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Theoretical studies on the electron paramagnetic resonance parameters for the tetragonal VO^{2+} center in CaO-Al$_2$O$_3$-SiO$_2$ system

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In this work, the high order perturbation formulae of the electron paramagnetic resonance (EPR) parameters, g & A for a VO^{2+} 3d^1 ion in tetragonal symmetry (compressed octahedron) are adopted to theoretically study these parameters of the tetragonal VO^{2+} center in CaO-Al$_2$O$_3$-SiO$_2$ system. Because the spin-orbit (SO) coupling parameter ζ_p (≈151 cm^{-1}) of ligand O^{2-} is close to that (≈248 cm^{-1}) of the central V^{4+} ion in the cluster [VO$_6$]$^{8-}$ with strong covalence, the effect of the SO coupling parameter ζ_p on EPR parameters are considered on the basis of cluster approach. The obtained EPR parameters show good agreement with the experimental values and need fewer adjustable parameters than previous studies. And the local structure of the tetragonal VO^{2+} center in CaO-Al$_2$O$_3$-SiO$_2$ system due to Jahn-Teller effect is obtained from the analysis of the EPR parameters. The results are discussed.

Keywords: VO^{2+}; CaO-Al$_2$O$_3$-SiO$_2$; electron paramagnetic resonance (EPR); crystal-fields; spin Hamiltonians.

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1. Introduction

It is well-known that electron paramagnetic resonance (EPR) technique is a powerful tool to study the environmental symmetry of the transition-metal ions doped into the crystals (or glasses) which is produced by the ligands around the metal ion and can also give valuable information about the electric fields of these impurity ions [1]. The vanadyl ion (VO^{2+}) with 3d^1 configuration is probably the most stable among the molecular paramagnetic transition metal ions and is often used as an impurity probe for detecting the site symmetry of the central ion and the bonding nature with the ligands in the EPR studies [2-3] Due to the strong V^{4+}-O^{2-} covalence bonding in VO^{2+}, many VO^{2+} complexes in crystals (or glasses) possess C_{4v} symmetry with the axial symmetry for g and A values [4-6]. For example, EPR investigations for VO^{2+} center in CaO-Al$_2$O$_3$-SiO$_2$ glass-ceramic system were performed by Farah and the anisotropic g factors ($g_\parallel$, $g_\perp$) and the hyperfine structure constants ($A_\parallel$, $A_\perp$) were also obtained for this center [6]. According to the EPR results, the oxygen octahedron around the central ion V^{4+} was found to suffer tetragonally compressed distortion [6]. According to the EPR results, the oxygen octahedron around the central ion V^{4+} was found to suffer tetragonally compressed distortion [6]. Based on the traditional crystal-field theory, theoretical calculations for EPR spectra of V^{4+} center in CaO-Al$_2$O$_3$-SiO$_2$ were carried out through the complete diagonalization energy matrix method (CDM) and perturbation theory method (PTM) by Wei *et al*, [7] and the theoretical results show good agreement with the observed values (see Table I) [7]. However, there may be some imperfections in their calculations. First, many adjusted parameters (*i.e.*, the crystal field parameters B_{20}, B_{40} and B_{44}, the orbital-reduction factor k and the core polarization constant κ) were introduced in their studies. Second, the contributions to EPR parameters from the ligand orbitals and SO coupling interactions were ignored for the strong covalent system CaO-Al$_2$O$_3$-SiO$_2$: VO^{2+} characterized by the small orbital-reduction factor $k(\approx 0.7 \ll 1)$ [7]. Since the SO coupling coefficient ζ_p (≈ 151 cm^{-1} [4]) of the ligand O^{2-} is close to that (≈ 248 cm^{-1} [1]) of the central V^{4+} ion, these contributions from ζ_p and the p- (s-) orbitals of the ligands may be somewhat important for this center due to strong covalency. Finally, No information about the local structures has been determined for the octahedral cluster [VO$_6$]$^{8-}$ in CaO-Al$_2$O$_3$-SiO$_2$ system, since previous computations failed to correlate with the defect structures around the impurity. Due to the reason that analysis of EPR spectra can provide useful information about local defect structures of the cluster [VO$_6$]$^{8-}$ in CaO-Al$_2$O$_3$-SiO$_2$ system, and this would be helpful in understanding the properties of this glass-ceramic system. Thus, further studies on the above EPR parameters are of scientific and practical meanings. So, in this paper, the EPR parameters are quantitatively analyzed based on high-order perturbation formulas of these parameters for a d^1 ion in tetragonally compressed octahedral, the contributions from the tetragonally compressed distortion as well as the SO coupling and the orbitals of the ligands are considered in these formulas.

