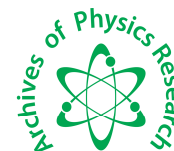




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# Theoretical investigations of the optical spectra and EPR parameters for $\text{VO}^{2+}$ in Zinc Potassium Phosphate Hexahydrate

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## ABSTRACT

The optical spectrum band positions and EPR parameters ( $g$  factors  $g_{//}$ ,  $g_{\perp}$  and hyperfine structure constants  $A_{//}$  and  $A_{\perp}$ ) for  $\text{VO}^{2+}$  ions in zinc potassium phosphate hexahydrate are theoretically studied from the complete diagonalization (of energy matrix) method (CDM). In the calculation, the contributions to the EPR parameters from the  $s$ - and  $p$ -orbitals as well as the spin-orbit coupling coefficient of the ligands are taken into account. The calculated EPR parameters and optical band positions show good agreement with the experimental data.

**Key words:** Electron paramagnetic resonance (EPR); Crystal-fields and Spin Hamiltonians;  $\text{VO}^{2+}$   $\text{ZnKPO}_4 \cdot 6\text{H}_2\text{O}$

## INTRODUCTION

Paramagnetic  $\text{VO}^{2+}$  ions which reflect the local symmetry and the structural properties of the host are widely used as probes in various crystalline materials and the electron paramagnetic resonance spectra of  $\text{VO}^{2+}$  ion in different diamagnetic host lattices have been studied by many workers to get information about the structure, dynamics and environment of the host lattices.<sup>[1-7]</sup> The  $\text{VO}^{2+}$  ion has the electronic configuration  $[\text{Ar}] 3d^1$  and the single unpaired spin leads to Paramagnetism in  $\text{VO}^{2+}$ . The behavior of the unpaired electron in  $\text{VO}^{2+}$  complexes is dominated by the strong  $\text{V}=\text{O}$  bond, as a results most of the complexes possess tetragonal symmetry with both  $g$  and  $A$  values found to be axially symmetric. For example, Ravikumar et al have studied the EPR and optical spectra of  $\text{VO}^{2+}$  ion doped zinc potassium phosphate hexahydrate ( $\text{ZnKPO}_4 \cdot 6\text{H}_2\text{O}$ , ZPPH) at room temperature<sup>[8]</sup>, and got the axial EPR parameters ( $g_{//}$ ,  $g_{\perp}$ ,  $A_{//}$ ,  $A_{\perp}$ ). According to the EPR and optical spectra, the paramagnetic impurity has entered the lattice only substitutionally and the local structure around the impurity is the  $C_{4v}$  symmetry.<sup>[8]</sup> But until now, these EPR experimental results have not been satisfactorily interpreted. For example, in the treatments of the  $g$  factors for a  $3d^1$  ion in tetragonally distorted octahedral based on the simple perturbation formulas and three adjustable

parameters ( $\epsilon^{*2}, \beta^{*2}, \kappa$ ) in Ref[8], the third-order and the higher order perturbation terms were ignored. And the ligand orbitals and spin-orbit coupling interactions were ignored as well. In order to investigate the observed results for the  $VO^{2+}$  ion in ZPPH to a good extent, the complete diagonalization (of energy matrix) method (CDM) based on the cluster approach are applied. In CDM, the contributions from the p- and s- orbitals as well as the spin-orbit coupling of the ligands are taken into account. The results are discussed.

## 2. Calculations

From the cluster approach, the one-electron basis functions for an octahedral  $d^n$  cluster can be written as:<sup>[9][10]</sup>

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

Where  $\varphi_\gamma$  (the subscript  $\gamma=e_g$  or  $t_{2g}$  represents the irreducible representation of  $O_h$  group) is the d-orbital of the  $3d^n$  ion.  $\chi_{p\gamma}$  and  $\chi_s$  are the p- orbital and s- orbital of ligand.  $N_\gamma$  (the normalization factors) and  $\lambda_\gamma$  (or  $\lambda_s$ ) (the orbital mixing coefficients) are the molecular orbital coefficients, The normalization relation can be written as<sup>[11]</sup>:

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

and the approximate relation can be given as<sup>[11]</sup>

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

Here  $N$  is the average covalency factor, characteristic of the covalency effect (or reduction of the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter) for the central ion in crystals.  $S_{d\gamma}$  (and  $S_{ds}$ ) are the group overlap integrals and can be calculated from the Slater-type self-consistent field functions with the impurity-ligand distance. 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.,  $\lambda_e / S_{dpe} \approx \lambda_s / S_{ds}$  within the same irreducible representation  $e_g$ . Thus, the spin-orbit coupling coefficients and the orbital reduction factors can be derived from the above equations:

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

where  $\zeta_d^0$  and  $\zeta_p^0$  are the spin-orbit coupling coefficients of the 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.

