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 $\Delta g$ 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 $\Delta g (= g - g_s)$ 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 $\Delta g$ 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$^{4+}$.
plete perturbation formulas of $\Delta g$ 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

$$\begin{align*}
H &= H_0 + H', \\
H_0 &= H_c + H_a, \\
H' &= H_0 + H_{SO}^{CF} + H_{Ze}^{CF} + H_{ld}^{CF} + H_{SO}^{CT} + H_{Ze}^{CT} + H_{ld}^{CT},
\end{align*}$$

(1)

where $H_c$, $H_a$, $H_{SO}$, $H_{Ze}$ and $H_{ld}$ 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 $\zeta_{CF}$, $\zeta_{CT}$, $\xi_{CF}$, $\xi_{CT}$, orbital reduction factors $k_{CF}$, $k_{CT}$ and $a_{CF}$, $a_{CT}$, and dipolar hyperfine structure parameters $P_{CF}$, $P_{CT}$ and $P_{CF}$, $P_{CT}$.

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 $t_z^3$, $e^3$ and $e^6$, 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

$$|^{a}A_2^{3/2}a_2\rangle = |[\xi^+\eta^+\zeta^+|\theta^+\theta^-\epsilon^+\epsilon^-].$$

(2)

In the above square bracket, the letters on the left column denote $t_z^3$ orbitals and those on the right column denote $e^6$ orbitals. There is only one excited configuration $(t_z^3)(e^6)^3$ (or $(T_z^3)^a$) having non-zero SO coupling interaction with the ground state $^4A_2$. Thus, the $\zeta$-components of the $^4T_z^3$ state with $M_S = 3/2$ can be written as

$$|^{4}T_z^{3/2}\zeta\rangle = |[\xi^+\eta^+\zeta^+|\theta^+\theta^-\epsilon^+\epsilon^-].$$

(3)

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

$$|\psi_T^a\rangle = N_T^{a} [ (|d_T\rangle + \lambda_T^{a}|p_T\rangle)$$

(4)

are taken as the one-electron basis functions for the octahedral 3d$^3$ cluster. The subscript $\gamma$ (= t$_y$ or e$_x$) stands for the irreducible representation of the O$_h$ group, the superscript $\alpha$ (a or b) denotes the antibonding and bonding orbitals. $|d_T\rangle$ is the d orbital of the 3d$^3$ ion and $|p_T\rangle$ is the p orbital of the ligand. $N_T^{a}$ is the normalization factor and $\lambda_T^{a}$ is the orbital mixing coefficient. Thus, we have the normalization condition

$$N_T^{a} = [1 + \lambda_T^{a} S_{dp}(\gamma) + (\lambda_T^{a})^2]^{-1/2},$$

(5)

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

$$f_T = (B/B_0 + C/C_0)/2 \approx (N_T^{a})^2 [1 + (\lambda_T^{a})^2 S_{dp}(\gamma) - 2\lambda_T^{a} S_{dp}(\gamma)],$$

(6)

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

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

(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 $\Delta g$ 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.

$$\Delta g = \Delta g_{CF} + \Delta g_{CT},$$

$$\Delta g_{CF} = -8k_{CF}^{3/2}/3E_1$$

$$- 2k_{CF}^{3/2} (2k_{CF}^{3/2} - k_{CF}^{3/2} + 2g_{S}^{3/2})/9E_1^2$$

$$+ 4k_{CF}^{3/2} (k_{CF} - 2g_{S})/9E_1^2$$

$$- 2k_{CF}^{3/2} (k_{CF} + g_{S})/3E_1^2$$

$$+ 4k_{CF}^{3/2} (k_{CF} + g_{S})/3E_1^2$$

$$- 4k_{CF}^{3/2} (k_{CF} + g_{S})/3E_1^2$$

$$+ 4k_{CF}^{3/2} (k_{CF} + g_{S})/3E_1^2,$$

$$\Delta g_{CT} = 8k_{CT}^{3/2} (3E_n),$$

$$A = A_{CF} + A_{CT},$$

$$A_{CF} = -P_{CF}^{3/2} (8k_{CF}^{3/2} (3E_1) + 2k_{CF}^{3/2} (2k_{CF}^{3/2} - k_{CF}^{3/2} + 2g_{S}^{3/2})/9E_1^2$$