2. Calculation

As for nd^1 ions in tetragonally compressed octahedra, the higher orbital doublet ^2e_g in original cubic symmetry would split into two orbital singlets $^2a_1$ (θ) and $^2b_1(\varepsilon)$. Meanwhile, the ground orbital triplet $^2t_{2g}$ in cubic symmetry can be divided into an orbital singlet $^2b_2$ (ζ) and a doublet $^2e(\eta, \xi)$, with the former lying lowest [8]. Thus, the energy intervals can be written as follows:

$$E_1 = E(^2e) - E(^2b_2) = -3D_s + 5D_t \tag{1}$$

$$E_2 = E(^2b_1) - E(^2b_2) = 10D_q \tag{2}$$

$$E_3 = E(^2a_1) - E(^2b_2) = 10D_q - 4D_s - 5D_t \tag{3}$$

Here, D_q, D_s and D_t are the cubic field parameter and the tetragonal field parameters, respectively. They can be calculated from the local geometry of the studied impurity centers and the point-charge model [9-11], and be expressed as follows:

$$D_q = -eq\langle r^4\rangle/(6\bar{R}^5) \tag{4}$$

$$D_s = 2eq\langle r^2\rangle(1/R_{\|}^3 - 1/R_{\perp}^3)/7 \tag{5}$$

$$D_t = -2eq\langle r^4\rangle(1/R_{\|}^5 - 1/R_{\perp}^5)/21 \tag{6}$$

Here $q(= -2e)$ is the effective charge of the oxygen ligand. $\langle r^2\rangle$ and $\langle r^4\rangle$ denote the expectation values of the radial wavefunction of d^1 orbital in cluster, which can be expressed in terms of the corresponding free-ion values and average covalency factor N with respect to the admixture between the central metal ion and the ligand orbitals [9-11]:

$$\begin{aligned}\langle r^2\rangle &\approx 3.3222N(a.u.),\\ \langle r^4\rangle &\approx 21.0698N(a.u.)\end{aligned} \tag{7}$$

$\bar{R}$ denotes the average metal-ligand (V-O) bonding length for the studied system (here, we take $\bar{R} \approx 1.985$ Å for the VO^{2+} in cubic case [13]). $R_{\|}$ and $R_{\perp}$ denote the metal-ligand distances parallel and perpendicular to the tetragonal axis, respectively. For the VO^{2+} center in CaO-Al$_2$O$_3$-SiO$_2$ system forming tetragonal [VO$_6$]$^{8-}$ cluster, due to Jahn-Teller effect (note: the Jahn-Teller ion V^{4+} can suffer the Jahn-Teller effect under octahedral environments, which may slightly modify the immediate environment by stretching or contraction of the impurity-ligand bonding lengths), the parallel and perpendicular metal-ligand lengths can be expressed in terms of the average distance and the tetragonal compression ΔR (see Fig. 1) as:

$$R_{\|} \approx \bar{R} - 2\Delta R, \qquad R_{\perp} \approx \bar{R} + \Delta R \tag{8}$$

As mentioned before, previous studies [7] did not consider the contributions to EPR parameters from the s-& p-orbitals and the SO coupling coefficients of the ligands. Thus, using the routines provided in Refs. [14], the high-order (third-order) perturbation formulae of the g tensor and A tensor for 3d^1 ion in tetragonally compressed octahedra including above contributions can be obtained based on cluster approach:

