Studies of the Spin Hamiltonian Parameters for Cubic V^{2+}, Cr^{3+}, and Mn^{4+} Centers in MgO and CaO, based on Two Mechanism Models

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The high-order perturbation formulas of the spin Hamiltonian (SH) parameters g-shift $\Delta g\ (= g - g_s)$ and the hyperfine structure constant A for a $3d^3$ ion in cubic octahedra are established, based on the two mechanism model. In this model, not only the contributions from the conventional crystal-field (CF) mechanism, but also those from the charge-transfer (CT) mechanism are taken into account. These formulas are applied to the investigation of the SH parameters of cubic V^{2+}, Cr^{3+} and Mn^{4+} centers in MgO and CaO. Based on these studies, the sign of Δg due to the CT mechanism is opposite to that due to the CF mechanism, while the signs of the A factor due to the CF and CT mechanisms are equal. The theoretical results, including the contributions from the CF and CT mechanisms, agree better with the observed values than those containing only the conventional CF mechanism.

Key words: Crystal-fields and Spin Hamiltonians; Electron Paramagnetic Resonance (EPR); V^{2+}; Cr^{3+}; Mn^{4+}.

1. Introduction

Recently, by applying the crystal-field (CF) mechanism, high-order perturbation formulas of the spin Hamiltonian (SH) parameters g-shift $\Delta g (= g - g_s$, where $g_s \approx 2.0023$ is the spin-only value) have been established for $3d^3$ ions in cubic octahedra [1, 2]. In these formulas, both the contributions from the spin-orbit (SO) coupling coefficients of the central transition-metal ions and the ligands are taken into account [1, 2]. These formulas (so-called two-SO-coupling-coefficient formulas) are superior to those containing only the contributions of the central ions (i.e. one-SO-coupling-coefficient formulas [3, 4]). Therefore, they are more suitable for systems with heavy-element ligand ions (such as Br^- and I^-), where the SO coupling coefficients ζ_p of the ligands are much greater than the corresponding coefficients ζ_d of the central $3d^3$ ions [1, 2]. The values of Δg for these systems are only slightly negative or even positive.

It is widely accepted that the values of $\Delta g(\sim -0.03)$ are relatively large and negative for the $3d^3$ ions V^{2+} and Cr^{3+} in oxides (such as MgO and CaO) [5, 6]. This can be approximately explained on the basis of the one- or two-SO-coupling-coefficient formulas based on the CF mechanism, because the covalency effect and the value of ζ_p for the ligand are small. However, for the isoelectronic Mn^{4+} in the same hosts, the magnitudes of $\Delta g(\sim -0.009)$ are much smaller [7, 8], and can hardly be interpreted within the limit of the CF mechanism, since these oxides are ionic crystals and the coefficient $\zeta_p{}^0(\approx 151\ \text{cm}^{-1}$ [9]) of O^{2-} is even smaller than the coefficient $\zeta_d{}^0(\approx 405\ \text{cm}^{-1}$ [10]) of Mn^{4+}. So, another mechanism besides the CF mechanism should be considered. In fact, the microscopic origin of the SH parameters (including Δg) for $3d^n$ ions in crystals result from not only the CF mechanism (related to the CF energy levels) but also the charge-transfer (CT) mechanism (related to the CT energy levels) [11, 12]. Unfortunately, the latter was usually neglected in studies of the SH parameters. Further, since the energies of the CT levels lower with increasing valence state [13], the contributions to the SH parameters from the CT mechanism for isoelectronic $3d^n$ ions having a high valence state may be important and cannot be neglected. In this paper, we establish the complete perturbation formulas of Δg and hyperfine structure constant A for $3d^3$ ions in cubic octahedral clusters based on the two mechanism model including both CF and CT contributions. By using these formulas, the SH parameters for cubic V^{2+}, Cr^{3+} and Mn^{4+} centers in MgO and CaO are investigated.

