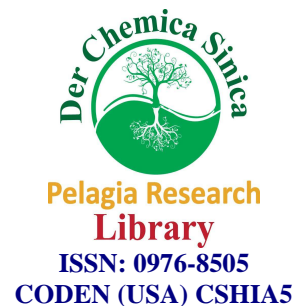




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Theoretical investigations on the EPR parameters of VO^{2+} in anatase

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ABSTRACT

The electron paramagnetic resonance (EPR) parameters g_{\parallel} , g_{\perp} and the hyperfine structure constants A_{\parallel} , A_{\perp} for VO^{2+} in anatase are calculated from the high order perturbation formulas of these parameters for a $3d^1$ ion in tetragonal symmetry (compressed octahedron). In these formulas, the contributions to the spin Hamiltonian parameters from the s - and p -orbitals as well as the spin-orbit coupling coefficient of the ligands are taken into account. On the basis of the studies, the angle between the metal-ligand bond and C_4 axis is found to be about 3.1° bigger than the host value in the oxygen octahedron around V^{4+} site. The calculated EPR results are in good agreement with observed values.

Key words: Electron paramagnetic resonance(EPR); Crystal and ligand fields; VO^{2+} ; Anatase (TiO_2)

INTRODUCTION

The vanadyl has advantages as probe in studying local structures and properties in doped crystals[1-8]. 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 useful tool to study the electronic and crystal-field properties for paramagnetic ions in crystals, the EPR experiments for VO^{2+} -doped anatase were carried out, and its spin Hamiltonian parameters g_{\parallel} and g_{\perp} and the hyperfine structure constants A_{\parallel} and A_{\perp} were determined in Ref[8]. Up to now, however, these experimental results were not interpreted. In order to investigate the EPR parameters of the VO^{2+} center in anatase to a good extent, in this work, the EPR parameters are quantitatively analyzed from the high order perturbation formulas of these parameters for a d^1 ion in tetragonal symmetry (compressed octahedron) by considering reasonable local lattice (angle) distortion around the impurity ion. In these formulas, the contributions from the spin-orbit coupling and the orbitals of the ligands are also taken into account based on the cluster approach.

MATERIALS AND METHODS

Anatase has a defective rock salt structure in which one in six of Ti lattice sites is vacant. Thus each oxygen has three Ti neighbours and belongs to three different octahedra while Ti is in a distorted octahedral oxygen coordination in which there are two long (along the C_4 axis) and four short bonds [8]. The cell structure around the interstitial site is the same, except for the distances of the oxygens along C_4 axis, it can be described in detail as follows: 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 $R_1 \approx 2.804 \text{ \AA}$, the rest four oxygen ions are at the apexes of a distorted tetrahedron with the same metal-ligand distance $R_2 \approx 1.937 \text{ \AA}$ and the angle θ_0 (between the metal-ligand bond R_2 and C_4 axis) is about 77.7° [9]. When VO^{2+} is doped into the lattice of anatase, we think it may occupy the interstitial site and the $\text{V}=\text{O}$ bond takes up the direction of the longest distance (along the C_4 axis). This situation is also found in other VO^{2+} -doped crystals (e.g., VO^{2+} in Tutton salt)[1,10], and then the cluster $(\text{VO}_6)^{8+}$ is forming. For a $3d^1$ (VO^{2+}) ion in

tetragonally distorted octahedra, its higher orbital doublet 2E_g of the original cubic case would split into two orbital singlets ${}^2A_1(\theta)$ and ${}^2B_1(\epsilon)$, while the original lower orbital triplet ${}^2T_{2g}$ would be separated into an orbital singlet ${}^2B_2(\zeta)$ and a doublet ${}^2E(\eta, \xi)$, with the ${}^2B_2(\zeta)$ lying lowest. [11]

From the cluster approach, the one-electron basic functions for a $3d^n$ ion in octahedra can be expressed as: [12,13]

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

Where φ_γ (the subscript $\gamma=e$ or t represents the irreducible representation of O_h group) is the d-orbital of the $3d^n$ ion. $\chi_{p\gamma}$ and χ_s is 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 [13]:

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

and the approximate relationships [14]

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

Here N is the average covalency factor. $S_{d\gamma}$ (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., $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ within the same irreducible representation e_g .