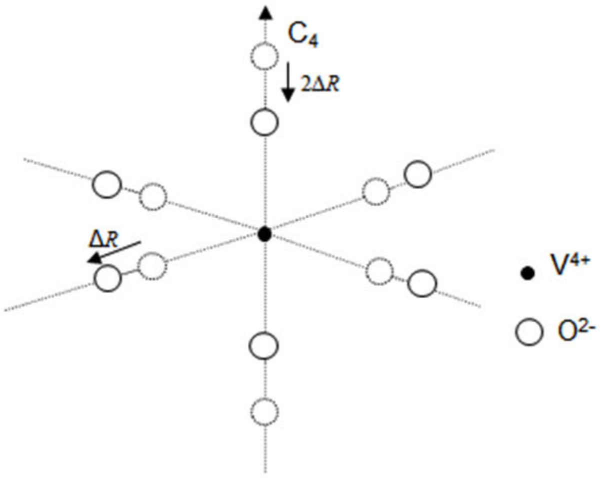

FIGURE 1. The local structure of [VO$_6$]$^{8-}$ cluster in CaO-Al$_2$O$_3$-SiO$_2$ system.

$$g_{\|} = g_e - \frac{8k'\zeta'}{E_2} - \frac{2k'\zeta^2}{E_1^2} - \frac{4k'\zeta\zeta'}{E_1E_2} - \frac{2\zeta^2}{E_1^2} \tag{9}$$

$$g_{\perp} = g_e - \frac{2k\zeta}{E_1} + \frac{k\zeta^2}{E_1^2} - \frac{2k\zeta'^2}{E_1E_2} + \frac{2k'\zeta'\zeta}{E_1E_2} - \frac{4\zeta'^2}{E_2^2} - \frac{\zeta^2}{E_1^2} \tag{10}$$

$$A_{\|} = P\left(-\kappa - \frac{4}{7}\right) + P'\left[(g_{\|} - g_e) + \frac{3}{7}(g_{\perp} - g_e)\right] \tag{11}$$

$$A_{\perp} = P\left(-\kappa - \frac{2}{7}\right) + P'\left[\frac{11}{14}(g_{\perp} - g_e)\right] \tag{12}$$

Where $g_e \approx 2.0023$ is the spin-only value. The energy denominators E_1 and E_2 stand for the energy divisions between the excited $^2b_1$, ^2e and the ground $^2b_2$ states, as mentioned in Eqs. (1-3). P and P' are the dipolar hyperfine constant related to the interaction within t_{2g} states and the interaction between t_{2g} and e_g states.

The SO coupling parameters ζ, ζ', the orbital reduction factors k, k' and the dipolar hyperfine constant P, P' in Eqs. (9-12) may be written as [15,16]:

$$\begin{aligned}\zeta &= N_t(\zeta_d + \lambda_t^2\zeta_p/2)\\ \zeta' &= (N_tN_e)^{1/2}(\zeta_d - \lambda_t\lambda_e\zeta_p/2)\end{aligned} \tag{13}$$

$$\begin{aligned}k &= N_t(1 + \lambda_t^2)\\ k' &= (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2]\end{aligned} \tag{14}$$

$$P = N_tP_0 \qquad P' = (N_tN_e)^{1/2}P_0 \tag{15}$$

ζ_d and ζ_p are the SO coupling coefficients of the free 3d^1 and ligand ions, respectively. $P_0(\approx 128 \times 10^{-4}$ cm^{-1} [17]) is the dipolar hyperfine structure parameter of the free VO^{2+} ion. A denotes the integral $R\langle ns \mid \partial/\partial y \mid np_y\rangle$ with the impurity-ligand distance R of 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 $t_{2g})$ and can be determined from the normalization conditions [15-16]

$$N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1 \tag{16}$$

$$N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1 \tag{17}$$

And the approximate relationships [15-16]

$$N^2 = N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}] \tag{18}$$

$$N^2 = N_e^2[1+\lambda_e^2 S_{dpe}^2+\lambda_s^2 S_{ds}^2-2\lambda_e S_{dpe}-2\lambda_s S_{ds}] \tag{19}$$

