Research on the Spin-Hamiltonian Parameters and Local Structure for the Tetragonal Mo^{5+} Centers in $CaWO_4$ Crystal

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The spin-Hamiltonian parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$(A), $A_\perp$(A), $A_\parallel$(B) and $A_\perp$(B), A(A) and A(B) belonging to isotopes $^{95}Mo^{5+}$ and $^{97}Mo^{5+}$) of Mo^{5+} ion at the tetragonally-compressed tetrahedral W^{6+} site in $CaWO_4$ crystal are calculated from the high-order perturbation formulae based on the two-mechanism model, where besides the contributions to spin-Hamiltonian parameters due to the crystal-field mechanism concerning the crystal-field excited states in the extensively-applied crystal-field theory, those due to charge-transfer mechanism concerning charge-transfer excited states (which are omitted in crystal-field theory) are included. The calculated results are in reasonable agreement with the experimental values. The calculations show that for the high-valence state d^n ions (e. g., Mo^{5+} considered) in crystals, the contributions due to charge-transfer mechanism should be taken into account in the studies of spin-Hamiltonian parameters. The local structure of Mo^{5+} center in $CaWO_4$ crystal due to the impurity-induced local lattice relaxation is estimated from the calculations. The results are discussed.

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1. Introduction

Tungstates crystals AWO_4 (where A indicates a divalent cation) with sheelite-type structure have attracted investigative efforts because they can be readily grown as good-sized, stable, colorlessly transparent and hard crystals. On being doped with rare earth and transition metal ions, they have the potential applications in solid state lasers, luminescence, phosphor and scintillator devices [1–6]. This fact caused a number of spectroscopic studies for AWO_4 crystals doped with rare earth and transition metal ions [1–12]. Decades ago, Azarbayejani and Merlo [12] measured the electron paramagnetic resonance (EPR) spectra of Mo^{5+}-doped $CaWO_4$ crystal and found that Mo^{5+} ion occupies the tetragonally-compressed W^{6+} site. The spin-Hamiltonian parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$(A), $A_\perp$(A), $A_\parallel$(B) and $A_\perp$(B), A(A) and A(B) belong to isotopes $^{95}Mo^{5+}$ and $^{97}Mo^{5+}$) of this Mo^{5+} tetrahedral center were reported from the measurement [12]. Up to date there is still lack of the theoretical explanations for these spin-Hamiltonian parameters.

For d^n ions in crystals, the spin-Hamiltonian parameters are generally calculated theoretically by the extensively-applied crystal-field (CF) theory where only the contributions due to CF mechanism concerning the interactions of CF excited states with the ground state are considered [13–15]. However, strictly speaking, the spin-Hamiltonian parameters originate from two contributions or mechanisms, one is the above CF mechanism and another is the charge-transfer (CT) mechanism concerning with the interactions of CT excited states with the ground state [16–18]. The neglect of CT mechanism in CF theory is due to the CT energy levels being often much higher than the CF energy levels [19], which results in the very weak influence of CT energy levels on the ground state. However, since the CT energy levels lower with the increase of the valence state of d^n ions [19], for the high-valence state d^n ions (e. g., Mo^{5+} considered here) in crystals, the reasonable and exact calculations of spin-Hamiltonian parameters should also take the contributions due to CT mechanism into account and so the two (CF and CT)-mechanism model should be used. In this paper, we calculate the spin-Hamiltonian parameters of Mo^{5+}-doped $CaWO_4$ crystals from the high-order perturbation formulae based on the two-mechanism model. In view of the fact that the spin-Hamiltonian parameters of a paramagnetic ion in crystals depend sensitively upon its immediate environment, the local (or defect) structure of Mo^{5+} centers caused by the impurity-induced local crystal relaxation in $CaWO_4$ crystals can be estimated from the calculations. The results are discussed.

