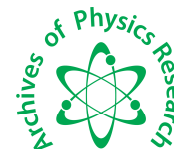




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Theoretical studies of the EPR parameters for VO^{2+} ions in $[\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$ single crystals

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ABSTRACT

In this work, the electron paramagnetic resonance (EPR) parameters g factors $g_{\parallel}$ and $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ of a tetragonal VO^{2+} center in $[\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$ crystal are theoretically studied 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 and the energy separations are correlated with the geometrical relationship of present studied tetragonal cluster. The calculated EPR parameters are in good agreement with the experimental data. The results are discussed.

Key words: Electron paramagnetic resonance (EPR); Crystal-fields and Spin Hamiltonians; VO^{2+} ; $[\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$

INTRODUCTION

Vanadyl ion (VO^{2+}) as the most stable cation among the molecular paramagnetic transition metal ions has been extensively used as a probe to study local structures and properties in doped crystals by means of Electronic paramagnetic resonance technique [1-10]. The VO^{2+} ion has the electronic configuration $[\text{Ar}] 3d^1$ and the single unpaired spin leads to Paramagnetism in VO^{2+} . The behavior of the unpaired electron in 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. This is supported by many EPR experiments^[1-10]. For example, Biyik et al have studied the EPR spectra of VO^{2+} ion doped ammonium tetroxalate dihydrate single crystals $([\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O})$, ATO hereafter) at room temperature^[6], and got the nearly axial EPR parameters ($g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$). According to the EPR spectra, the NH_4^+ ion is replaced by VO^{2+} ion which forming a $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ complex with its nearest neighbours has a tetragonally distorted octahedral symmetry^[6]. However, these EPR experimental results have not been satisfactorily interpreted. In order to investigate the observed results for the VO^{2+} ion in ATO to a good extent, the high order perturbation formulas of these parameter in tetragonal symmetry are applied. In these formulas, the energy separations are correlated with the local structure and the contributions from the s - and p - orbitals and the spin-orbit coupling coefficients of the ligands are taken into account for present covalent system^[6]. The results are discussed.

2. Calculations

For a $3d^1(\text{VO}^{2+})$ ion in tetragonally compressed octahedra, its higher orbital doublet ${}^2\text{E}_g$ of the original cubic case would split into two orbital singlets ${}^2\text{A}_{1g}(|z^2\rangle)$, and ${}^2\text{B}_{1g}(|x^2-y^2\rangle)$ while the original lower orbital triplet ${}^2\text{T}_{2g}$ would be separated into an orbital doublet ${}^2\text{E}_g(|xz\rangle \text{ and } |yz\rangle)$ and a singlet ${}^2\text{B}_{2g}(|xy\rangle)$, the latter lying lowest^{[6][11]}. From the cluster approach, the one-electron basis functions for an octahedral d^n cluster can be written as:^{[12][13]}

$$\psi_t = N_t^{1/2} (\varphi_t - \lambda_t \chi_{pt})$$

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

Where φ_γ (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 χ_s are the p-orbital and s-orbital of ligand. N_γ (the normalization factors) and λ_γ (or λ_s) (the orbital mixing coefficients) are the molecular orbital coefficients. The normalization relation can be written as: [13]

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

and the approximate relation can be expressed as [13]

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

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_{dpy} (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:

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

where ζ_d^0 and ζ_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. here $R \approx 0.197 \text{ nm}$ is taken for the VO^{2+} in cubic field [14]. From the distance R and Slater-type SCF functions [15][16], one can calculate the group overlap integrals which are collected in the Table 1.

By using the perturbation procedure similar to that in Refs[17][18], the two-SO-coupling coefficient formulas of the g factors and the hyperfine structure constants for the $3d^1$ ion in tetragonally compressed octahedra can be derived from the cluster approach [19].

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

where g_s (≈ 2.0023) is the spin-only value, P_0 is the dipolar hyperfine structure parameter of the free $3d^1$ ion. 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 obtained from the strong cubic field approach as follows:

$$\begin{aligned} E_1 &= E({}^2B_1) - E({}^2B_2) = 10 D_q \\ E_2 &= E({}^2E_2) - E({}^2B_2) = -3 D_s + 5 D_t \end{aligned} \quad (6)$$

Here D_q is the cubic field parameter and D_s , D_t tetragonal ones. From the superposition model and the geometrical relationship of the studied $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ cluster, they can be determined as follow:

$$\begin{aligned} D_s &= (4/7) \bar{A}_2(R_0) [(R_0/R_{\perp})^{t_2} - (R_0/R_{\parallel})^{t_2}] \\ D_t &= (16/21) \bar{A}_4(R_0) [(R_0/R_{\perp})^{t_4} - (R_0/R_{\parallel})^{t_4}] \end{aligned} \quad (7)$$

Where the t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents, $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference bonding length R_0 ($\approx 0.197 \text{ nm}$). For $3d^n$ octahedral clusters, the ratio $\bar{A}_2(R_0) \approx 10.8 \bar{A}_4(R_0)$ and