Here $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. N is the average covalency factor, characteristic of the covalency effect (or reduction of the SO coupling coefficient and the dipolar hyperfine structure parameter) for the central ion in the studied system. generally, 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. Thus, the integrals $S_{dpt} \approx 0.04553$, $S_{dpe} \approx 0.1198$, $S_{ds} \approx 0.0896$ and $A \approx 1.0283$ can be calculated from the Slater-type SCF functions [18-19] and the metal-ligand bonding length $R(\approx 1.985$ Å [13]). According to the optical spectra parameter for VO^{2+} doped in glasses and crystals, [20-21] the average covalency factor $N(\approx 0.81)$ can be adopted here. Then, the molecular orbital coefficients $N_t \approx 0.8289$, $N_e \approx 0.8819$, $\lambda_t \approx 0.5021$, $\lambda_e \approx 0.4359$ and $\lambda_s \approx 0.3271$ can be obtained from Eqs. (16-19). And the parameters $\zeta \approx 221$ cm^{-1}, $\zeta' \approx 198$ cm^{-1} $k \approx 0.9334$ and $k' \approx 0.6893$ can be determined from Eqs. (13-15) and the free-ion values $\zeta_d \approx 248$ cm^{-1} for V^{4+} [5] and $\zeta_p \approx 151$ cm^{-1} for O^{2-} [4].

In Eqs. (11) and (12), the core polarization constant k is taken as 0.84, which is the same as $\kappa(\approx 0.84)$ adopted in the previous work, [7]. Thus, there are only one unknown parameters ΔR in the formulae of the EPR parameters. Substituting the related values (*i.e.*, ζ, ζ', k and k') into Eqs. (9)-(12) and fitting the calculated results to the experimental data, one can obtain:

$$\Delta R \approx 0.1 \text{ Å} \tag{20}$$

The theoretical results are shown in Table I. For comparison, the calculated results based on the formulae of the EPR parameters within the scheme of the conventional crystal-field theory and various fitted parameters in Refs. [7] are also given in the table.

TABLE I. The EPR parameters of the tetragonal VO^{2+} center in CaO-Al_2O_3-SiO_2 system

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
Cal[a]	1.9359	1.9791	-168.3	-58.1
Cal[b]	1.9246	1.9703	-164.3	-65.1
Cal[c]	1.9370	1.9733	-157.9	-61.3
Expt[d]	1.936	1.979	162.1	60.6

[a] Ref. 7.

[b] Calculations by using Eqs. (9)-(12) and including the tetragonal distortion in equation (20), but without considering the ligand orbital contributions (*i.e.*, taking $\lambda_\gamma = 0$, $\zeta_p = 0$ and then $\zeta' = \zeta = N\zeta_d$, $k = k' = N$ and $P = P' = NP_0$) in this work.

[c] Calculations by using Eqs. (9)-(12) and including both the tetragonal distortion in Eq. (20) and the ligand orbital contributions in this work.

[d] Ref. 6.

3. Discussion

From Table I, we find that the theoretical results (Cal^c) based on the high-order perturbation formulae including the contributions from the ligand orbitals and SO coupling interactions show better agreement with the experimental values than those (Cal^b) neglecting the above contributions. This means that the contributions to the EPR parameters from the ligand orbitals and SO coupling interactions are important and should be considered in the explanations of these parameters for present system. In addition, these results exhibit a slight improvement compared with those (Cal^a) based on the formulae of the traditional crystal-field theory and various fitted parameters in previous work [7], although fewer adjustable parameters (the tetragonal distortion parameter ΔR, the core polarization constant κ) than those (the crystal field parameters B_{20}, B_{40} and B_{44}, the orbital reduction factor k, the core polarization constant κ) in Ref. [7] are adopted in this work.

(1) The studied system CaO-Al_2O_3-SiO_2:VO^{2+} exhibits strong covalency and significant impurity-ligand orbital admixtures, characterized by the small covalency factor $N(\approx 0.81 < 1)$ and the considerable mixing coefficients ($\Delta_t \approx 0.5021$, $\lambda_e \approx 0.4359$ and $\lambda_s \approx 0.3271$). In view of the high valence state of V^{4+}, the covalency and hence the significant admixture between the metal and ligand orbitals can be expected. In addition, the validity of the average covalency factor N can be further demonstrated by the relationship: $N^2 \approx 1 - h(L)k(M)$ [22], where the parameter $h(L)$ and $k(M)$ are the characteristic of the ligand and central metal ions, respectively. From the values $h(O^{2-})$ and $k(V^{2+}) \approx 0.1$ and $k(V^{3+}) \approx 0.2$ [22] one can reasonably obtain $k(V^{4+}) \approx 0.3$ here by extrapolation. Thus, the value $N \approx 0.84$ is obtained which is very close to that adopted ($N \approx 0.81$) in this work.

