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Theoretical investigations on the EPR parameters and optical spectra of VO^{2+} in $KZnClSO_4.3H_2O$

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ABSTRACT

In this work, the electron paramagnetic resonance (EPR) parameters g factors $g_{//}$ and $g_\perp$ and the hyperfine structure constants $A_{//}$ and $A_\perp$ of a tetragonal VO^{2+} center in $KZnClSO_4.3H_2O$ 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. The calculated EPR parameters and optical band positions in this work are in good agreement with the experimental data.

Key words: Crystal-fields and Spin Hamiltonians; VO^{2+} ; $KZnClSO_4.3H_2O$.

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[1-8]. The VO^{2+} ion has the electronic configuration [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 V=O bond, as a results most of the complexes possess C_{4v} symmetry with both g and A values found to be axially symmetric. This is supported by many EPR experiments. For example, Deva etal have studied the EPR and optical spectrum of VO^{2+} ion in $KZnClSO_4.3H_2O$ (Potassium zinc chloro sulphate triphydrate, PZCST) crystal [9]. From the EPR spectrum, they suggest that the VO^{2+} ion can occupy the substitutional and interstitial positions of Zn^{2+} in the PZCST crystal lattice. the spin Hamiltonian parameters $g_\parallel$ and $g_\perp$ and the hyperfine structure constants $A_\parallel$ and $A_\perp$ for the VO^{2+} ion in PZCST were theoretically treat on the basis of molecular calculations and various adjustable parameters. The contributions to g factors and A constants from the spin-orbit coupling coefficient of the ligand O^{2-} were ignored for the significant covalent system. the contributions from the ligand s-orbital were neglected as well. Actually, for the sake of the high valence state of the impurity V^{4+}, the covalence effect and hence the admixtures between the orbitals of the metal and the ligand ions may become significant. This point can be illustrated by V^{4+} ion in other complexes(for example, V^{4+} doped TiO_2[10]), and can be also illustrated by the lower observed hyperfine structure constants($A_\parallel \approx$-173 cm^{-1} and $A_\perp \approx$-64 cm^{-1}[9]) than VO^{2+} ion in some oxides(e.g., $A_\parallel \approx$-175.5 cm^{-1} and $A_\perp \approx$-68.2 cm^{-1} for GeO_2: VO^{2+}[11]). In addition, the third-order perturbation terms were neglected in their theoretical treatment. In order to explain the experimental spin hamiltonian parameters of PZCST crystal: VO^{2+} to a better extent, in this work, the anisotropic g factors and hyperfine structure constants of this center were investigated by the perturbation formulas of a $3d^1$ ion in tetragonally compressed octahedra. In these formulas, the contributions from the s- and p- orbitals and the spin-orbit coupling coefficients of the ligands are taken into account based on the cluster approach.

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MATERIALS AND METHODS

For a $3d^1$(VO^{2+}) ion in tetragonally compressed octahedra, its higher orbital doublet ^2E_g of the original cubic case would split into two orbital singlets $^2A_{1g}$ ($|z^2>$),and $^2B_{1g}$ ($|x^2-y^2>$) while the original lower orbital triplet $^2T_{2g}$ would be separated into an orbital doublet $2E_g$ ($|xz>$ and $|yz>$) and a singlet $^2B_{2g}$ ($|xy>$), the latter lying lowest[9]. From crystal- and ligand-field theory, the LCAO molecular-orbitals can be expressed as the one-electron basic functions:[12][13]

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

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

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 are the p- orbital and s- orbital of ligand. N_γ(the normalization coefficient)and λ_γ (or λ_s)(the orbital mixing coefficients.) are the molecular orbital coefficients. The normalization relation can be given as:[14]

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

And the approximate relation can be expressed as[14]:

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

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}) denote 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.

By using the perturbation procedure similar to that in [15,16], 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.

$$g_\square = g_s - 8 k'\zeta'/E_1 - 2k\zeta'^2/E_2^2 + 2 k'\zeta'^2/E_1^2$$
$$g_\square = g_s - 2k\zeta'/E_2 + 2 k'\zeta'\zeta[1/E_1 E_2 - 1/E_1^2]$$

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

where g_s (≈ 2.0023) is the spin-only value, P is the dipolar hyperfine structure parameter of the free $3d^1$ ion. For free V^{4+} ion, we have $P \approx 172 \times 10^{-4} cm^{-1}$[17]. κ is the isotropic core polarization constant. Based on the cluster approach, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' can be written as:

$$\zeta = N_t (\zeta_d + \lambda_t^2 \zeta_p/2) \qquad \zeta' = (N_t N_e)^{1/2} (\zeta_d - \lambda_t \lambda_e \zeta_p/2)$$
$$k = N_t (1 + \lambda_t^2/2) \qquad k' = (N_t N_e)^{1/2} [1 - \lambda_t (\lambda_e + \lambda_s A)/2] \tag{5}$$

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. here $R \approx 0.197nm$ is taken for the VO^{2+} in cubic field[18]. From the distance R and Slater-type SCF functions[19,20], the integrals $S_{dpt} \approx 0.047726$, $S_{dpe} \approx 0.12396$, $S_{ds} \approx 0.09863$, and $A \approx 1.02055$ are obtained.

