Investigation of the Spin Hamiltonian Parameters of a Tetragonal VO^{2+} Center in $(NH_4)_2SbCl_5$

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The spin Hamiltonian parameters $g_{\parallel}$ and $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ of a tetragonal VO^{2+} center in $(NH_4)_2SbCl_5$ are investigated, using the perturbation formulas for a $3d^1$ ion in tetragonally compressed octahedra. 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 Cl^- ligand are taken into account, based on the cluster approach. According to these studies, compression of the ligand octahedra results from the strong axial crystal-fields due to the short V^{4+}-O^{2-} bond in the $[VOCl_4]^{2-}$ cluster. The obtained spin Hamiltonian parameters agree well with the experimental data and need fewer adjustable parameters than the previous studies. The covalency of the studied system is also discussed.

Key words: Electron Paramagnetic Resonance; Crystal-Fields and Spin Hamiltonians; VO^{2+}; $(NH_4)_2SbCl_5$.

1. Introduction

Vanadyl (VO^{2+}) has advantages as probe in studying local structures and properties in doped crystals [1 – 7]. Especially, pentacoordinated clusters (with approximately C_{4v} symmetry) having an apical ligand different from the other four are of particular importance because of the short metal-oxygen bond along the C_4 axis and significant covalency of the systems [8 – 10]. For example, the tetragonal VO^{2+} center (i. e. $[VOCl_4]^{2-}$ cluster) was observed in $(NH_4)_2SbCl_5$:VO^{2+}, and its spin Hamiltonian parameters $g_{\parallel}$ and $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ were measured by means of electron paramagnetic resonance [11]. These experimental results were theoretically treated on the basis of molecular orbital calculations and various adjustable parameters [11]. However, the contributions (to $g_{\perp}$ and $A_{\perp}$) from the spin-orbit coupling coefficient of the ligand Cl^-, which is much larger than that of the central ion, were not taken into account [11]. The contributions from the ligand s-orbitals were neglected as well, and, many adjusted parameters (i. e., the molecular orbital coefficients β, β_1 and γ, the spin-orbit coupling coefficient λ, the dipolar hyperfine structure parameter P and the core polarization constant κ) were introduced in the studies. Finally, the molecular orbital coefficients corresponding to the orbitals of the central ion were almost unity (that for ^2E representation was even larger than unity), suggesting a dominant (more than 98%) ionic nature of the bonds [11]. In fact, the $[VOCl_4]^{2-}$ cluster may have significant covalency due to the high valence state of V^{4+}. This point can be illustrated by the observed hyperfine structure constants $A_{\parallel} \approx -168.8(1) \cdot 10^{-4}$ cm^{-1} and $A_{\perp} \approx -62.0(1) \cdot 10^{-4}$ cm^{-1} (note: only the absolute values were given in [11]), which are lower than those for VO^{2+} in some oxides (e. g., $A_{\parallel} \approx -175.5 \cdot 10^{-4}$ cm^{-1} and $A_{\perp} \approx -68.2 \cdot 10^{-4}$ cm^{-1} for GeO_2:VO^{2+} [12]). In order to interpret further the experimental spin Hamiltonian parameters of $(NH_4)_2SbCl_5$:VO^{2+}, in this work the anisotropic g factors and the hyperfine structure constants of this center were investigated by the perturbation formulas of these parameters for 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.

2. Calculations

In VO^{2+} doped $(NH_4)_2SbCl_5$, V^{4+} may occupy the host pentacoordinated Sb^{3+} site due to their similar charge, despite the size mismatch [11]. Since V^{4+} has an extra charge compared with the replaced Sb^{3+}, the apical ligand Cl^- along the pseudo-C_4 axis can be substituted by an oxygen ion as charge compensation. Thus, the tetragonal $[VOCl_4]^{2-}$ cluster is formed. Because of the smaller ionic radius and greater charge of O^{2-} compared to Cl^-, the former would shift towards the central V^{4+} due to its stronger electrostatic attraction. Therefore, the studied cluster has a shorter and stronger V^{4+}-O^{2-} bond along the C_4 axis compared to the other four longer and weaker V^{4+}-Cl^- bonds in the perpendicular direction, corresponding to a compressed octahedron.

