Theoretical Study of the Spin Hamiltonian Parameters of Vanadium Ions V^{2+} in $CsMgX_3$ (X = Cl, Br, I)

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The spin Hamiltonian *g* factors and the hyperfine structure constants for V^{2+} in $CsMgX_3$ (X = Cl, Br, I) are theoretically studied by using the perturbation formulas of these parameters for a $3d^3$ ion in octahedral symmetry, based on the cluster approach. In such formulas, the contributions from the s-orbitals of the ligands were usually neglected. Here they are taken into account. The theoretical results (particularly the *g* factor for $CsMgI_3$) show a significant improvement compared with those in absence of the ligand s-orbital contributions in the previous studies.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-field Theory; V^{2+}; $CsMgX_3$ (X = Cl, Br, I).

1. Introduction

$CsMgX_3$ (X = Cl, Br, I) is attracting attention due to its luminescence in doped crystals [1 – 3]. The properties of $CsMgX_3$ depend largely on the electronic and local structure of excited impurity ions (transition-metal or rare earth). Electron paramagnetic resonance (EPR) experiments were carried out on $CsMgX_3$ doped with transition-metal ions [4, 5]. For example, the spin Hamiltonian *g* factors and the hyperfine structure constants were measured for V^{2+} in $CsMgX_3$ [5]. Later, systematic and instructive studies have been made on these *g* factors using a perturbation formula of the *g* factor for a $3d^3$ ion in octahedral symmetry, based on the cluster approach [6]. In this formula, both the spin-orbit (S.O.) coupling coefficients of the central metal and the ligand ions as well as the p-orbitals of the ligands are taken into account. However, the agreement between theory and experiment was not very good for X = I, where the S.O. coupling coefficient of the ligand is even much larger than that of V^{2+}. To some extent, the contributions from the S. O. coupling of the ligand I^- seem to be overestimated, leading to theoretical *g* factors significantly (about 40%) larger than the experimental ones. In order to better determine the spin Hamiltonian parameters of $CsMgX_3$:V^{2+} in this work, the s-orbitals of the ligands are introduced in the single-electron wavefunctions of the $3d^3$ octahedral cluster. Based on the cluster approach, the previous theoretical model and formulas are improved in consideration of the ligand s-orbital contributions. Then the above formulas are applied to the studied $CsMgX_3$:V^{2+}.

2. Theory and Calculation

$CsMgX_3$ is isomorphous with $CsNiCl_3$. Its structure is hexagonal with parallel linear chains of $[MgX_6]^{3-}$ octahedra shearing faces [5, 7]. For a V^{2+} ($3d^3$) ion in octahedral symmetry, the perturbation formulas of the *g*-shift $\Delta g (= g - g_s$, where $g_s = 2.0023$ is the spin-only value) and the hyperfine structure constant based on the cluster approach (or the two-S.O.-coupling coefficient model) can be written as [8, 9]

$$\begin{aligned} g = g_s &- 8\zeta' k'/(3E_1) \\ &- 2\zeta(2k'\zeta - k\zeta' + 2g_s\zeta')/(9{E_1}^2) \\ &+ 4\zeta'^2(k - 2g_s)/9{E_3}^2 - \zeta^2(k + g_s)/(3{E_2}^2) \\ &- 4\zeta\zeta' k'[1/(3E_1E_2) + 1/(9E_1E_3) + 1/(3E_2E_3)], \end{aligned}$$

$$\begin{aligned} &A = P'\{-8\zeta' k'/(3E_1) \\ &-2\zeta(2k'\zeta - k\zeta' + 2g_s\zeta')/(9{E_1}^2) \\ &+4\zeta'^2(k - 2g_s)/9{E_3}^2 - \zeta^2(k + g_s)/(3{E_2}^2) \\ &-4\zeta\zeta' k'[1/(3E_1E_2) + 1/(9E_1E_3) + 1/(3E_2E_3)]\} - P\kappa. \end{aligned} \quad (1)$$

Table 1. The group overlap integrals, the spectral parameters Dq, B and C (in cm^{-1}), N_γ and λ_γ (and λ_s), S.O. coupling coefficients (in cm^{-1}), orbital reduction factors and dipolar hyperfine structure parameters (in 10^{-4} cm^{-1}) for V^{2+} in $CsMgX_3$ (X = Cl, Br, I).