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:

$$E_1 = E(^2B_2) - E(^2B1) = 10 D_q$$
$$E_2 = E(^2B_2) - E(^2E2) = -3 D_s + 5D_t \tag{6}$$

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Here D_q is the cubic field parameter and D_s, D_t tetragonal ones. Thus, by using the formulas of g factors and hyperfine structure constants, and fitting the calculated results to the experimental data, one can have

$$N \approx 0.81 \qquad \kappa \approx 0.538$$

The values $N_t \approx 0.8299$, $N_e \approx 0.8871$, $\lambda_t \approx 0.5029$, $\lambda_e \approx 0.4294$ and $\lambda_s \approx 0.3471$ are calculated from equations (2) and (3). Then the parameters $\zeta \approx 221.67$ cm^{-1}, $\zeta' \approx 198.80$ cm^{-1}, $k \approx 0.9349$ and $k' \approx 0.6902$ can be determined from equation (5) 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 calculated EPR parameters and three optical spectrum band positions are collected in table 1 and 2.

Table 1.   The EPR parameters for PZCST: VO^{2+} crystal

	$g_\parallel$	$g_\perp$	$A_\parallel/10^{-4} \cdot cm^{-1}$	$A_\perp/10^{-4} \cdot cm^{-1}$
Cal[a]	1.927	1.986	-183	65
Cal[b]	1.936	1.974	-171	-64
Expt[[9]	1.936	1.988	-173	-64

[a] Calculations by using the simple perturbation formulas and adjusting various parameters in the previous work[9]
[b] Calculations by using equation (4) and including the ligand orbital contributions in this work.

Table 2.   The optical spectrum band positions for VO^{2+} in PZCST crystal

assignment	Cal/ cm^{-1}	Expt[9]/ cm^{-1}
$^2B_2 \rightarrow {}^2E$	14407	14405
$^2B_2 \rightarrow {}^2B_1$	16497	16497
$^2B_2 \rightarrow {}^2A_1$	25764	25765

RESULTS AND DISCUSSION

From Table 1, one can find that the calculated EPR parameters of VO^{2+} in $KZnClSO_4.3H_2O$ based on the higher perturbation formulas including the ligand orbital contributions are in good agreement with the observed values, This suggests that the formulas and the related parameters adopted in this work can be regarded as suitable. The theoretical g factors and hyperfine structure constants obtained in this study are slightly better than those in the ref[9]. Based on the formulas of the g factors and A constants within the scheme of the conventional crystal-field theory in Ref[9], the observed values were interpreted by various adjustable parameters(β^2, ε^2 P, κ) and neglecting the contributions from the SO coupling coefficient and the orbitals of the ligands. 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 small covalency factor N ($\approx 0.81 < 1$) in equation (3) and the obvious mixing coefficients ($\lambda_t \approx 0.5029$, $\lambda_e \approx 0.4294$ and $\lambda_s \approx 0.3471$) obtained in present 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.

It can be seen from Table 2 that the calculated energy separations show very good agreement with the experimental data. The crystal-field parameters D_q and D_s, D_t are about 1649.7 cm^{-1}, 3382.5 cm^{-1}, 851.5 cm^{-1}, respectively. If one assumes a decrease of the metal-ligand distances parapell(i.e the V=O bond length) to the tetragonal axis by about 0.03nm, the tetragonal field parameters(D_s, D_t) can be obtained from Newman′s superposition model. This value is closed to 0.047nm which can be obtained from refs[2] and [18]. This suggests that the oxygen octahedron around V^{4+} ion is significantly compressed along the C_4 axis. Considering that the radius of V^{4+}(≈ 0.063nm[23]) is smaller than that of Zn^{2+}(≈ 0.074nm[24]) and that the difference in electronegativities between the two ions, the local lattice distortion can be understood.

CONCLUSION

In this paper, the EPR parameters for a tetragonal VO^{2+} center in $KZnClSO_4.3H_2O$ crystal are theoretically studied from the high order perturbation formulas of these parameters including the ligand contributions. The calculated

EPR parameters and optical band positions are in good agreement with the observed values.

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