For the VO^{2+} ($3d^1$) ion in compressed octahedra, its higher orbital doublet ^2E_g of the original cubic case would split into two orbital singlets $^2B_{1g}$ $(|x^2-y^2\rangle)$ and $^2A_{1g}$ $(|z^2\rangle)$, while the original lower orbital triplet $^2T_{2g}$ would be separated into an orbital doublet ^2E_g $(|xz\rangle$ and $|yz\rangle)$ and a singlet $^2B_{2g}$ $(|xy\rangle)$, the latter lying lowest [13, 14].

As mentioned before, the treatments in [11] did not include the contributions (to the spin Hamiltonian parameters in the perpendicular direction) from the spin-orbit coupling interaction of the ligands, which can be much larger than those from the central ion. By considering the above contributions and the perturbation procedure similar to that in [15, 16], the formulas of the g factors and the hyperfine structure constants for the $3d^1$ ion in tetragonally compressed octahedra can be expressed on the basis of the cluster approach:

$$\begin{aligned}
g_\parallel &= g_s - 8k'\zeta'/E_1 - k\zeta^2/E_1^2 + 2k'\zeta'^2/E_2^2,\\
g_\perp &= g_s - 2k\zeta/E_1 + 2k'\zeta'\zeta[1/(E_1E_2) - 1/E_2^2],\\
A_\parallel &= P[-\kappa - 4/7 + (g_\parallel - g_s) + 3(g_\perp - g_s)/7],\\
A_\perp &= P'[-\kappa + 2/7 + 11(g_\perp - g_s)/14],
\end{aligned} \tag{1}$$

where g_s (≈ 2.0023) is the pure spin value and κ is the core polarization constant. The denominators E_1 and E_2 are the energy separations between the excited $^2B_{1g}$ and ^2E_g and the ground $^2B_{2g}$ states [13, 14]. They can be expressed in terms of the tetragonal field parameters Ds and Dt and the cubic field parameter Dq:

$$E_1 = 3Ds - 5Dt, \quad E_2 = 10Dq. \tag{2}$$

Based on the cluster approach, the spin-orbit coupling coefficients ζ and ζ', the orbital reduction factors k and k', and the dipolar hyperfine structure parameters P and P' in (1) may be written as

$$\begin{aligned}
\zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),\\
\zeta' &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2),\\
k &= N_t(1 + \lambda_t^2/2),\\
k' &= (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2],\\
P &= N_tP_0, \quad P' = (N_tN_e)^{1/2}P_0,
\end{aligned} \tag{3}$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the $3d^1$ and the ligand ions in free states, respectively. P_0 is the dipolar hyperfine structure parameter of the free $3d^1$ ion. 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 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 γ $(= e_g$ and $t_{2g})$. They are usually determined from the normalization conditions

$$\begin{aligned}
&N_t(1 - 2\lambda_tS_{dpt} + \lambda_t^2) = 1,\\
&N_e(1 - 2\lambda_eS_{dpe} - 2\lambda_sS_{ds} + \lambda_e^2 + \lambda_s^2) = 1,
\end{aligned} \tag{4}$$

and the approximate relationship

$$\begin{aligned}
N^2 &= N_t^2[1 + \lambda_t^2S_{dpt}^2 - 2\lambda_tS_{dpt}],\\
N^2 &= N_e^2[1 + \lambda_e^2S_{dpe}^2 + \lambda_s^2S_{ds}^2 - 2\lambda_eS_{dpe} - 2\lambda_sS_{ds}].
\end{aligned} \tag{5}$$

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 spin-orbit coupling coefficient and the dipolar hyperfine structure parameter) for the central ion in crystals. In general, the mixing coefficients increase with increasing 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.