2. Calculations

For a $3d^3$ ion in a cubic MX_6 cluster, the complete Hamiltonian containing the CF and CT mechanisms can be written as

$$\begin{aligned} H &= H_0 + H', \\ H_0 &= H_c + H_a, \\ H' &= H_b + {H_{SO}}^{CF} + {H_{Ze}}^{CF} + {H_{hf}}^{CF} \\ &\quad + {H_{SO}}^{CT} + {H_{Ze}}^{CT} + {H_{hf}}^{CT}, \end{aligned} \tag{1}$$

where H_c, H_a, H_b, H_{SO}, H_{Ze} and H_{hf} are, respectively, the cubic field (c), the diagonal (a) and off-diagonal (b) terms of the electrostatic Coulomb interaction, the SO coupling, the Zeeman term and the hyperfine interactions. The superscripts CF and CT stand for terms in the CF and CT mechanisms with the corresponding SO coupling coefficients ζ_{CF}, ζ_{CF}' and ζ_{CT}, ζ_{CT}', orbital reduction factors k_{CF}, k_{CF}' and k_{CT}, k_{CT}', and dipolar hyperfine structure parameters P_{CF}, P_{CF}' and P_{CT}, P_{CT}'.

Considering the contributions of CT excitations to the SH parameters, one can write the many- electron wave-functions of CT configurations in terms of seven-electron wave-functions out of $t_2{}^n$, e^a and e^b, where the superscripts n, a and b denote the non-bonding orbitals, anti-bonding orbitals (corresponding to the CF mechanism [1, 2]) and bonding orbitals (corresponding to the CT mechanism [11, 12]), respectively. Thus, the ground state $^4A_2$ of the $3d^3$ MX_6 cluster can be expressed as

$$|^4A_2 \tfrac{3}{2} a_2\rangle = -[\xi^+\eta^+\zeta^+|\theta^+\theta^-\varepsilon^+\varepsilon^-]. \tag{2}$$

In the above square bracket, the letters on the left column denote $t_2{}^n$ orbitals and those on the right column denote e^b orbitals. There is only one excited configuration $(t_2{}^n)^4(e^b)^3$ (or $^4T_2{}^n$) having non-zero SO coupling interaction with the ground state $^4A_2$. Thus, the ζ-components of the $^4T_2{}^n$ state with $M_S = 3/2$ can be written as

$$|^4T_2^n \tfrac{3}{2} \zeta\rangle = -[\xi^+\eta^+\zeta^+\zeta^-|\theta^+\theta^-\varepsilon^+]. \tag{3}$$

From the LCAO-MO (molecular orbital) model, the MO orbitals

$$|\psi_\gamma{}^x\rangle = N_\gamma{}^x(|d_\gamma\rangle + \lambda_\gamma{}^x|p_\gamma\rangle) \tag{4}$$

are taken as the one-electron basis functions for the octahedral $3d^3$ cluster. The subscript $\gamma(= t_{2g}$ or $e_g)$ stands for the irreducible representation of the O_h group, the superscript $x(=$ a or b) denotes the antibonding and bonding orbitals. $|d_\gamma\rangle$ is the d orbital of the $3d^3$ ion and $|p_\gamma\rangle$ is the p orbital of the ligand. $N_\gamma{}^x$ is the normalization factor and $\lambda_\gamma{}^x$ is the orbital mixing coefficient. Thus, we have the normalization condition

$$N_\gamma{}^x = [1 + \lambda_\gamma{}^x S_{dp}(\gamma) + (\lambda_\gamma{}^x)^2]^{-1/2}, \tag{5}$$

where $S_{dp}(\gamma)$ is the group overlap integral. In addition, these LCAO coefficients for the antibonding orbitals satisfy the approximate relationship [1, 2]

$$\begin{aligned} f_\gamma &= (B/B_0 + C/C_0)/2 \\ &\approx (N_\gamma{}^a)^2[1 + (\lambda_\gamma{}^a)^2 S_{dp}{}^2(\gamma) - 2\lambda_\gamma{}^a S_{dp}(\gamma)], \end{aligned} \tag{6}$$

where B_0 and C_0 are the Racah parameters of the free $3d^3$ ion. Nevertheless, the orthogonality relationship

$$\lambda_\gamma{}^b \approx [\lambda_\gamma{}^a S_{dp}(\gamma) - 1]/[2\lambda_\gamma{}^a - S_{dp}(\gamma)] \tag{7}$$

is held for the bonding and antibonding orbitals.