$$- 4k_{CF}^{3/2} (k_{CF} - 2g_{S})/9E_1^2$$

$$+ 4k_{CF}^{3/2} (k_{CF} + g_{S})/3E_1^2,$$
and those in the CT mechanism are
\[
\begin{align*}
\zeta_{CT} &= N_{P}N_{N}^{2}[\lambda_{g} + (\lambda_{g})^{2}c_{dp}^{0}/2], \\
\zeta'_{CT} &= N_{P}N_{N}^{2}[(\lambda_{g}^{2} - \lambda_{g}^{2})c_{dp}^{0}/2], \\
k_{CT} &= N_{P}N_{N}^{2}[1 + (\lambda_{g}^{2})/2], \\
k'_{CT} &= N_{P}N_{N}^{2}[1 + \lambda_{g}^{2}c_{dp}^{0}/2], \\
P_{CT} &= (N_{P}^{2})P_{0}, \\
P'_{CT} &= N_{P}N_{N}^{2}P_{0},
\end{align*}
\]
and those in the CT mechanism are
\[
\begin{align*}
\zeta_{CT} &= N_{P}N_{N}^{2}[\lambda_{g} - S_{dp}(t_{2g})c_{dp}^{0} - \lambda_{g}^{2}c_{dp}^{0}/2], \\
\zeta'_{CT} &= N_{P}N_{N}^{2}[\lambda_{g}^{2} - \lambda_{g}^{2}S_{dp}(t_{2g})c_{dp}^{0}/2], \\
k_{CT} &= N_{P}N_{N}^{2}[1 + (\lambda_{g}^{2})S_{dp}(t_{2g})], \\
k'_{CT} &= N_{P}N_{N}^{2}[1 + \lambda_{g}^{2}S_{dp}(t_{2g})], \\
P_{CT} &= (N_{P}^{2})P_{0}, \\
P'_{CT} &= N_{P}N_{N}^{2}P_{0}.
\end{align*}
\]
Here \(c_{dp}^{0}\) and \(c_{dp}^{0}\) 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 \(\Delta g\) becomes that of the twoSO-coupling-coefficient, based on the CF mechanism [1, 2]. Further, if the terms related to \(c_{dp}^{0}\) and \(\lambda_{g}^{2}\) are also neglected (i.e. \(c_{dp}^{0} = 0\) and \(\lambda_{g}^{2} = 0\)), 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 \(\Delta g\) 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 \(D_{J}\) 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 \(D_{Q} \propto R^{-3}\) 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 \(R_{HI}\), may be obtained from the empirical formula [20, 21] \(R \approx R_{HI} + (r_{I} - r_{H})/2\). For the studied cubic centers, the impurity radii are \(r_I(V^{2+}) \approx 0.88\) Å, \(r_I(Cr^{3+}) \approx 0.63\) Å, \(r_I(Mn^{4+}) \approx 0.60\) Å, and the radii of the replaced ions are \(r_{H}(Mg^{2+}) \approx 0.66\) Å and \(r_{H}(Ca^{2+}) \approx 0.99\) Å [22], \(R_{HI}(MgO) \approx 2.15\) Å and \(R_{HI}(CaO) \approx 2.405\) Å [22]. The distances \(R\) for various centers are shown in Table 1. The spectral parameters \(B, C\) and \(D_{Q}\) are also collected there. Thus, the coefficients \(f_{x}\) 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 \(S_{dp}(g)\) in (5) – (7) are determined and shown in Table 1. Thus, the LCAO coefficients \(N_{P}\) and \(\lambda_{g}\) 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 \(c_{dp}^{0}(\approx 167, 273\) and 405 cm\(^{-1}\)) [10, 23] and \(P_{0}(\approx 128.10^{-4}, -39.7.10^{-4}\) and 235·10\(^{-4}\) 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]
\[
E_{n} \approx 30000[\chi(L) - \chi(M)]\text{cm}^{-1},
\]
where \(\chi(L)\) and \(\chi(M)\) are, respectively, the optical electronegativities of the ligand and 3d\(^n\) ions. In the given systems, \(\chi(O^{2-}) \approx 3.2\), \(\chi(Cr^{3+}) \approx 1.9\) and \(\chi(Mn^{4+}) \approx 3.0\) [13]. For V\(^{2+}\), the value of \(\chi\) 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 \(\kappa \approx -2\chi/(3r^{-3})\),
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.