From Eq(1), the spin-orbit coupling coefficients ζ , ζ' and the orbital reduction factors k , k' may be written as:

$$\zeta = N_t (\zeta_d^0 + \lambda_t^2 \zeta_p^0 / 2) \quad \zeta' = (N_t N_e)^{1/2} (\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0 / 2) \\ k = N_t (1 + \lambda_t^2 / 2) \quad k' = (N_t N_e)^{1/2} [1 - \lambda_t (\lambda_e + \lambda_s A) / 2] \quad (4)$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients for a free $3d^n$ and ligand ions, respectively. A denotes the integral $R \left\langle ns \left| \frac{\partial}{\partial y} \right| np_y \right\rangle$, where R is the impurity-ligand distance in the studied system.

From the perturbation theory, the two SO-coupling-coefficient formulas of the g factors and the hyperfine structure constants for a $3d^1$ ion in tetragonal octahedra symmetry with the ground state ${}^2B_2(\zeta)$ can be obtained from the cluster approach [14]:

$$g_{\parallel} = g_s - 8k' \zeta' / E_1 - 2k \zeta^2 / E_2^2 + 2k' \zeta'^2 / E_1^2 \\ g_{\perp} = g_s - 2k \zeta / E_2 + 2k' \zeta \zeta' [1/E_1 E_2 - 1/E_1^2] \\ A_{\parallel} = P_0 [-\kappa - 4N^2/7 + (g_{\parallel} - g_s)] + 6(g_{\perp} - g_s)/14 \\ A_{\perp} = P_0 [-\kappa + 2N^2/7 + 11(g_{\perp} - g_s)/14] \quad (5)$$

where g_s (≈ 2.0023) is the spin-only value. P_0 is the dipolar hyperfine structure parameter of the free $3d^1$ ion ($P_0 \approx 172 \times 10^{-4} \text{cm}^{-1}$ for free V^{4+} ion [15]). 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 and 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 :

$$E_1 = 10 D_q \quad E_2 = -3 D_s + 5 D_t \quad (6)$$

From the superposition model [16] and the geometrical relationship of the studied impurity center, the tetragonal

field parameters can be determined as follows:

$$D_s = (2/7) \bar{A}_2(R_0) [2(R_0/R_1)^2 + 2(R_0/R_{V-O})^2 + 2(2\cos^2\theta - \sin^2\theta)(R_0/R_2)^2]$$

$$D_f = 8 \bar{A}_4(R_0) \{ (-1/42) [(35\cos^4\theta - 30\cos^2\theta + 3)(R_0/R_2)^4 + 2(R_0/R_1)^4 + 2(R_0/R_{V-O})^4] + (R_0/R_2)^4 \sin^4\theta / 6 \}$$
(7)

Here R_{V-O} is the V=O bond length ($\approx 1.97 \text{ \AA}$ [17]), θ represents the angle between the metal-ligand bond R_2 and C_4 axis, $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters (with the reference bonding length R_0), while t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents^[18]. The relationships $\bar{A}_4(R_0) \approx \frac{3}{4} D_q$ and $\bar{A}_2(R_0) = 9 \square 12 \bar{A}_4(R_0)$ have been proved to be reasonable for many $3d^n$ ions in octahedral environments [18-20], we take $\bar{A}_2(R_0) \approx 12 \bar{A}_4(R_0)$ here. The average metal-ligand distance $\bar{R} = (R_{V-O} + R_1 + 4R_2)/6 \approx 2.087 \text{ \AA}$ is taken as the reference bonding length R_0 . From the distance R_0 and the Slater-type SCF functions [21,22], the integrals can be calculated and collected in Table 1. For VO^{2+} in anatase, to our knowledge, no optical spectra data were reported. However, the value $Dq \approx 1800 \text{ cm}^{-1}$ of the central V^{4+} ion located at the interstitial site in rutile was obtained from the crystal-field analysis [23]. Considering that the average metal-ligand distance \bar{R} ($\approx 2.087 \text{ \AA}$) for the studied system is slightly larger than that (about 2.043 \AA [23]) 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 $Dq \approx 1750 \text{ cm}^{-1}$ can be approximately estimated for present system here.