By using Macfarlane's perturbation-loop method [4] and the above one-electron basis functions as well as the CT configurations, the complete perturbation formulas of Δg and A for $3d^3$ ions in cubic octahedra are established on the basis of the two mechanism models including both the CF and CT contributions, i. e.

$$\begin{aligned} \Delta g &= \Delta g_{CF} + \Delta g_{CT}, \\ \Delta g_{CF} &= -8k'_{CF}\zeta'_{CF}/3E_1 \\ &\quad - 2\zeta'_{CF}(2k'_{CF}\zeta_{CF} - k_{CF}\zeta'_{CF} + 2g_s\zeta'_{CF})/9E_1^2 \\ &\quad + 4\zeta'^2_{CF}(k_{CF} - 2g_s)/9E_3^2 \\ &\quad - 2\zeta^2_{CF}(k_{CF} + g_s)/3E_2^2 \\ &\quad + 4k'_{CF}\zeta'_{CF}\zeta_{CF}/9E_1E_3 \\ &\quad - 4k'_{CF}\zeta'_{CF}\zeta_{CF}/3E_1E_2 \\ &\quad + 4k'_{CF}\zeta'_{CF}\zeta_{CF}/3E_2E_3, \\ \Delta g_{CT} &= 8k'_{CT}\zeta'_{CT}/(3E_n), \\ A &= A_{CF} + A_{CT}, \\ A_{CF} &= -P'_{CF}[8k'_{CF}\zeta'_{CF}/3E_1 + 2\zeta'_{CF}(2k'_{CF}\zeta_{CF} - k_{CF}\zeta'_{CF} \\ &\qquad + 2g_s\zeta'_{CF})/9E_1^2 \\ &\quad - 4{\zeta_{CF}}'^2(k_{CF} - 2g_s)/9E_3^2 \end{aligned}$$

$$\begin{aligned} &+2\zeta_{\mathrm{CF}}^2(k_{\mathrm{CF}}+g_{\mathrm{s}})/3E_2^2 \\ &-4k'_{\mathrm{CF}}\zeta'_{\mathrm{CF}}\zeta_{\mathrm{CF}}(1/9E_1E_3-1/3E_1E_2 \\ &\qquad +1/3E_2E_3)]-\kappa P_{\mathrm{CF}}, \end{aligned}$$

$$A_{\mathrm{CT}}=8P'_{\mathrm{CT}}k'_{\mathrm{CT}}\zeta'_{\mathrm{CT}}/3E_1-(\kappa/2)P_{\mathrm{CT}}, \tag{8}$$

where $E_i (i = 1 \sim 3)$ are the zeroth-order energy denominators (which are related to the CF excitations and defined in [1,2]) and E_n is the energy difference between the CT excited $^4\mathrm{T}_2^n$ and the ground $^4A_2$. κ is the core polarizability constant. The corresponding parameters in the CF mechanism are

$$\begin{aligned} \zeta_{\mathrm{CF}}&=(N_{\mathrm{t}}^{\mathrm{a}})^2[\zeta_{\mathrm{d}}^0+(\lambda_{\mathrm{t}}^{\mathrm{a}})^2\zeta_{\mathrm{p}}^0/2], \\ \zeta'_{\mathrm{CF}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{a}}[\zeta_{\mathrm{d}}^0-\lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{a}}\zeta_{\mathrm{p}}^0/2], \\ k_{\mathrm{CF}}&=(N_{\mathrm{t}}^{\mathrm{a}})^2[1+(\lambda_{\mathrm{t}}^{\mathrm{a}})^2/2], \\ k'_{\mathrm{CF}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{a}}[1+\lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{a}}/2], \\ P_{\mathrm{CF}}&=(N_{\mathrm{t}}^{\mathrm{a}})^2P_0, \\ P'_{\mathrm{CF}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{a}}P_0, \end{aligned} \tag{9}$$