(2) The positive sign of the tetragonal compression $\Delta R(\approx 0.1$ Å) obtained in this work suggest that the oxygen octahedron around impurity V^{4+} ion exhibits tetragonally compressed distortion along C_4 axis, which is consistent with the ground state ${}^2b_2$ based on the experimental EPR results $g_{\parallel} < g_{\perp} < g_e$ and $| A_{\parallel} | > | A_{\perp} |$).

The local structure distortion can be explained by the Jahn-Teller effect. Because in compression, the ground state is nondegenerate singlet $^2b_2$, while in elongation, the ground state is degenerate doublet ^2e, it can be expected that the latter is unstable. Similar distortions caused by Jahn-Teller effect are also found for V^{4+} (or other d^1 ions, such as Nb^{4+} [23] and W^{5+} [24]) in many other glasses and crystals [20,25-26]. In addition, the crystal field parameters $D_q(\approx 1685\ \mathrm{cm}^{-1})$, $D_s(\approx -3257\ \mathrm{cm}^{-1})$ and $D_t(\approx 876\ \mathrm{cm}^{-1})$ obtained in present calculations are similar as V^{4+} in other crystals and glasses [2,20-21]. So, the tetragonal compression ΔR obtained in this work is reliable.

(3) The calculated results show that the hyperfine structure constants $A_{\|}$ and $A_{\perp}$ are negative as given in Table I, and the absolute values of them are in good agreement with the experimental values. It should be pointed out that the signs of the hyperfine structure constants are very difficult to determine. Thus, many experiments give them as absolute ones [1,2,6,21]. Our calculations indicate that both signs of $A_{\|}$ and $A_{\perp}$ are negative, this point is in accordance with the Ref. [7] and also be supported by the theoretical results for V^{4+} ions in many crystals [1,13,26] and glasses [20,25]. In fact, from the formulae of A constants (Eqs. (11) and (12)), one can find that the negative signs of A constants are determined by the negative anisotropic g-shifts ($g_{\|} - g_e$, $g_{\perp} - g_e$) and the negative terms related to core polarization constant κ which indicates the contribution to A constants by the unpaired s-electron. And the large value of $\kappa(\approx 0.84)$ leads to large magnitudes of the hyperfine structure constants. It seems that the displacement toward central ion for the two ligands along C_4 axis is larger than that (see Fig. 1) for the planar ligands may lead to more V^{4+} 3d-3s admixture and hence the larger κ. In addition, many previous works suggest that κ is within the range 0.6-1.0 for V^{4+} (or VO^{2+}) ions in various crystals and glasses [1,2,13,20,25,26]. The value of $\kappa(\approx 0.84)$ adopted in this work lies within the range and can be regarded as rational.

(4) The calculation errors of this work can be discussed as follows. First, the approximation of the theoretical model (the cluster approach) and third-order perturbation formulae adopted here can lead to some errors. Second, the covalency factor N obtained from those of the similar $[VO_6]^{8-}$ cluster may also introduce some errors into the calculated results. In fact, if one assumes an increase of the factor N by about 0.3%, the calculated results can be improved and show better agreement with the observed values (especially, the constants $A_{\|}$ and $A_{\perp}$) than Cal^c in Table I. Third, the bond length of VO^{2+} in cubic field is applied in the calculations of the group overlap integrals, which is not the actual metal-ligand distance. This would introduce small errors into the integrals and hence bring forward an influence on the final EPR parameters. The errors of the final g factors are estimated to be no more than 1% as the integrals change by 10%. Finally, the contributions to the EPR parameters from charge-transfer (CT) mechanism are not involved. Fortunately, these contributions are very small for the cluster $[VO_6]^{8-}$ [27] and can be reasonably ignored.

4. Conclusions

The defect structure and EPR parameters for the tetragonal VO^{2+} center in CaO-Al_2O_3-SiO_2 system are quantitatively studied from the high order (third order) perturbation formulae of these parameters including both the tetragonal distortion and the ligand orbitals contributions. The $[VO_6]^{8-}$ cluster is found to suffer the tetragonal compression by about 0.1 Å along the C_4 axis due to the Jahn-Teller effect. The negative signs of the constants $A_{\|}$ and $A_{\perp}$ are suggested in this work.

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