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

$$N \approx 0.838, \quad \kappa \approx 0.599, \quad \theta \approx 80.8^\circ$$

The normalization factors (N_γ) and the orbital mixing coefficients λ_γ (or λ_s) are calculated from equations (2) and (3). Then the parameters ζ , ζ' , k , k' can be determined from equation (4) and the free-ion values $\zeta_d^0 \approx 248 \text{ cm}^{-1}$ for V^{4+} [26] and $\zeta_p^0 \approx 151 \text{ cm}^{-1}$ for O^{2-} [27], they are also collected in Table 1. The corresponding EPR parameters are shown in Table 2.

Table 1. The group overlap integrals, molecular orbital coefficients N_γ and λ_γ (and λ_s), spin-orbit coupling coefficients (in cm^{-1}) and the orbital reduction factors for VO^{2+} in anatase

S_{dpt}	S_{dpe}	S_{ds}	A	N_t	N_e	λ_t
0.0329	0.0941	0.0743	1.3587	0.8507	0.8904	0.4531
λ_e	λ_s	ζ	ζ'	k	k'	
0.3852	0.3041	224.2	204.4	0.9381	0.7129	

Table 2. The EPR parameters for VO^{2+} in anatase

	g_\parallel	g_\perp	$A_\parallel / 10^{-4} \cdot \text{cm}^{-1}$	$A_\perp / 10^{-4} \cdot \text{cm}^{-1}$
Ca	1.9'	1.9'	-186.3	-73
Ca	1.9'	1.9'	-187.6	-72.1
Ca	1.9'	1.9'	-186.1	-72.7
Exl	1.9'	1.9'	188.8	69.2

^a Calculations by using equation (5) but neglecting the ligand orbital contributions and local angular distortion (i.e., taking $\zeta = \zeta' = N \zeta_d^0$ and $k = k' = N$, $\theta_0 \approx 77.7^\circ$) in this work..

^b Calculations by using equation (5) neglecting the ligand orbital contributions but considering the local angular distortion in this work.

^c Calculations by using equation (5) including the ligand orbital contributions and the local angular distortion in this work.

^d In Ref.[8], the hyperfine structure constants were given in unit G. and the signs of them were not given. Based on the theoretical calculations in this work and various experimental results for V^{4+} (or VO^{2+}) in oxides [15], these signs are suggested to be negative.

RESULTS AND DISCUSSION

From table 2, one can find that the calculated results of VO^{2+} in anatase by using high order perturbation formulas including the ligand orbital contributions and the local angular distortion are in good agreement with the experimental values, This suggests that the formulas and the related parameters adopted in this work can be regarded as suitable.

(1) The calculated results including the contributions from ligand orbitals and the local angular deformation are better than those neglecting above contributions (see g_{\parallel}). In fact, neglectation of the ligand orbital contributions may lead to larger product $k'\zeta'$ (see Eq.5), and hence to smaller g_{\parallel} . Moreover, The above discrepancy of g_{\parallel} between the calculated results (cal^a, cal^b) and the observed values can not be removed by adjusting the average covalency factor N and the local angle θ . In view of the high valence state of V^{4+} , the strong 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 ($\approx 0.838 < 1$) in equation (3) and the obvious mixing coefficients (see table 1) 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 with high valence state.

(2) Based on the local angular distortion ($\Delta\theta = \theta - \theta_0 \approx 3.1^\circ$), $D_s \approx 3187.9 \text{ cm}^{-1}$ and $D_t \approx 812.4 \text{ cm}^{-1}$ are calculated in this work. These values are close to other VO^{2+} doped crystals[4,28]. For instance, $D_s \approx 3381 \text{ cm}^{-1}$ and $D_t \approx 852 \text{ cm}^{-1}$ were determined from the optical spectra of VO^{2+} in $\text{KZnClSO}_4 \cdot 3\text{H}_2\text{O}$ [28]. Then the related parameters and local angular distortion adopted in the calculation can be regarded as suitable. Interestingly, similar local lattice deformation is also found in other d^1 ions doped crystals. For example, substitutional Mo^{3+} or interstitial V^{4+} in rutile[23,29]. This also supports the validity of the calculation in this work.