From the superposition model [17] and the geometrical relationship of the studied $[VOCl_4]^{2-}$ cluster, the tetragonal field parameters can be determined as

$$\begin{aligned}
Ds &= (4/7)[\bar{A}_2(Cl^-) - \bar{A}_2(O^{2-})],\\
Dt &= -(16/21)[\bar{A}_4(Cl^-) - \bar{A}_4(O^{2-})].
\end{aligned} \tag{6}$$

Here $\bar{A}_2(L)$ and $\bar{A}_4(L)$ are the intrinsic parameters for the ligand L (= Cl^-, O^{2-}). For $3d^n$ octahedral clusters, $\bar{A}_4 \approx (3/4)Dq$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ have been proved to be valid in many crystals [18 – 21] and can be reasonably adopted here. According to the optical absorption spectra of some V^{4+} doped oxides and chlorides [14, 22], the cubic field parameters $Dq(O^{2-}) \approx 2000\ \mathrm{cm}^{-1}$ and $Dq(Cl^{-}) \approx 1440\ \mathrm{cm}^{-1}$ can be obtained. Thus, the total (or effective) cubic field parameter $Dq \approx [Dq(O^{2-}) + 4Dq(Cl^{-})]/5 \approx 1552\ \mathrm{cm}^{-1}$ is calculated for the $[VOCl_4]^{2-}$ cluster.

For the studied system, since the ionic radius r_i (≈ 0.63 Å [23]) of the impurity V^{4+} is smaller than the radius r_h (≈ 0.76 Å [23]) of the host Sb^{3+}, the effective distance R from the central V^{4+} to the planar Cl^{-} ligands can be estimated from the empirical formula $R \approx R_\mathrm{H} + (r_\mathrm{i} - r_\mathrm{h})/2$ [24, 25], which has been proved to be valid for many transition-metal ions in crystals by investigations on the experimental superhyperfine constant, EXAFS measurements and crystal-field spectrum analyses. Here R_H (≈ 2.62 Å [11]) is the host Sb^{3+}-Cl^{-} distance perpendicular to the C_4 axis in the pure crystal. Thus, we obtain $R \approx 2.555$ Å here. From the distance R and the Slater-type SCF functions [26, 27], the integrals $S_\mathrm{dpt} \approx 0.0184$, $S_\mathrm{dpe} \approx 0.0591$, $S_\mathrm{ds} \approx 0.0331$ and $A \approx 1.3236$ are obtained. The average covalency factor N (≈ 0.87) can be obtained for the isoelectronic octahedral Ti^{3+} cluster in LiF [28]. Since the covalency of the V^{4+}-Cl^{-} bonds in this work is stronger than that of the Ti^{4+}-F^{-} bonds in LiF:Ti^{3+}, one can approximately take $N \approx 0.82$ here. Thus, the mixing coefficients $\lambda_\mathrm{t} \approx 0.482$, $\lambda_\mathrm{e} \approx 0.438$ and $\lambda_\mathrm{s} \approx 0.245$ are calculated from (4) and (5), and the parameters $\zeta \approx 260\ \mathrm{cm}^{-1}$, $\zeta' \approx 155\ \mathrm{cm}^{-1}$, $k \approx 0.919$, $k' \approx 0.681$, $P \approx 141 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ and $P' \approx 143 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ are also determined from (3) and the free-ion values $\zeta_\mathrm{d}^0 \approx 248\ \mathrm{cm}^{-1}$ [13] and $P_0 \approx 172 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ [29] for V^{4+} and $\zeta_\mathrm{p}^0 \approx 587\ \mathrm{cm}^{-1}$ for Cl^{-} [30]. Note that the contributions from the spin-orbit coupling and the orbitals of the ligand Cl^{-} are treated as the cubic octahedral cluster, and those from the apical oxygen ion is ignored because of its much smaller ζ_p^0 ($\approx 151\ \mathrm{cm}^{-1}$ [31]) compared with that of Cl^{-}.

The core polarization constant in the formulas of the hyperfine structure constants is taken as $\kappa \approx 0.66$. This value is close to that (≈ 0.75 [32, 33]) for the isoelectronic Ti^{3+} and can be regarded as suitable. Substituting these parameters into (1), the spin Hamiltonian parameters for the tetragonal VO^{2+} center are calculated and shown Table 1. For comparisons, the theoretical results of the molecular orbital calculations in [11] and those based on the conventional formulas (of [15, 16]) in the absence of the ligand orbital and spin-orbit coupling contributions (i. e., taking $\lambda_\mathrm{i} = 0$, $\zeta_\mathrm{p}^0 = 0$ and then $\zeta = \zeta' = N\zeta_\mathrm{d}^0$, $k = k' = N$ and $P = P' = NP_0$) are also obtained and collected in Table 1.