$\bar{A}_4(R_0) \approx \frac{3}{4} D_q$ have been proved to be valid in many crystals^{[19][20]}, and can be reasonably adopted here. For $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, to our knowledge, no optical spectra data were reported. However, the value $Dq \approx 2040 \text{ cm}^{-1}$ was estimated in the interpretation of the EPR parameters for $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ in DADT crystal^[21], and here we take $Dq \approx 2040 \text{ cm}^{-1}$. The crystal structure data $R_{\perp}$ and $R_{\parallel}$ denote the metal-ligand distances parallel and perpendicular to the tetragonal axis, respectively. Here we take the $R_{\perp} \approx R_0 \approx 0.197 \text{ nm}$ ^[14] and $R_{\parallel}$ as the adjustable parameter. Thus, by using the formulas of g factors and hyperfine structure constants, and fitting the calculated results to the experimental data, one can have

$$N \approx 0.94 \quad \kappa \approx 0.792 \quad R_{\parallel} \approx 1.55 \text{ nm}$$

the molecular orbital coefficients ($N_{\gamma}, \lambda_{\gamma}, \lambda_s$) can be got from equations (2) and (3) and shown in Table 1. the spin-orbit coupling coefficients (ζ, ζ'), the orbital reduction factors (k, k'), P, P' can be also obtained from the equation (4) and the free-ion values $\zeta_d \approx 248 \text{ cm}^{-1}$ and $P_0 \approx 136 \times 10^{-4} \text{ cm}^{-1}$ for V^{4+} ^[22] and $\zeta_p \approx 151 \text{ cm}^{-1}$ for O^{2-} ^[23] and also shown in table 1. The calculated EPR parameters are collected 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 ATO single crystal

S_{dpt}	S_{dpe}	S_{ds}	A	N_t	N_e	λ_t	
0.04773	0.12396	0.09863	1.02055	0.95254	0.99309	0.27593	
λ_e	λ_s	ζ	ζ'	k	k'	P	P'
0.26446	0.21010	241.7	235.9	0.9888	0.9084	129	132

Table 2. The EPR parameters for ATO: VO^{2+} crystal

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}/10^{-4} \cdot \text{cr}$	$A_{\perp}/10^{-4} \cdot \text{cm}^{-1}$
Cal ^a	1.9	1.9	-189.2	-68.2
Expt ^[b]	1.9	1.9	-195	-63.2

^a Calculations by using equation (5) and including the ligand orbital contributions in this work.

^b The signs of the experimental hyperfine structure constants were not given in Ref. [6]. Based on the theoretical calculations in this work and various observed results for V^{4+} (or VO^{2+}) in oxides [24], these signs should be negative.

DISCUSSION

(1) From Table 2, one can find that the calculated results based on the higher perturbation formulas including the ligand and orbital and spin-orbit coupling contributions are in good agreement with the experimental data. This suggests that the formulas and the related parameters adopted in this work can be regarded as suitable. In view of the high valence state of V^{4+} , the significant covalency (or admixture) between the metal and ligand orbitals can be expected. This point can be illustrated by the covalency factor N ($\approx 0.94 < 1$) 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 V^{4+} (vanadyl) ions^{[19][25][26]}. 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 0.01 and 0.03 for the calculated $g_{\parallel}$ and $g_{\perp}$.

(2) Based on the analysis of the EPR parameters, one can have the $R_{\parallel} \approx 0.155 \text{ nm}$, this means that the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ octahedron around V^{4+} ion is significantly compressed ($\Delta R = R_0 - R_{\parallel} \approx 0.042 \text{ nm}$). Similar local distortions were also found in other VO^{2+} ions doped crystals. For example, $\Delta R \approx 0.047 \text{ nm}$ and 0.039 nm were found for VO^{2+} in $\text{KZnClO}_4 \cdot 3\text{H}_2\text{O}$ ^{[14][25]} and DADT crystal^[21]. Therefore, the local distortion obtained in this study can be regarded as reasonable.

(3) The core polarization $\kappa \approx 0.792$ obtained in this work is closed to that of (≈ 0.735) VO^{2+} in DADT crystal^[21] and within the range 0.6-1.0 which is supported by many studies^{[19][28][29]}, this also suggests that the related parameters used here can be regarded as reasonable.

(4) the observed values of $A_{\parallel}$ and $A_{\perp}$ from the EPR experiment given in Ref[6] are positive. However, the theoretical calculations are negative (see Table 2). In fact, these negative signs of the hyperfine structure constants are supported by the experimental results for many octahedral VO^{2+} or V^{4+} clusters in various crystals^{[24][30]}. This means that the calculated results obtained here can be regarded as suitable.

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 VO^{2+} ions in ATO. On the basis of the studies, the oxygen octahedron around V^{4+} ion is significantly compressed along the C_4 axis ($\Delta R \approx 0.042 \text{ nm}$). The calculated EPR

parameters based on the above contributions and the local structure in this work are in good agreement with the experimental data.

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