and those in CT mechanism are

$$\begin{aligned} \zeta_{\mathrm{CT}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{t}}^{\mathrm{b}}\{[\lambda_{\mathrm{t}}^{\mathrm{a}}-S_{\mathrm{dp}}(\mathrm{t_{2g}})]\zeta_{\mathrm{d}}^0-\lambda_{\mathrm{t}}^{\mathrm{a}}\zeta_{\mathrm{p}}^0/2\}, \\ \zeta'_{\mathrm{CT}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{b}}\{[\lambda_{\mathrm{t}}^{\mathrm{a}}-S_{\mathrm{dp}}(\mathrm{e_{2g}})]\zeta_{\mathrm{d}}^0+\lambda_{\mathrm{t}}^{\mathrm{a}}\zeta_{\mathrm{p}}^0/2\}, \\ k_{\mathrm{CT}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{t}}^{\mathrm{b}}\{\lambda_{\mathrm{t}}^{\mathrm{a}}/2-(\lambda_{\mathrm{t}}^{\mathrm{a}})^2S_{\mathrm{dp}}(\mathrm{t_{2g}})+\lambda_{\mathrm{t}}^{\mathrm{a}}S_{\mathrm{dp}}^2(\mathrm{t_{2g}})\}, \\ k'_{\mathrm{CT}}&=N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{b}}\{\lambda_{\mathrm{e}}^{\mathrm{a}}+\lambda_{\mathrm{t}}^{\mathrm{a}}/2+\lambda_{\mathrm{t}}^{\mathrm{a}}S_{\mathrm{dp}}(t_{2\mathrm{g}})S_{\mathrm{dp}}(\mathrm{e_g}) \\ &\qquad -\lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{a}}S_{\mathrm{dp}}(t_{2\mathrm{g}})\}, \\ P_{\mathrm{CT}}&=(N_{\mathrm{t}}^{\mathrm{b}})^2P_0, \\ P'_{\mathrm{CT}}&=N_{\mathrm{t}}^{\mathrm{b}}N_{\mathrm{e}}^{\mathrm{b}}P_0. \end{aligned} \tag{10}$$

Here ζ_{d}^0 and ζ_{p}^0 are the SO coupling coefficient of the $3d^3$ ion and that of the ligand in the free state. P_0 is the dipolar hyperfine structure parameter of the free $3d^3$ ion. It can be seen that, if only the terms related to the anti-bonding orbitals are considered (i.e. the contributions from the CT mechanism are ignored), the above formula (8) of Δg becomes that of the two-SO-coupling-coefficient, based on the CF mechanism [1,2]. Further, if the terms related to ζ_{p}^0 and $\lambda_\gamma^{\mathrm{x}}$ are also neglected (i.e. $\zeta_{\mathrm{p}}^0 = 0$ and $\lambda_\gamma^{\mathrm{x}} = 0$), it would be reduced to that of the one-SO-coupling-coefficient formula [3,4].