Table 1. The spin Hamiltonian parameters of the tetragonal VO^{2+} center in $(NH_4)_2SbCl_5$.

	Cal.[a]	Cal.[b]	Cal.[c]	Expt.[d] [11]
$g_\parallel$	1.9483	1.9172	1.9478	1.9478 (1)
$g_\perp$	1.9795	1.9671	1.9796	1.9793 (1)
$A_\parallel$ ($10^{-4}\ \mathrm{cm}^{-1}$) [d]	−165.4	−171.6	−168.2	−168.8 (1)
$A_\perp$ ($10^{-4}\ \mathrm{cm}^{-1}$) [d]	−64.0	−63.3	−63.1	−62.8 (1)

[a] Calculations by using the molecular orbital coefficients close to unity based on the molecular orbital calculations in the previous work [11].

[b] Calculations by using the perturbation formulas (1) and neglecting the contributions from the ligand orbital and spin-orbit coupling contributions (i. e., taking $\lambda_\gamma = 0$, $\zeta_\mathrm{p}^0 = 0$ and then $\zeta = \zeta' = N\zeta_\mathrm{d}^0$, $k = k' = N$ and $P = P' = NP_0$, corresponding to the conventional formulas in [15, 16]).

[c] Calculations by using (1) and including the contributions from the ligand orbital and spin-orbit coupling contributions based on the cluster approach.

[d] The signs of the experimental hyperfine structure constants are not given in [11]. Based on the theoretical calculations in the present work (and also [11]) and various observed results for VO^{2+} (or V^{4+}) in some compressed octahedra [12, 30], these signs should be negative.

3. Discussion

From Table 1, one can find that the calculated spin Hamiltonian parameters based on the perturbation formulas established in this work by considering the ligand orbital and spin-orbit coupling contributions show better agreement with the experimental data than those in the absence of the above contributions. This means that the contributions to the spin Hamiltonian parameters (including $g_\perp$ and $A_\perp$) from the ligand orbitals and spin-orbit coupling interaction are important and should be considered in the analyses of electron paramagnetic resonance results. Further, inclusion of the ligand s-orbital contributions, which were ignored in [11], can also yield better theoretical results than those containing only ligand p-orbital contributions. In addition, the resulting spin Hamiltonian parameters exhibit a slight improvement compared with those based on the molecular calculations in the previous work [11], although fewer adjustable parameters (the covalency factor N and the core polarization constant κ) than those in [11] (the molecular orbital coefficients β, β_1 and γ, the spin-orbit coupling coefficient λ, the dipolar hyperfine structure parameter P and the core polarization constant κ) are adopted in this work.

1. The small N ($\approx 0.82 < 1$) as well as the moderate mixing coefficients ($\lambda_t \approx 0.482$, $\lambda_e \approx 0.438$ and $\lambda_e \approx 0.245$) obtained here reveal significant admixture between the metal and ligand orbitals in the studied system containing considerably covalent V^{4+} of high valence state. Meanwhile, the ratios $(\zeta + \zeta')/2/\zeta_d^0$ (≈ 0.84) and $(P+P')/2/P_0$ (≈ 0.83), as well as the average $(k+k')/2$ (≈ 0.80) in the present work, approximately account for the covalency effect. This point may be illustrated by the comparable optical electronegativity ($\approx$ 2.6 [22]) for V^{4+} with that ($\approx$ 3.0 [22]) for Cl^-, as indication of significant covalency for this metal-ligand combination. In contrast, the molecular orbital coefficients in [11] were very close to unity, especially the coefficient γ for the E_g state was even larger than unity. These coefficients could be interpreted as dominant ionicity of the bonds. However, the above interpretation would be incompatible with the much smaller adjusted spin-orbit coupling coefficient 148 cm^{-1} [11] than the free-ion value ζ_d^0 ($\approx$ 248 cm^{-1} [13]). Therefore, the theoretical calculations and the related parameters based on the cluster approach applied in this work can be regarded as more suitable. The validity of the average covalency factor N can be further illustrated by the relationship [34]

$$N^2 = 1 - h(\mathrm{L})\,k(\mathrm{M}), \tag{7}$$

where the parameters h(L) ($\approx$ 1.0 and 2.0) are the characteristic of the ligands L (= O^{2-} and Cl^-), and k(M) is the characteristic of the central metal ion. From the values $k(V^{2+}) \approx 0.1$ and $k(V^{3+}) \approx 0.15$, one can reasonably obtain $k(V^{4+}) \approx 0.20$ here by extrapolation. Thus, we have N of about 0.89 and 0.77 for O^{2-} and Cl^-, respectively, whose average (≈ 0.83) is close to that ($N \approx 0.82$) adopted in this work.

