Investigations of the EPR parameters for the interstitial V^{4+} in anatase from two microscopic spin Hamiltonian methods

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ABSTRACT

The spin Hamiltonian parameters $g_{//}$ and $g_{\perp}$ for the interstitial V^{4+} in anatase are theoretically studied from the complete diagonalization (of energy matrix) method (CDM) and the perturbation theory method (PTM) which are improved in this paper. The two methods are based on the two-spin–orbit-parameter model considering the contributions from the spin–orbit (SO) coupling of central $3d^n$ ion and ligand. The theoretical results from both methods are not only consistent with the experimental values, but also close to each other. This means that both methods can be effective in the investigations of spin Hamiltonian(SH) parameters.

Key words: Electron paramagnetic resonance(EPR); Crystal-fields and Spin Hamiltonians; V^{4+} Anatase (TiO_2)

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INTRODUCTION

Over the last few decades, anatase(TiO_2) doped with transition-metal ions has been widely investigated for its interesting optical, electronic and magnetic properties [1-6]. Usually, these properties may be related to the electronic and crystal-field behaviors of the impurity ions in host. Science electron paramagnetic resonance (EPR) is a powerful tool to study the electronic and crystal-field properties for paramagnetic ions in crystals, the EPR experiments for V^{4+}-doped anatase were carried out, and its spin Hamiltonian parameters $g_{//}$ and $g_{\perp}$ and the hyperfine structure constants $A_{//}$ and $A_{\perp}$ were given [7]. Up to now, however, these experimental results have not been satisfactorily interpreted, for example, these results were theoretically treated on the basis of the simple second-order perturbation formulas of the g factors for a $3d^1$ ion in tetragonally distorted octahedra based on the conventional-field theory and various adjustable

parameters (i.e.,the radial average functions $<r^2>$, $<r^4>$, spin-orbit coefficient) [7]. Only the spin-orbit coupling interaction of the interstitial V^{4+} center was considerd for the covalent system (the orbital reduction actor k was estimated to be about 0.76<1) in Ref.[7], and the contributions from the ligand orbitals and spin-orbit coupling interactions were ignored. Actually, 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 V^{4+}. In addition, the hyperfine structure constants were not interpreted. In order to investigate the EPR parameters for the interstitial V^{4+} center in anatase to a better extent, in this work, two methods are improved based on the two-spin–orbit-parameter model: one is the perturbation theory method(PTM), the other is the complete diagonalization (of energy matrix) method(CDM). Both of them are considering the contributions from the p- and s- orbitals as well as the spin-orbit coupling of the ligands and the related energy separations are quantitatively determined from the local structure of this center.

Calculations

2.1 calculation by PTM

Anatase is one of the three mineral forms of titanium dioxide, it crystallizes in the tetragonal system with space group D_{4h}^{19}(I4amd)[7,8]. When V^{4+} is doped into the lattice of anatase, it may occupy the interstitial site. The oxygen octahedron around this site is tetragonally distorted: two oxygen ions along the C_4 axis are far from the impurity with the distance $R_1 \approx 2.804$ Å, the rest four oxygen ions are at the apexes of a distorted tetrahedron with the same metal-ligand distance $R_2 \approx 1.937$ Å and the angle θ (between the metal-ligand distance R_2 and C_4 axis) is about 77.7°[8]. For a $3d^1(V^{4+})$ ion in tetragonally distorted octahedra, its higher orbital doublet ^2E_g of the original cubic case would split into two orbital singlets $^2A_1$ (θ) and $^2B_1(\varepsilon)$, while the original lower orbital triplet $^2T_{2g}$ would be separated into an orbital singlet $^2B_2$ (ζ) and a doublet ^2E (η, ξ) [9] , with the former lying lowest for present system[7]. As mentioned before, the contributions from the ligand orbitals and spin-orbit coupling interactions were ignored and the energy separations were not correlated with the local structure around the impurity center in the explanations of Spin Hamiltonian(SH) parameters in previous work, by considering the above contributions, the two-SO-parameter model is used in the studies of Spin Hamiltonian(SH) parameters for interstitial V^{4+} in anatase.

From the cluster approach for a $3d^n$ ion in octahedra, the LCAO molecular-orbitals can be taken as the one-electron basic functions: [10, 11]

$$\psi_t = N_t^{1/2}(\varphi_t - \lambda_t \chi_{pt})$$
$$\psi_e = N_e^{1/2}(\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s) \qquad (1)$$

Where φ_γ (the subscript $\gamma = e$ or t stands for the irreducible representation of O_h group) is the d-orbital of the $3d^n$ ion . $\chi_{p\gamma}$ and χ_s are the p- orbital and s- orbital of ligand. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients. Thus, we have the normalization relationship[11, 12]:

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

and the approximate relationships[12]

$$N^{\,2} = N_t^{\,2}\,[\,1 + \lambda_t^{\,2}\,S_{dpt}^{\,2} - 2\,\lambda_t\,S_{dpt}\,]$$
$$N^{\,2} = N_e^{\,2}\,[\,1 + \lambda_e^{\,2}\,S_{dpe}^{\,2} + \lambda_s^{\,2}\,S_{ds}^{\,2} - 2\,\lambda_e\,S_{dpe} - 2\,\lambda_s\,S_{ds}] \tag{3}$$

Here N is the average covalency factor, characteristic of the covalency effect of (or reduction of the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter) for the central ion in crystals. $S_{dp\gamma}$ (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 proportionality 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 [12]. Thus, the spin-orbit coupling coefficients and the orbital reduction factors can be written as[12]:

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

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the $3d^n$ and 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.