The Hamiltonian for the  $d^1$  ion in crystal-field can be written as<sup>[9]</sup>:

$$H = H_f + H_{so}(\zeta, \zeta') + H_{CF}(D_q, D_s, D_t) \tag{5}$$

Here  $H_f$  is the free-ion Hamiltonian.  $H_{so}(\zeta, \zeta')$  is the spin-orbit coupling interactions including two SO coupling parameters  $\zeta$  and  $\zeta'$ .  $H_{CF}$  is the crystal-field Hamiltonian for  $3d^1$  ion in tetragonal symmetry,  $D_q, D_s, D_t$  are the cubic field and the tetragonal field parameters respectively. According to the strong field basis functions in tetragonal

symmetry, one can get the 10×10 complete Hamiltonian matrix elements of the crystal field and spin-orbit coupling based on the two-SO-parameter model. Diagonalizing the energy matrix, one can get the eigenvalues (the energy levels and the optical spectrum band positions) and the wave functions of the ground state. For the spin doublet ground state, the wave function can be written as:

$$\begin{aligned}
 |\Phi^+\rangle &= c_1|\psi_{\xi}^-\rangle + c_2|\psi_{\eta}^-\rangle + c_3|\psi_{\zeta}^+\rangle + c_4|\psi_{\theta}^+\rangle + c_5|\psi_{\epsilon}^+\rangle \\
 |\Phi^-\rangle &= c_1|\psi_{\xi}^+\rangle + c_2|\psi_{\eta}^+\rangle + c_3|\psi_{\zeta}^-\rangle - c_4|\psi_{\theta}^-\rangle - c_5|\psi_{\epsilon}^-\rangle
 \end{aligned}
 \tag{6}$$

Where  $\psi$  is the LCAO molecular-orbitals for a 3d<sup>n</sup> ion in octahedra based on the cluster approach(see Eq.(1)). Considering the equivalence between the SH and Zeeman interaction, the g factors are:

$$\begin{aligned}
 g_{\parallel} &= 2\langle\Phi^+|L_z + g_e S_z|\Phi^+\rangle = 4(2c_3c_5k' - c_2c_1k) + g_e(1 - 2c_2^2 - 2c_1^2) \\
 g_{\perp} &= 2\langle\Phi^+|L_x + g_e S_x|\Phi^+\rangle = 2(-2\sqrt{3}c_1c_4k' + 2c_3c_2k - 2c_1c_5k) + g_e(2c_3^2 + 2c_2^2 - 1)
 \end{aligned}
 \tag{7}$$

where  $g_e$  ( $\approx 2.0023$ ) is the free-electron value,  $k'$  and  $k$  are the orbital reduction factors as mentioned in Eq.(4).  $L_z(L_x)$  and  $S_z(S_x)$  are the operators of orbit and spin angular momentums, respectively. The constants  $A_{\parallel}$  and  $A_{\perp}$  are related to the g factors. They can be written as<sup>[11]</sup>:

$$\begin{aligned}
 A_{\parallel} &= P[-\kappa - 4/7 + (g_{\parallel} - g_s)/7] \\
 A_{\perp} &= P'[-\kappa + 2/7 + 11(g_{\perp} - g_s)/14]
 \end{aligned}
 \tag{8}$$

Where  $P(=N_iP_0)$  and  $P'(= (N_iN_e)^{1/2}P_0)$  are the dipolar hyperfine constants, they are related to the interaction within  $t_{2g}$  state and between  $t_{2g}$  and  $e_g$  states, respectively.  $P_0$  is the dipolar hyperfine structure parameter of the free 3d<sup>1</sup> ion.  $\kappa$  is the isotropic core polarization constant. For present system, we have  $\zeta_d^0 \approx 248 \text{ cm}^{-1}$ <sup>[12]</sup>  $P_0 \approx 172 \times 10^{-4} \text{ cm}^{-1}$ <sup>[13]</sup> for  $V^{4+}$  and  $\zeta_p^0 \approx 151 \text{ cm}^{-1}$ <sup>[14]</sup> for  $O^{2-}$  respectively. the group overlap integrals  $S_{dpy}$  (and  $S_{ds}$ ) can be calculated from the Slater-type self-consistent field(SCF) functions<sup>[15,16]</sup> with the impurity -ligand distance R. For present system, the impurity-ligand length is unknown, but the V-O bond length ( $\approx 0.197\text{nm}$ ) is obtained for  $VO^{2+}$  in cubic field<sup>[17]</sup>, and we take  $R \approx 0.197\text{nm}$  here. thus we can calculate the group overlap integrals which are collected in the Table 1<sup>[18]</sup>. Applying the above parameters to the related equations, the spin-orbit coupling coefficients( $\zeta, \zeta'$ )、the molecular orbital coefficients ( $N_{\gamma}, \lambda_{\gamma}, \lambda_s$ ) can be got and shown in Table 1. Thus, by fitting the calculated optical band positions and EPR parameters to the experimental values. One can have

$$N \approx 0.778, \quad \kappa \approx 0.8, \quad D_q \approx 1490.7 \text{ cm}^{-1}, \quad D_s \approx -3854 \text{ cm}^{-1}, \quad D_t \approx 186 \text{ cm}^{-1},$$

