ABSTRACT

In this work, the electron paramagnetic resonance (EPR) parameters $g$ factors $g_∥$ and $g_⊥$ and the hyperfine structure constants $A_∥$ and $A_⊥$ of a tetragonal VO$^{2+}$ center in KZnClSO$_4$.3H$_2$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. 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$_2$O.

INTRODUCTION

Vanadyl ion (VO$^{3+}$) 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 et al have studied the EPR and optical spectrum of VO$^{2+}$ ion in KZnClSO$_4$.3H$_2$O (Potassium zinc chloro sulphate trihydrate, 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 $g_∥$ and $g_⊥$ and the hyperfine structure constants $A_∥$ and $A_⊥$ for the VO$^{2+}$ ion in PZCST were theoretically treated 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$^-$ 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($A_∥$=-173 cm$^{-1}$ and $A_⊥$=-64 cm$^{-1}$[9]) than VO$^{2+}$ ion in some oxides(e.g., $A_∥$=-175.5 cm$^{-1}$ and $A_⊥$=-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.
MATERIALS AND METHODS

For a 3d(VO$^{2+}$) ion in tetragonally compressed octahedra, its higher orbital doublet 2$^2$E of the original cubic case would split into two orbital singlets 2$^1$A$_{1g}$ (|z$^2$>,) and 2$^1$B$_{1g}$ (|x$^2$−y$^2$>) while the original lower orbital triplet 2$^3$T$_{2g}$ would be separated into an orbital doublet 2E$_g$ (|yz> and |xz>) and a singlet 2$^1$B$_{2g}$ (|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]

ψ_{e} = N_{e}^{1/2} (\phi_{e} - \lambda_{e} \chi_{d})

ψ_{g} = N_{g}^{1/2} (\phi_{g} - \lambda_{g} \chi_{d})

(1)

Where $\phi_{e}$ (the subscript $e$ or $t$ represents the irreducible representation of O$_h$ group) is the d-orbital of the 3d$^n$ ion. $\chi_{d}$ and $\chi_{f}$ are the p- orbital and s- orbital of ligand. $N_{s}$ (the normalization coefficient) and $\lambda_{s}$ (or $\lambda_{f}$) (the orbital mixing coefficients) are the molecular orbital coefficients. The normalization relation can be given as:[14]

$N_{s} (1 - 2 \lambda_{s} \chi_{d} + \lambda_{s}^2) = 1$

$N_{f} (1 - 2 \lambda_{f} \chi_{d} - 2 \lambda_{f} \chi_{d} + \lambda_{f}^2 + \lambda_{f}^2) = 1$

(2)

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

$N_{e} = N_{e}^2 \left[ 1 + \lambda_{e}^2 \chi_{d}^2 - 2 \lambda_{g} \chi_{d} \right]$

$N_{g} = N_{g}^2 \left[ 1 + \lambda_{g}^2 \chi_{d}^2 + 2 \lambda_{e} \chi_{d} - 2 \lambda_{g} \chi_{d} - 2 \lambda_{s} \chi_{d} \right]$

(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. $S_{dpt}$ (and $S_{d}$) 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., $\lambda_{s}/S_{dpt} = \lambda_{s}/S_{s}$ within the same irreducible representation $e_c$.

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:

$g_{e} = g_{r} - 8 k \zeta / E_{z} + 2 k \lambda_{s} / E_{z}^2$

$g_{e} = g_{r} - 2 k \zeta / E_{z} + 2 k \lambda_{s} / E_{z}^2$

$A_{e} = P[-k^4 N_{e}^2 / 2 + (g_{e} - g_{r}) + 6(g_{e} - g_{r})]$

$A_{e} = P[-k^2 N_{e}^2 / 2 + 11(g_{e} - g_{r})]$

(4)