By using the perturbation procedure similar to that of Pilbrow and Gourier[13,14], the two SO-coupling-coefficient formulas of the g factors and the hyperfine structure constants for a $3d^1$ ion under octahedral tetragonal symmetry can be obtained from the cluster approach:

$$g_\square = g_s - 8\,k'\zeta'/E_1 - 2k\zeta^{\prime 2}/E_2^{\,2} + 2\,k'\zeta^{\prime 2}/E_1^{\,2}$$

$$g_\square = g_s - 2k\zeta/E_2 + 2\,k'\zeta'\zeta[1/E_1\,E_2 - 1/E_1^{\,2}]$$

$$A_\square = P[-\kappa - 4\,N^2/7 + (g_\square - g_s) + 6(g_\square - g_s)/14]$$
$$A_\square = P[-\kappa + 2\,N^2/7 + 11(g_\square - g_s)/14] \tag{5}$$

where g_s (≈ 2.0023) is the spin-only value. P is the dipolar hyperfine structure parameter of the free $3d^1$ ion. κ is the isotropic core polarization constant. The energy denominators E_1 and E_2 stand for the energy separations between the excited $^2B_1$, ^2E and the ground $^2B_2$ states. They can be expressed in terms of the tetragonal field parameters D_s and D_t and the cubic field parameter D_q

$$E_1 = 10\,D_q$$
$$E_2 = -3\,D_s + 5D_t \tag{6}$$

From the superposition model [15] and the geometrical relationship of the studied impurity center, the tetragonal field parameters can be determined as follows:

$$D_s = (4/7\,)\,\overline{A}_2\,(R_0)[(R_0/R_1)^{t2} + (2\cos^2\theta - \sin^2\theta)(\,R_0/R_2)^{t2}] \tag{7}$$

$D_t = \{(-1/42)[\ 4(R_0/R_1)^{t4}+(35\cos^4\theta - 30\cos^2\theta + 3)(\ R_0/R_2)^{t4}]+(R_0/R_2)^{t4}\sin^4\theta/6\}\ \overline{A}_4\ (R_0)$

Here $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters (with the reference bonding length R_0), while t_2 (≈ 3)and t_4(≈ 5) are the power-law exponents[16]. For $3d^n$ octahedral clusters, the relationships $\overline{A}_4(R_0) \approx \frac{3}{4}D_q$ and $\overline{A}_2(R_0) = 9 \quad 12\overline{A}_4(R_0)$ have been proved to be reasonable in many crystals[16,17,18], we take $\overline{A}_2(R_0) \approx 11.3\overline{A}_4(R_0)$ here. The average metal-ligand distance

$\overline{R} = (R_1 + 2R_2)/3 \approx 2.226$ Å is taken as the reference bonding length R_0. From the distance R_0 and the Slater-type SCF functions[19,20] , the integrals $S_{dpt} \approx 0.0209$, $S_{dpe} \approx 0.0664$, $S_{ds} \approx 0.0585$, and $A \approx 1.4496$ are obtained.

Substituting above parameters into E.q.(5) and fitting the calculated g factors and the hyperfine structure constants to the experimental data, we have:

$$Dq \approx 1600cm^{-1}, \quad N \approx 0.831, \quad \kappa \approx 0.44$$

The values $N_t \approx 0.839$, $N_e \approx 0.868$, $\lambda_t \approx 0.459$, $\lambda_e \approx 0.366$ and $\lambda_s \approx 0.322$ are calculated from equations (2) and (3). Then the parameters $\zeta \approx 221cm^{-1}$, $\zeta' \approx 201cm^{-1}$, $k \approx 0.928$ and $k' \approx 0.690$ can be determined from equation (4) and the free-ion values $\zeta_d \approx 248$ cm^{-1} for V^{4+} [21] and $\zeta_p \approx 151$ cm^{-1} for O^{2-} [22].The corresponding EPR parameters are shown in Table 1.