Now, the above formulas are applied to the SH parameters Δg and A for V^{2+}, Cr^{3+} and Mn^{4+} in MgO and CaO. From the optical spectra of these octahedral $3d^3$ centers [14], the Racah parameters B and C and cubic field parameter D_{q} for V^{2+} and Cr^{3+} in MgO can be obtained. The spectral parameters for MgO: Mn^{4+} can be approximately estimate from those [15,16] of the cubic Mn^{4+} and Cr^{3+} clusters in similar $SrTiO_3$ by using the approximate relationship L (MgO: Mn^{4+}) / L (MgO:Cr^{3+}) $\approx$ L ($SrTiO_3$: Mn^{4+}) / L ($SrTiO_3$:Cr^{3+}). The parameters for doped CaO can be estimated from those of MgO and the relationship $D_{\mathrm{q}} \propto R^{-5}$ for the impurity-ligand distance [17,18] and the fact that B and C increase slightly with increasing distance R [19]. The distance R, which is usually different from the host cation-anion distance R_{H}, may be obtained from the empirical formula [20,21] $R \approx R_{\mathrm{H}} + (r_i - r_h)/2$. For the studied cubic centers, the impurity radii are r_i (V^{2+}) ≈ 0.88 Å, r_i(Cr^{3+}) ≈ 0.63 Å, r_i(Mn^{4+}) ≈ 0.60 Å, and the radii of the replaced ions are r_h(Mg^{2+}) ≈ 0.66 Å and r_h(Ca^{2+}) ≈ 0.99 Å [22], R_{H}(MgO) ≈ 2.105 Å and R_{H}(CaO) ≈ 2.405 Å [22]. The distances R for various centers are shown in Table 1. The spectral parameters B, C and Dq are also collected there. Thus, the coefficients f_γ in (6) can be calculated by using the free-ion values B_0 and C_0 (they are 766, 2855 cm^{-1} for V^{2+}, 1030, 3850 cm^{-1} for Cr^{3+}, and 1160 and 4303 cm^{-1} for Mn^{4+}, respectively) [10,23]. From the Slater-type SCF functions [24,25] and the above distances R, the integrals $S_{\mathrm{dp}}(\gamma)$ in (5) – (7) are determined and shown in Table 1. Thus, the LCAO coefficients N_γ^{x} and $\lambda_\gamma^{\mathrm{x}}$ related to the CF and CT mechanisms are calculated and collected in Table 1. According to (9) and (10) as well as the values of ζ_{d}^0($\approx$ 167, 273 and 405 cm^{-1} [10,23]) and P_0($\approx 128\cdot10^{-4}$, $-39.7\cdot10^{-4}$ and $235\cdot10^{-4}$ cm^{-1}) for free V^{2+}, Cr^{3+} and Mn^{4+} ions [26], the SO coupling coefficients, the orbital reduction factors and the dipolar hyperfine structure parameters related to CF and CT mechanisms for the studied systems can be determined.

The CT energy level E_n for teh ligand-to-metal charge transfer (LMCT) can be obtained from the approximate relationship [13]

$$E_n \approx 30000[\chi(L)-\chi(M)]\,\mathrm{cm}^{-1}, \tag{11}$$

where $\chi(L)$ and $\chi(M)$ are, respectively, the optical electronegativities of the ligand and $3d^n$ ions. In the given systems, $\chi(O^{2-}) \approx 3.2$, χ (Cr^{3+}) ≈ 1.9 and $\chi(Mn^{4+}) \approx 3.0$ [13]. For V^{2+}, the value of χ can be obtained by extrapolation, i.e. $\chi(V^{2+}) \approx 1.4$. These values are also shown in Table 1.

The core polarization constant in the formula of the A factor can be expressed as $\kappa \approx -2\chi/(3\langle r^{-3}\rangle)$,

Table 1. The spectral parameters, group overlap integrals and LCAO coefficients related to the CF and CT mechanisms of V^{2+}, Cr^{3+} and Mn^{4+} in MgO and CaO.