2. The local structure (or tetragonal distortion) of the studied system is originated from the much stronger axial crystal-fields due to the short V^{4+}-O^{2-} bond. Since the oxygen ligand has a smaller ionic radius and a greater charge than the original Cl^-, the former would be attracted towards the central V^{4+} due to the stronger electrostatic interaction. Therefore, in this cluster, the V^{4+}-O^{2-} bond along the C_4 axis is much shorter and stronger than the other four V^{4+}-Cl^- bonds. This results in the considerably compressed ligand octahedron, corresponding to the tetragonal field parameters $Ds \approx -2592$ cm^{-1} and $Dt \approx 320$ cm^{-1}.

3. The signs of the experimental $A_\parallel$ and $A_\perp$ were not given in [11]. Nevertheless, the theoretical studies in this work and the molecular orbital calculations for some VO^{2+} complexes in previous works [11, 35] yield negative signs of the A factors due to the relatively larger contributions from κ compared with those from the g-shifts $g_\parallel - g_s$ and $g_\perp - g_s$. These negative signs of the hyperfine structure constants are also supported by the experimental results for many octahedral VO^{2+} or V^{4+} clusters in various crystals [30, 36]. As for the magnitudes of the hyperfine structure constants, the smaller values ($A_\parallel \approx -168.8(1) \cdot 10^{-4}$ cm^{-1} and $A_\perp \approx -62.0(1) \cdot 10^{-4}$ cm^{-1} [11]) for the studied system than those (e. g., $A_\parallel \approx -175.5 \cdot 10^{-4}$ cm^{-1} and $A_\perp \approx -68.2 \cdot 10^{-4}$ cm^{-1} for GeO_2:VO^{2+} [12] and $A_\parallel \approx -182.8 \cdot 10^{-4}$ cm^{-1} and $A_\perp \approx -72.0 \cdot 10^{-4}$ cm^{-1} for $[VO(H_2O)_5]^{2+}$ [37]) for some VO^{2+} doped oxides are usually ascribed to the covalency of the system, as mentioned for many transition-metal complexes [38]. In addition, the significant anisotropy of the A factors can be attributed to the considerable compression along the C_4 axis in the VO^{2+} center due to the strong axial crystal-fields of the apical oxygen ion.

4. The calculation errors can be analyzed as follows. First, approximation of the perturbation formulas and the cluster approach adopted here can induce some errors. Second, neglecting of the spin-orbit coupling of the apical oxygen ion can lead to very small ($\leq 0.5\%$) errors of the resultant spin Hamiltonian parameters due to its low magnitude. In addition, the impurity-ligand distance R is obtained from the empirical formula [24, 25], which would also bring some errors to the group overlap integrals in the calculations. Had the observed superhyperfine constants for the studied system been reported, a better or more exact impurity-ligand distance R could be obtained. Since (i) these integrals are small and (ii) the tetragonal field parameters in (6) are approximately independent of the impurity-ligand distances, the errors in the theoretical spin Hamiltonian parameters due to the uncertainty of R are estimated to be not greater than 2% even though these integrals vary by 10%. Finally, the displacement of the impurity V^{4+} due to the electrostatic attraction of the axial oxygen ion is not considered in the calculations. The impurity shift would slightly increase the bond angles of the Cl^- ligands related to the C_4 axis and hence the tetragonal field parameters, and so lead to the appreciably larger g factors and smaller A factors. According to the estimations, the errors in the final spin Hamiltonian parameters due to the above structural variation would be not more than 1%, even

when the relative ratio of the impurity displacement to the V^{4+}-Cl^- distance R amounts to 30%. Therefore, the above displacement can be safely neglected for the sake of simplicity and reduction in the number of adjustable parameters, and then the structure of a square pyramid for the impurity center is adopted here.

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