<table>
<thead>
<tr>
<th>Ions</th>
<th>MgO</th>
<th>CaO</th>
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<th>CaO</th>
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<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ (Å)</td>
<td>2.215</td>
<td>2.350</td>
<td>2.090</td>
<td>2.225</td>
<td>2.075</td>
<td>2.210</td>
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<td>$B$ (cm$^{-1}$)</td>
<td>683</td>
<td>101</td>
<td>690</td>
<td>101</td>
<td>710</td>
<td>101</td>
</tr>
<tr>
<td>$C$ (cm$^{-1}$)</td>
<td>2420</td>
<td>101</td>
<td>3320</td>
<td>101</td>
<td>3330</td>
<td>101</td>
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<tr>
<td>$D_b$ (cm$^{-1}$)</td>
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<td>101</td>
<td>1590</td>
<td>101</td>
<td>1160</td>
<td>101</td>
</tr>
<tr>
<td>$f'_b$</td>
<td>0.870</td>
<td>0.901</td>
<td>0.766</td>
<td>0.777</td>
<td>0.740</td>
<td>0.743</td>
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<tr>
<td>$E_b$ (cm$^{-1}$)</td>
<td>5400</td>
<td>101</td>
<td>3900</td>
<td>101</td>
<td>3900</td>
<td>101</td>
</tr>
<tr>
<td>$S_{dp}(d_{2g})$</td>
<td>0.022</td>
<td>0.014</td>
<td>0.023</td>
<td>0.015</td>
<td>0.018</td>
<td>0.011</td>
</tr>
<tr>
<td>$S_{dp}(d_{3g})$</td>
<td>0.068</td>
<td>0.048</td>
<td>0.071</td>
<td>0.049</td>
<td>0.057</td>
<td>0.039</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0.396</td>
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</table>

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.

<table>
<thead>
<tr>
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<th>MgO</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{CF}$</td>
<td>-0.0233</td>
<td>-0.0336</td>
<td>-0.0248</td>
<td>-0.0335</td>
<td>-0.0406</td>
<td>-0.0459</td>
</tr>
<tr>
<td>$\Delta_{CT}$</td>
<td>0.0004</td>
<td>0.00005</td>
<td>0.00025</td>
<td>0.00030</td>
<td>0.0316</td>
<td>0.0357</td>
</tr>
<tr>
<td>$\Delta$ (tot)</td>
<td>-0.0229</td>
<td>-0.0331</td>
<td>-0.0223</td>
<td>-0.0305</td>
<td>-0.0090</td>
<td>-0.0102</td>
</tr>
<tr>
<td>$\Delta$ (Expt.)</td>
<td>-0.0220 (5)</td>
<td>-0.0340 (5)</td>
<td>-0.0223 (5)</td>
<td>-0.0291 (5)</td>
<td>-0.0086 (3)</td>
<td>-0.0092 (5)</td>
</tr>
<tr>
<td>$A_{CT}$</td>
<td>0.563</td>
<td>0.558</td>
<td>0.382</td>
<td>0.396</td>
<td>0.292</td>
<td>0.303</td>
</tr>
<tr>
<td>$A_{CT}$</td>
<td>0.472</td>
<td>0.441</td>
<td>0.653</td>
<td>0.670</td>
<td>0.704</td>
<td>0.722</td>
</tr>
<tr>
<td>$A_{CT}$</td>
<td>-1.452</td>
<td>-1.642</td>
<td>-0.986</td>
<td>-0.989</td>
<td>-0.899</td>
<td>-0.883</td>
</tr>
<tr>
<td>$A_{CT}$</td>
<td>-1.904</td>
<td>-2.059</td>
<td>-1.197</td>
<td>-1.134</td>
<td>-1.037</td>
<td>-0.977</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.563</td>
<td>0.558</td>
<td>0.382</td>
<td>0.396</td>
<td>0.292</td>
<td>0.303</td>
</tr>
</tbody>
</table>