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

$\zeta = N_{s} (\zeta_{s} + \lambda_{s} \zeta_{d}^2 / 2)$

$\zeta' = (N_{t} N_{s} / 2) (\zeta_{s} - \lambda_{e} \zeta_{d} / 2)$

$k = N_{t} (1 + \lambda_{s} \zeta_{d}^2 / 2)$

$k' = (N_{t} N_{s} / 2) [1 - \lambda_{s} (\zeta_{s} + \lambda_{s} A) / 2]$

(5)

where $\zeta_{d}$ and $\zeta_{s}$ are the spin-orbit coupling coefficients of the 3d$^n$ and ligand ions in free states, respectively. $A$ denotes the integral $R_{ns} \int \left[ \frac{\partial}{\partial \phi_{d}} n_{P_{d}} \right] \phi_{d}$. Where $R$ is the impurity-ligand distance in the studied system. Here R=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 $S_{dpt}$=0.047726, $S_{dpt}$=0.12396, and $S_{d}$=0.09863, and $A$=1.02055 are obtained.

The energy denominators $E_{1}$ and $E_{2}$ stand for the energy separations between the excited $^2$B$_{1}$, $^2$E and the ground $^2$B$_{2}$ states. They can be obtained from the strong cubic field approach as follows:

$E_{1}$ = $E(2B_{1})$ - $E(2B_{2})$ = 10 D$_{q}$

$E_{2}$ = $E(2B_{2})$ - $E(2E)$ = -3 D$_{q}$+5D$_{t}$

(6)
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

$$N = 0.81 \quad \kappa = 0.538$$

The values $N_t = 0.8299$, $N_e = 0.8871$, $\lambda_t = 0.5029$, $\lambda_e = 0.4294$ and $\lambda_e = 0.3471$ are calculated from equations (2) and (3). Then the parameters $\zeta = 0.047\text{nm}$ which can be obtained from refs[2] and [18].

$$0.5029, \approx \text{theoretical } g\text{ factors and hyperfine structure constants obtained in this study are slightly better than those in the ref[9].}$$

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 ($\beta$, $\epsilon^2$, $P$, $\kappa$) 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 $N = (0.81\cdot1)$ in equation (3) and the obvious mixing coefficients ($\lambda_t = 0.5029$, $\lambda_e = 0.4294$ and $\lambda_e = 0.3471$) 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 $D_t$, $D_s$, $D_e$ are about 1649.7 cm$^{-1}$, 1649.6 cm$^{-1}$, 851.5 cm$^{-1}$, respectively. If one assumes a decrease of the metal-ligand distances parallel(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 close 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.

### RESULTS AND DISCUSSION

From Table 1, one can find that the calculated EPR parameters of VO$^{2+}$ in KZnCISO$_4$·3H$_2$O 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 ($\beta$, $\epsilon^2$, $P$, $\kappa$) 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 $N = (0.81\cdot1)$ in equation (3) and the obvious mixing coefficients ($\lambda_t = 0.5029$, $\lambda_e = 0.4294$ and $\lambda_e = 0.3471$) 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.

CONCLUSION

In this paper, the EPR parameters for a tetragonal VO$^{2+}$ center in KZnCISO$_4$·3H$_2$O crystal are theoretically studied from the high order perturbation formulas of these parameters including the ligand contributions. The calculated

### Table 1. The EPR parameters for PZCST: VO$^{3+}$ crystal

<table>
<thead>
<tr>
<th></th>
<th>$g_{|}$</th>
<th>$g_{\perp}$</th>
<th>$A_1/10^4\text{cm}^{-1}$</th>
<th>$A_2/10^4\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal$^a$</td>
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<td>65</td>
</tr>
<tr>
<td>Cal$^b$</td>
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<td>1.974</td>
<td>-171</td>
<td>-64</td>
</tr>
<tr>
<td>Expt$^b$</td>
<td>1.936</td>
<td>1.988</td>
<td>-173</td>
<td>-64</td>
</tr>
</tbody>
</table>

$^a$ 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>
<thead>
<tr>
<th>Assignment</th>
<th>Cal/ cm$^{-1}$</th>
<th>Expt[9]/ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3!B_2!!!\to^5!E$</td>
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<td>14405</td>
</tr>
<tr>
<td>$^3!B_2!!!!\to^5!B_2$</td>
<td>16497</td>
<td>16497</td>
</tr>
<tr>
<td>$^3!B_2!!!!\to^7!A_1$</td>
<td>25764</td>
<td>25765</td>
</tr>
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</table>

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

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

REFERENCES