The calculated results are shown in Table 2. For comparisons, the theoretical results of the molecular calculations based on three adjustable parameters in Ref[8] and those based on the traditional formulas in the absence of the ligand orbital and spin-orbit coupling contributions in Ref[11] are also obtained and collected in Table 2.

**Table 1. The group overlap integrals, molecular orbital coefficients  $N_{\gamma}$  and  $\lambda_{\gamma}$ (and  $\lambda_s$ ), spin-orbit coupling coefficients(in  $\text{cm}^{-1}$ ) and the orbital reduction factors for  $VO^{2+}$  in ZPPH**

$S_{dpt}$	$S_{dpe}$	$S_{ds}$	A	$N_i$	$N_e$	$\lambda_e$
0.0477	0.1239	0.0986	1.0206	0.7990	0.8588	0.5515
$\lambda_e$	$\lambda_s$	$\zeta$	$\zeta'$	$k$	$k'$	
0.4644	0.3699	216.5047	189.4143	0.9205	0.6360	

**Table 2. The optical spectrum band positions ( in  $\text{cm}^{-1}$ ) and EPR parameters for  $\text{VO}^{2+}$  ions in ZPPH**

	calculation			Experiment <sup>[8]</sup>
	Cal <sup>a</sup>	Cal <sup>b</sup>	Cal <sup>c</sup>	
${}^2\text{B}_2 \rightarrow {}^2\text{E}$	12492	--	12384	12496
	--	--	12599	
${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$	14920	--	14921	14921
${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$	29406	--	29400	29403
$g_{\parallel}$	1.936	1.922	1.936	1.936
$g_{\perp}$	1.976	1.978	1.971	1.976
$A_{\parallel}$	224	200	201	201
$A_{\perp}$	78	76	78	76

<sup>a</sup> calculations by using the simple perturbation formulas and three adjustable parameters in previous work<sup>[8]</sup>

<sup>b</sup>Calculations by using the high-order perturbation formulas which were given in Ref[11] but neglecting the ligand orbital contributions(i.e., taking  $\zeta = \zeta = N \zeta'_d$  and  $k = k' = N$ ) in this work.

<sup>c</sup>Calculations by using CDM in this work

### DISCUSSION

From Table 2, one can find that the calculated results based on the complete diagonalization of energy matrix method (CDM) including the ligand and orbital and spin-orbit coupling contributions are in good agreement with the experimental data. This means that the related parameters adopted in this work can be regarded as suitable.

(1) Seen from Table 2, the calculated results based on CDM are better than those (Cal<sup>b</sup> in Table 2) based on the simple formulas in the absence of the contributions from the ligand orbitals. In view of the high valence state of  $\text{V}^{4+}$ , the significant covalency ( or admixture) between the metal and ligand orbitals can be expected. This point can be illustrated by the small covalency factor  $N$  ( $\approx 0.778 < 1$ ) in equation (3) and the obvious mixing coefficients (see Table 1) obtained from the cluster approach in this work. This situation is also found in other crystals doped  $\text{V}^{4+}$  (vanadyl) ions.<sup>[11][18][19]</sup> 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 0.07 and 0.04 for the calculated  $g_{\parallel}$  and  $g_{\perp}$ . Obviously, for the impurity ion  $\text{V}^{4+}$  with high valence state in crystals, the above contributions would not to be ignored.

(2)The calculated hyperfine structure constants obtained in present work are better than those in the previous studies and are in good agreement with the experimental data. Many studies show that the core polarization  $\kappa$  in various  $\text{V}^{4+}$ (or  $\text{VO}^{2+}$ ) clusters in crystals is in the range 0.6-1.0<sup>[11][18][20][21]</sup>. The value  $\kappa \approx 0.8$  obtained in this work is within the range. This also suggests that the related parameters used here can be regarded as reasonable.

### CONCLUSION

In this work, the contributions from the ligand orbitals and spin-orbit coupling interactions are considered in the theoretical investigations of the EPR parameters for the  $\text{VO}^{2+}$  ions in ZPPH and the calculated EPR parameters based on the above contributions in this work are in good agreement with the experimental data.

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