where $\chi$ is characteristic of the density of unpaired spins at the nucleus of the central metal ion and $(r - \bar{r})$ is the expectation value of the inverse cube of the radial wave-function of the 3d orbital [27]. By using the values of $(r - \bar{r})$ for $V^{2+}$, $Cr^{3+}$ and $Mn^{4+}$ [27] and $\chi$ for those in MgO and CaO (note: the value of $\chi$ 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 $\kappa$ 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 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 $\Delta g_{\text{CT}}$ due to the CT mechanism are opposite in sign and about 2%, 10% and 78% in magnitude compared with $\Delta g_{\text{CF}}$ due to the CF mechanism for $V^{2+}$, $Cr^{3+}$ and $Mn^{4+}$, respectively. So, the experimental g factors for the studied 3d 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 $|\Delta g_{\text{CT}}/\Delta g_{\text{CF}}|$) increases with increasing valence state of the 3d 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. $\Delta g_{\text{CF}}$ 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 $\Delta g$ from the CT mechanism are much larger and should be taken into account. (ii) According to
(10), the contributions of $\xi_d$ and $\xi_p$ are of the same sign in $\xi_{CT}$. Thus, it can be expected that for large ligands (e.g., Br\textsuperscript{-}, I\textsuperscript{-}) with much larger $\xi_p$ importance of $\Delta\xi_{CF}$ would increase even more rapidly. (iii) The ratio $|\Delta\xi_{CF}/\Delta\xi_{CT}|$ decreases slightly from MgO to CaO for each 3d\textsuperscript{3} ion, suggesting that the magnitude of $\Delta\xi_{CF}$ increases more significantly than $\Delta\xi_{CT}$ does in the latter.

2.) Compared with the case of $\Delta g$, 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 ($\kappa P_{CF}$ 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\textsuperscript{3} ion, the ratio $|A_{CT}/A_{CF}|$ decreases slightly from MgO to CaO. Seen from (8), both $A_{CF}$ and $A_{CT}$ increase with increase of $\kappa$ 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\textsuperscript{2+} and Mn\textsuperscript{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\textsuperscript{4+} center in Mn doped CaO powder with some uncertainty [8]. As measured by many workers [6, 26, 28, 29], the values of $\Delta g$ are usually $\sim$ 0.001 for Mn\textsuperscript{2+} in CaO (and other similar oxides), which are almost by one order in magnitude smaller than those ($\sim$ 0.009) of the experimental data for Mn\textsuperscript{4+} in oxides [7, 26]. According to the observed EPR spectrum (i.e., $\Delta g \approx$ $\sim$ 0.0092(5) and $A \approx$ $\sim$ 72.8 $\cdot$ 10$^{-4}$ cm$^{-1}$) [8] and the studies in this work, it should be indeed attributed to the cubic Mn\textsuperscript{4+} center rather than the Mn\textsuperscript{2+} one.

In summary, the SH parameters for the cubic V\textsuperscript{2+}, Cr\textsuperscript{3+} and Mn\textsuperscript{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\textsuperscript{3} systems with a high valence of the central ions.