X	S_{dpt}	S_{dpe}	S_{ds}	A	Dq	B	C	f_γ	N_t	N_e	λ_t	λ_e	λ_s	ζ	ζ'	k	k'	P	P'
Cl	0.0261	0.0769	0.0455	1.2609	960	635	2400	0.835	0.922	0.943	0.302	0.319	0.178	181	129	0.968	0.854	118	119
Br	0.0223	0.0705	0.0384	1.2010	880	616	2320	0.808	0.906	0.927	0.327	0.345	0.178	284	26	0.960	0.831	116	117
I	0.0188	0.0619	0.0345	1.0800	790	590	2224	0.775	0.881	0.906	0.350	0.370	0.195	458	−148	0.950	0.807	113	114

The energy denominators E_1, E_2 and E_3 are defined in [8]. In treatments of the cluster approach, the contributions of the s-orbitals of ligands are usually neglected [6, 8, 9]. Here they are considered. Thus, the total single electron wavefunction including the contributions from the s-orbitals of ligands may be expressed as

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

where φ_γ (γ = e and t denote the irreducible representations of the O_h group) are the d-orbitals of the central metal ion. $\chi_{p\gamma}$ and χ_s stand for the p- and s-orbitals of the ligands. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients. From the semiempirical method [8] one can denote the ratio of the electrostatic repulsion in the crystal to that of the free ion as

$$f_\gamma = \langle \psi_\gamma^2 | e^2/r_{12} | \psi_\gamma^2 \rangle / \langle \varphi_\gamma^2 | e^2/r_{12} | \varphi_\gamma^2 \rangle. \tag{3}$$

Utilizing the Mulliken approximation [10] and neglecting the small terms of λ_γ^3 and λ_γ^4 from the above formula, we have the following relationship

$$f_t = N_t^2 \left(1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}\right), \tag{4}$$

$$f_e = N_e^2 \left(1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}\right).$$

In addition, the normalization conditions for the wavefunctions can be expressed as

$$\begin{aligned} &N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1, \\ &N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1. \end{aligned} \tag{5}$$

$S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the admixture coefficients increase with increasing group overlap integrals, and one can approximately assume a proportional relationship 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. Usually, f_γ can be determined from the ratio of the Racah parameters for a $3d^3$ ion in a crystal to those in free state, i.e., $f_t \approx f_e \approx (B/B_0 + C/C_0)/2$.

From the cluster approach containing the ligand s-orbital contributions, the S. O. coupling coefficients ζ, ζ', the orbital reduction factors k, k', and the dipolar hyperfine structure parameters P and P' for the $3d^3$ ion in an octahedral cluster may be written as

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2), \\ \zeta' &= (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \\ k' &= (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2], \\ P &= N_t P_0, \quad P' = (N_t N_e)^{1/2} P_0, \end{aligned} \tag{6}$$

where ζ_d^0 and ζ_p^0 are the S. O. coupling coefficients of the free $3d^3$ and the ligand ions, respectively. P_0 is the dipolar hyperfine structure parameter for the $3d^3$ ion in free state. A denotes the integral $R\langle ns | \frac{\partial}{\partial y} | np_y \rangle$, where R is the metal-ligand distance of the studied system. Obviously, when taking $S_{ds} = \lambda_s = 0$ and $A = 0$, the above formulas return to those in absence of the ligand s-orbital contributions [6, 8, 9].

The distance R is about 2.496, 2.662 and 2.899 Å for X = Cl, Br and I, respectively [7]. From the distance R and the Slater-type SCF functions [11, 12], the group overlap integrals $S_{dp\gamma}$ (as well as the integrals S_{ds} and A) are obtained. These values are shown in Table 1.

The spectral parameters Dq, B and C can be obtained from optical spectra of these systems and similar $[VX_6]^{4-}$ clusters in VX_2 [13 – 15]. By using (4) – (6) and the free-ion parameters $B_0 \approx 766$ cm^{-1} and $C_0 \approx 2855$ cm^{-1} [16] for V^{2+}, the parameters f_γ and hence N_γ and λ_γ can be calculated. From the free-ion values $\zeta_d^0 \approx 167$ cm^{-1} [16], $P_0 \approx 128 \times 10^{-4}$ cm^{-1} [17] for V^{2+} and $\zeta_p^0 \approx 587$, 2460 and 5060 cm^{-1} for X = Cl, Br and I [18], the parameters ζ, ζ', k, k', P and P' are calculated from (6) and shown in Table 1. The core polarization constant in the formula of the hyperfine structure constant can be expressed as $\kappa \approx -2\xi/(3\langle r^{-3}\rangle)$, where ξ is characteristic of the

Table 2. Spin Hamiltonian parameters for V^{2+} in $CsMgX_3$ (X = Cl, Br, I).