2.2 calculation by CDM
The Hamiltonian for the d^1 ion in crystal-field can be written as: [10]

$H = H_f + H_{so}(\zeta,\zeta') + H_{CF}(D_q,D_s, D_t)$

Where H_f is the free-ion Hamiltonian. $H_{so}(\zeta,\zeta')$ is the spin-orbit coupling interactions including two SO coupling parameters ζ and ζ'. H_{CF} is the crystal-field Hamiltonian for $3d^1$ ion in tetragonal symmetry. By using the strong field basis functions[10] in tetragonal symmetry, we obtain the 10×10 complete Hamiltonian matrix elements of the crystal field and spin-orbit coupling based on the two-SO-parameter model. For the spin doublet ground state, we have the wave function:

$$|\Phi^+> = c_1|\psi^-_\xi> + c_2|\psi^-_\eta> + c_3|\psi^+_\zeta> + c_4|\psi^+_\theta> + c_5|\psi^+_\varepsilon>$$
$$|\Phi^-> = c_1|\psi^+_\xi> + c_2|\psi^+_\eta> + c_3|\psi^-_\zeta> - c_4|\psi^-_\theta> - c_5|\psi^-_\varepsilon> \tag{8}$$

Where ψ is the LCAO molecular-orbitals for a $3d^n$ ion in octahedra based on the cluster approach(see E.q.(1)). Considering the equivalence between the SH and Zeeman interaction, the g factors are:

$g_\parallel = 2<\Phi^+|L_z+g_sS_z|\Phi^+> = 4(2c_3c_5k'-c_2c_1k)+g_s(1-2c_2^2-2c_1^2)$

$$g_\perp = 2<\Phi^+ |L_x + g_s S_x| \Phi^-> = 2(-2\sqrt{3}\, c_1 c_4\, k' + 2c_3 c_2 k - 2c_1 c_5\, k') + g_s(2c_3{}^2 + 2c_2{}^2 - 1) \qquad (9)$$

here k' and k are the orbital reduction factors as mentioned in Eq.(4). The calculated

$g_\parallel$ and $g_\perp$ are also shown in Table 1 for comparison.

Table 1.   The EPR parameters for the interstitial V^{4+} center in anatase

	$g_\parallel$	$g_\perp$	$A_\parallel/10^{-4}\ \cdot cm^{-1}$	$A_\perp/10^{-4}\ \cdot cm^{-1}$
Cal[a]	1.916	1.967	-161	-47
Cal[b]	1.932	1.960	-159	-48
Cal[c]	1.932	1.958	--	--
Expt[d]	1.932	1.960	-158	-48

[a] *Calculations by using equation (5) but neglecting the ligand orbital contributions (i.e., taking $\zeta = \zeta' = N\,\zeta_d$ and $k = k' = N$) in this work..;* [b] *Calculations by using equation (5) and including the ligand orbital contributions in this work.;* [c] *Calculations by the complete diagonalization (of energy matrix) method (CDM) in this work.*

[d] *The signs of the experimental hyperfine structure constants were not given in Ref. [7]. Based on the theoretical calculations in this work and various observed results for V^{4+} (or VO^{2+}) in oxides [26], these signs should be negative.*

DISCUSSION

From Table 1, one can find that the calculated results of interstitial V^{4+} in anatase from both PTM and CDM approaches based on the two-SO-parameter model are not only consistent with the observed values, but also close to each other. This suggests that both microscopic SH approaches based on the two-SO-parameters model are effective in the theoretical investigations of SH parameters for $3d^1$ ion in crystals.

(1) the cubic field parameter Dq ($\approx 1600 cm^{-1}$) obtained in this work is close to that of V^{4+} ion in

various oxides. For example, the value Dq$\approx 1800 cm^{-1}$ of the central V^{4+} ion located at the

interstitial site in rutile was obtained from crystal-field analysis[23]. Considering that the average

metal-ligand distance $\bar{R}$ (≈ 2.226 Å) for the studied system is larger than that(about 2.043 Å) for

the interstitial V^{4+} in rutile and the crystal-field strength around the impurity may be mainly dependent upon its average distance from the six nearest oxygen ions and Dq decreases with increasing distance $\bar{R}$ [24,25], the value Dq$\approx 1600 cm^{-1}$ obtained in this work may be regarded as reasonable. The energy separations between the excited ^2E and the ground $^2B_2$ state(calculated from equations (6)) is about $9600 cm^{-1}$ which is consistent with the calculated results by other models[7], this means that the related parameters adopted in this work can be regarded suitable.
(2) The calculated results based on the perturbation formulas in equation (5) and the complete diagonalization (of energy matrix) method (CDM)(see E.q(9)) of this work are better than those (Cal.[a] in table 1) based on the simple formulas by neglecting the contributions from the ligand

orbitals. In view of the high valence state of V^{4+}, the 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 ($\approx 0.831 < 1$) in equation (3) and the obvious mixing coefficients ($\lambda_t \approx 0.459$, $\lambda_e \approx 0.366$ and $\lambda_s \approx 0.322$) obtained in this work. Therefore, the formulas of the EPR parameters containing the ligand orbital and spin-orbit coupling contributions seem to be more applicable than the simple ones in the absence of these contributions for the investigations on the EPR parameters of impurity ions in covalent systems.

CONCLUSIONS

In this paper, the contributions from the ligand orbitals and spin-orbit coupling interactions are considered in the theoretical investigations of the EPR parameters for the interstitial V^{4+} in anatase and the theoretical EPR parameters based on the above contributions in this work are in good agreement with the experimental data.

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