CONCLUSION

In this paper, the contributions from the ligand orbitals and spin-orbit coupling interactions and local angular distortion are considered in the theoretical investigations of the EPR parameters for VO^{2+} in anatase and the theoretical EPR parameters based on the above contributions in this work are in good agreement with the experimental data.

REFERENCES

- [1] Kipal R, Shukla S, *Phys. Scr.*, **2012**, 85, 015706.
- [2] Bozkurt E, Karabulut B, Kartal L, Soydas Y, *Chem. Phys. Letts.*, **2009**, 477, 65.
- [3] Bryik R, *Physica B*, **2009**, 404, 3483
- [4] Sreeramachandra L, Prasad S, Subramanian, *J. Chem. Phys.*, **1987**, 86(2), 629.
- [5] Biyik R, Tapramaz R, Karabulut B, *Z.Naturforsch.*58a, **2003**, 499.
- [6] Padiyan D P, Muthukrishnan C, Murugesan R, *J. Mol. Struct*, **2003**, 648, 1.
- [7] Karabulut B, Ilkin I, Tapramaz R, *Z.Naturforsch.*60a, **2005**, 95.
- [8] Luca V, Thomson S, Howe F, *J. Chem. Soc., Faraday Trans*, **1997**, 93, 2195.
- [9] Gallay R, Klink J, Moser J, *Phys. Rev. B*, **1986**, 34 (5), 3060
- [10] Borcherts R H, Kikuchi C, *J. Chem. Phys.*, **1964**, 41, 1896.
- [11] Abragam A, Bleaney B, *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, London, **1970**, pp381.
- [12] Sugano S, Tanabe Y, Kamimura H, *Multiplets of Transition-Metal Ions in Crystals*. Academic Press, New York, **1970**, pp249-279.
- [13] Gao X Y, Wu S Y, Wei W H, Yan W Z, *Z.Naturforsch.*60a, **2005**, 145.
- [14] Lin J Z, Wu S Y, Fu Q, Lu G D, *Z.Naturforsch.*61a, **2006**, 583.
- [15] McGarvey B R, *J. Phys. Chem*, **1967**, 71, 51.
- [16] Newman D J, Ng B, *Rep. Prog. Phys*, **1989**, 52, 699.
- [17] Vainshtein B K, Fridkin V M, Indenbom V L. *Modern crystallography II-structure of crystals*, Springer-Verlag Berlin Heidelberg, New York, **1982**.
- [18] Yu W L, Zhang X M, Yang L X, *Phys. Rev. B*, **1994**, 50, 6756.
- [19] Edgar A, *J. Phys. C: Solid State Physics*, **1977**, 10, 2019.
- [20] Newman D J, Pryce D C, Runciman W A, *Am. Mineral*, **1978**, 63, 1278.
- [21] Clementi E D, Raimondi D L, *J. Chem. Phys.*, **1963**, 38(11), 2686
- [22] Clementi E, Raimondi D L, Reinhardt W P, *J. Chem. Phys.*, **1967**, 47(4),1300.

- [23] Lin J Z, Wu S Y, Fu Q, *Radiat. Eff. Defects. Solids.*, **2006**, 161(10), 571.
[24] Moreno M, Barriuso M T, Aramburu J A, *Int. J. Quantum Chem.*, **1994**, 52, 829.
[25] Moreno M, *J. Phys. Chem. Solids*, **1990**, 51, 835.
[26] Chakravarty A S, *Introduction to the Magnetic Properties of solids*. A Wiley Interscience Publication, Canada, **1980**, 655.
[27] Hodgson E K, Fridovich I, *Biochem. Biophys. Res. Commun*, **1973**, 54, 270.
[28] Deva B, Raju P, Narasimhulu K V, Rao J L, *J. Phys. Chem. Solids*, **2003**, 64, 1339.
[29] Shao Y W, Hu Y X, Wang X F, Fu C J, *Radiat. Eff. Defects. Solids*, **2010**, 165, 298.