	Δg				$A(10^{-4}\ \mathrm{cm}^{-1})$			
X	Cal.[a]	Cal.[b]	Cal.[c]	Expt. [6]	Cal.[a]	Cal.[b]	Cal.[c]	Expt. [6]
Cl	−0.0392	−0.0315	−0.0311	−0.0283 (6)	−75.9	−75.1	−75.1	−75.0 (10)
Br	−0.0621	−0.0048	−0.0069	−0.0048 (20)	−74.9	−70.5	−71.0	−70.0 (20)
I	−0.0453	0.0535	0.0380	0.0377(100)	−74.3	−63.6	−65.0	−67.0 (20)

[a] Calculations based on the conventional crystal-field model (i. e., $\zeta = \zeta' = \zeta_d{}^0\sqrt{f_\gamma}$, $k = k' = \sqrt{f_\gamma}$ and $P = P' = P_0\sqrt{f_\gamma}$). [b] Calculations based on the cluster approach (i. e., two-S.O.-coupling coefficient formulas) including only the contributions from the p-orbitals of the ligands, i. e., treatment in [6]. [c] Calculations based on the cluster approach in consideration of the contributions from both the p- and s-orbitals of the ligands in the present work.

density of unpaired spins at the nucleus of the central metal ion and $\langle r^{-3}\rangle$ is the expectation value of the inverse cube of the radial wavefunction of the 3d-orbital [19]. From the values $\langle r^{-3}\rangle \approx 2.748$ a.u. [19] for V^{2+} and $\xi \approx -2.32 \sim -2.67$ a.u. [17] for the similar octahedral $[VCl_6]^{4-}$ cluster in $CdCl_2$ and VCl_2 solution, we approximately take $\kappa \approx 0.61$ for the studied $CsMgX_3{:}V^{2+}$ here.

Substituting these parameters into (1), the g factors and the hyperfine structure constants for the studied systems are obtained and collected in Table 2. For comparisons, the calculated results by neglecting the contributions of the s-orbitals of the ligands (i.e., $S_{ds} = \lambda_s = 0$ and $A = 0$, corresponding to the treatment in [6]) and those based on the conventional crystal-field model (i.e., $\zeta = \zeta' = \zeta_d{}^0\sqrt{f_\gamma}$, $k = k' = \sqrt{f_\gamma}$ and $P = P' = P_0\sqrt{f_\gamma}$) are also given in Table 2.

3. Discussion

From Table 2 one can find that the theoretical spin Hamiltonian parameters for the studied systems including the ligand s-orbital contributions show better agreement than those in absence of these contributions (or the results of conventional crystal-field model) with the observed values. This means that the theoretical model established in this work and the related parameters adopted here can be regarded as reasonable.

Compared with the results of the conventional crystal-field model, the cluster approach in [6] indeed yields improved g factors for all systems, particularly it offers the correct (or positive) sign of Δg for X = I by producing a negative value of ζ'. However, the theoretical Δg (by neglecting the ligand s-orbital contributions) for X = I is about 40% larger than the experimental value, suggesting that the contributions from the S.O. coupling of the ligand I^- are overestimated. In fact, inclusion of the s-orbitals of the ligands decreases explicitly the parameters N_e and λ_e [see (5)] and reduces less the magnitudes of k' and ζ' [see (6)], and finally leads to a smaller value of Δg [see (1)]. Obviously, the above effect of reduction is sensitive to the magnitude of the S.O. coupling coefficient of the ligand. Thus, the significant improvement of the calculated g factor (especially for X = I) by considering the ligand s-orbital contributions can be understood. Further, the previous assumption that the contributions of the s-orbitals of the ligands may be negligible for $3d^n$ ions in octahedra (e.g., $KNiF_3$) [20, 21] seems not always suitable for the ligand having a too much larger S.O. coupling coefficient (e.g., I^-), and so the ligand s-orbital contributions should be considered in studies of the g factors. On the other hand, the hyperfine structure constant, which may be largely proportional to the normalization factors [see (1) and (6)], is not so much dependent on the ligand (p- and s-) orbitals.

In the above calculations, only the contributions from the crystal-field mechanism (related to the crystal-field energy levels) are considered, while those from the charge-transfer (CT) mechanism (related to the charge-transfer energy levels) are ignored. According to our recent studies for $3d^3$ ions in oxides [22], the contributions to the g-shift from the CT mechanism can be estimated as

$$\begin{aligned}\Delta g_{CT} &\sim k_{CT}{}'\zeta_{CT}{}'/E_n\\ &\sim N_e{}^b(\lambda_e+\lambda_t/2)N_e{}^b(\lambda_t\zeta_d{}^0+\lambda_t\zeta_p{}^0/2)/E_n,\end{aligned} \tag{7}$$

with the CT energy separation [23]

$$E_n \approx 30{,}000[\chi(L)-\chi(M)]. \tag{8}$$

Here χ (L) and χ (M) are, respectively, the optical electronegativities of the ligand and the metal ions. In the studied systems, $\chi(Cl^-) \approx 3.4$, $\chi(Br^-) \approx 3.3$ and $\chi(I^-) \approx 3.0$ [23]. The value $\chi(V^{2+}) \approx 0.9$ can be obtained from those for similar isoelectronic Cr^{3+} and Mn^{4+} by extrapolation. Thus, one can approximately estimate $\Delta g_{CT} \sim 0.0003$, 0.0008 and 0.002 for X = Cl, Br and I, respectively. Thus, the CT contributions to the g factor seem to be insignificant because of the large energy difference between the CT levels and the ground state.

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