Ions	V^{2+}		Cr^{3+}		Mn^{4+}	
Hosts	MgO	CaO	MgO	CaO	MgO	CaO
R (Å)	2.215	2.350	2.090	2.225	2.075	2.210
B (cm^{-1})	683 [10]	720^b	690 [10]	710^b	750^a	755^b
C (cm^{-1})	2420 [10]	2460^b	3320 [10]	3330^b	3590^a	3595^b
D_q (cm^{-1})	1400 [10]	1040^b	1590 [10]	1160^b	1310^a	1130^b
f_γ	0.870	0.901	0.766	0.777	0.740	0.743
E_n (cm^{-1})	54000	54000	39000	39000	6100	6100
$S_{dp}(t_{2g})$	0.022	0.014	0.023	0.015	0.018	0.011
$S_{dp}(e_g)$	0.068	0.048	0.071	0.049	0.057	0.039
N_t^a	0.940	0.953	0.886	0.888	0.869	0.867
N_e^a	0.951	0.961	0.904	0.902	0.886	0.880
λ_t^a	0.353	0.310	0.513	0.509	0.560	0.568
λ_e^a	0.291	0.264	0.440	0.456	0.497	0.521
N_t^b	0.570	0.522	0.716	0.714	0.747	0.752
N_e^b	0.472	0.441	0.653	0.670	0.704	0.722
λ_t^b	−1.452	−1.642	−0.986	−0.988	−0.899	−0.883
λ_e^b	−1.904	−2.059	−1.197	−1.134	−1.037	−0.977
κ	0.563	0.558	0.382	0.396	0.292	0.303

[a] The parameters for MgO: Mn^{4+} are estimated from the relationship L (MgO: Mn^{4+}) / L (MgO:Cr^{3+}) ≈ L ($SrTiO_3$: Mn^{4+}) / L ($SrTiO_3$:Cr^{3+}). [b] The parameters for CaO:M^{n+} are obtained from those for MgO:M^{n+} by using the relationship $D_q \propto R^{-5}$ [17, 18] and the fact that B or C increases slightly with increasing distance R [19].

Table 2. The SH parameters $\Delta g (= g - g_s)$ and the hyperfine structure constant A (in units of 10^{-4} cm^{-1}) for V^{2+}, Cr^{3+} and Mn^{4+} in MgO and CaO.

	V^{2+}		Cr^{3+}		Mn^{4+}	
	MgO	CaO	MgO	CaO	MgO	CaO
Δg_{CF}	−0.0233	−0.0336	−0.0248	−0.0335	−0.0406	−0.0459
Δg_{CT}	0.0004	0.0005	0.0025	0.0030	0.0316	0.0357
Δg (tot)	−0.0229	−0.0331	−0.0223	−0.0305	−0.0090	−0.0102
Δg_{CT} (Expt.)	−0.0220 (5) [5]	−0.0340 (5) [6]	−0.0223 (5) [5]	−0.0291 (5) [6]	−0.0086 (3) [7]	−0.0092 (5) [8]
A_{CF}	−66.32	−68.14	12.7	13.5	−59.2	−61.8
A_{CT}	−11.70	−11.81	3.8	4.0	−15.2	−15.5
A (tot)	−78.02	−79.95	16.5	17.5	−74.4	−77.3
A_{CT} (Expt.)	−74.24 (2)[a] [5]	−76.04 (5)[a] [6]	16.0 (3) [5]	17.0 (1) [6]	−71.3[a] [7]	−72.8[a] [8]

[a] The signs of the experimental values of the A factors for V^{2+} and Mn^{4+}were not given in [5–8]. The negative signs are determined from those of the observed A values for these ions in various crystals [26] and the theoretical calculations in the present work.

where χ is characteristic of the 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 wave-function of the 3d orbital [27]. By using the values of $\langle r^{-3} \rangle$ for V^{2+}, Cr^{3+} and Mn^{4+} [27] and χ for those in MgO and CaO (note: the value of χ for CaO:Mn^{4+} is determined from the approximate relationship $\chi(\text{CaO:Mn}^{4+})/\chi(\text{MgO:Mn}^{4+}) \approx \chi(\text{CaO:Cr}^{3+})/\chi\ (\text{MgO:Cr}^{3+})$). Thus, the values of κ for various centers are obtained and shown in Table 1.

Substituting these parameters into (8), the g-shifts and the hyperfine structure constants for the $3d^3$ ions V^{2+}, Cr^{3+} and Mn^{4+} in MgO and CaO are calculated and shown in Table 2. For comparison, the theoretical results by considering only the contributions from the CF mechanism are also collected in Table 2.

3. Discussion

From Table 2 we find that the theoretical SH parameters, by considering both the CF and CT mechanisms, agree well with the observed values, whereas those by neglecting the CT contributions agree not. This suggests that the complete perturbation formulas based on the two mechanism model established in this work can be regarded as suitable.

1.) The contributions Δg_{CT} due to the CT mechanism are opposite in sign and about 2%, 10% and 78% in magnitude compared with Δg_{CF} due to the CF mechanism for V^{2+}, Cr^{3+} and Mn^{4+}, respectively. So, the experimental g factors for the studied $3d^3$ impurity centers in MgO and CaO can be reasonably explained by considering both mechanisms (see Table 2). (i) As mentioned before, the relative importance of the CT mechanism (characterized by $|\Delta g_{CT}/\Delta g_{CF}|$) increases with increasing valence state of the $3d^3$ ions, i.e. $V^{2+} < Cr^{3+} < Mn^{4+}$. Therefore, for V^{2+} the contributions from the CT mechanism may be ignored, and the two-SO-coupling-coefficient formula (i.e. Δg_{CF} in (8)) based on the CF mechanism is almost sufficient to yield suitable results. However, for Cr^{3+} and Mn^{4+}, especially the latter, the contributions to Δg from the CT mechanism are much larger and should be taken into account. (ii) According to

(10), the contributions of ζ_d^0 and ζ_p^0 are of the same sign in ζ'_{CT}. Thus, it can be expected that for large ligands (e.g., Br^-, I^-) with much larger ζ_p^0 importance of Δg_{CT} would increase even more rapidly. (iii) The ratio $|\Delta g_{CT}/\Delta g_{CF}|$ deceases slightly from MgO to CaO for each $3d^3$ ion, suggesting that the magnitude of Δg_{CF} increases more significantly than Δg_{CT} does in the latter.

2.) Compared with the case of Δg, the signs of A_{CF} and A_{CT} are equal and the relative importance of A_{CT} (characterized by $|A_{CT}/A_{CF}|$) are about $20 \sim 30\%$. (i) In fact, the contributions to A consist of two parts, i.e., the spin part (κP_{CF} in the CF mechanism and $\kappa P_{CT}/2$ in the CT mechanism) and the orbital part (the rest terms in (8)). Although the spin part (which depends upon the covalency reduction effect) is dominant, the contributions from the CT mechanism cannot be neglected. For each $3d^3$ ion, the ratio $|A_{CT}/A_{CF}|$ deceases slightly from MgO to CaO. Seen from (8), both A_{CF} and A_{CT} increase with increase of κ in CaO, only the increase of the latter is less obvious due to the factor 1/2. (ii) The signs of the experimental A factors for V^{2+} and Mn^{4+} were not determined in [5–8]. However, the negative signs can be verified from those of the observed A values for these ions in various crystals [23] and the theoretical calculations in the present work. (3) The observed SH parameters were assigned to the Mn^{4+} center in Mn doped CaO powder with some uncertainty [8]. As measured by many workers [6, 26, 28, 29], the values of Δg are usually -0.001 for Mn^{2+} in CaO (and other similar oxides), which are almost by one order in magnitude smaller than those (~ -0.009) of the experimental data for Mn^{4+} in oxides [7, 26]. According to the observed EPR spectrum (i.e. $\Delta g \approx -0.0092(5)$ and $A \approx -72.8 \cdot 10^{-4}$ cm^{-1}) [8] and the studies in this work, it should be indeed attributed to the cubic Mn^{4+} center rather than the Mn^{2+} one.

In summary, the SH parameters for the cubic V^{2+}, Cr^{3+} and Mn^{4+} centers in MgO and CaO are theoretically investigated based on the two mechanism model including both the CF and CT contributions. Obviously, this model can also be applied to other $3d^3$ systems with a high valence of the central ions.

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