2. Calculation

The one-electron basis functions in the two-mechanism model for a tetrahedral d^n cluster can be expressed as the linear combinations of d orbitals $|d_\gamma\rangle$ of d^n ions and the p orbitals $|\pi_\gamma\rangle$ and $|\sigma_\gamma\rangle$ of ligand [17, 18]:

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$$\psi_{\mathrm{e}}^{\chi} = N_{\mathrm{e}}^{\chi}\left(|d_{\mathrm{e}}\rangle + \sqrt{3}\lambda_{\pi}^{\chi}|\pi_{\mathrm{e}}\rangle\right),$$

$$\psi_{\mathrm{t}}^{\chi} = N_{\mathrm{t}}^{\chi}\left(|d_{\mathrm{t}}\langle + \lambda_{\sigma}^{\chi}|\sigma_{\mathrm{t}}\langle + \lambda_{\pi}^{\chi}|\pi_{\mathrm{t}}\rangle\right), \qquad (1)$$

where the subscript γ (= t or e) indicates the irreducible representation of T_d group and the superscript χ (= a or b) stands for the anti-bonding orbitals related to CF mechanism and bonding orbitals concerning CT mechanism. N_γ (normalization coefficients) and λ_β (the orbital mixing coefficients, $\beta = \sigma$ or π) are the molecular orbital (MO) coefficients.

The perturbation formulae of spin-Hamiltonian parameters for d^1 center in crystals depend upon its ground state and symmetry [13–15]. From the observed $g_\parallel > g_\perp$, one can conclude that the ground state of Mo^{5+} in $\mathrm{CaWO_4}$ is $|d_z^2\rangle$. Thus, from the above one-electron basis functions and by adding the spin–orbit interaction term $H_{\mathrm{SO}}^{\mathrm{CT}}$, the Zeeman (or magnetic) interaction term $H_{\mathrm{Ze}}^{\mathrm{CT}}$ and the hyperfine interaction term $H_{\mathrm{hf}}^{\mathrm{CT}}$ connected with CT mechanism to the traditional perturbation Hamiltonian in the CF mechanism, the high-order perturbation formulae based on the two-mechanism model for g factors of tetragonal d^1 tetrahedral cluster with the ground state $|d_z^2\rangle$ are derived in Ref. [18] and those for hyperfine structure constants A_i are derived here. They are

$$g_\parallel = g_{\mathrm{e}} + \Delta g_\parallel^{\mathrm{CF}} + \Delta g_\parallel^{\mathrm{CT}},$$

$$\Delta g_\parallel^{\mathrm{CF}} = \frac{3\zeta'^{2}_{\mathrm{CF}}(k_{\mathrm{CF}} - g_{\mathrm{e}})}{(E_1^{\mathrm{CF}})^2},$$

$$\Delta g_\parallel^{\mathrm{CT}} = \frac{3\zeta_{\mathrm{CT}}^2 k'_{\mathrm{CT}}}{E_1^{\mathrm{CT}}E_2^{\mathrm{CT}}},$$

$$g_\perp = g_{\mathrm{e}} + \Delta g_\perp^{\mathrm{CF}} + \Delta g_\perp^{\mathrm{CT}},$$

$$\Delta g_\perp^{\mathrm{CF}} = \frac{6\zeta_{\mathrm{CF}}k'_{\mathrm{CF}}}{E_1^{\mathrm{CF}}} - \frac{3\zeta'_{\mathrm{CF}}(\zeta_{\mathrm{CF}}k'_{\mathrm{CF}} + \frac{1}{2}\zeta'_{\mathrm{CF}}g_{\mathrm{e}})}{(E_1^{\mathrm{CF}})^2},$$

$$\Delta g_\perp^{\mathrm{CT}} = \frac{6\zeta_{\mathrm{CT}}k_{\mathrm{CT}}}{E_1^{\mathrm{CT}}},$$

$$A_\parallel = A_\parallel^{(1)} + A_\parallel^{(2)\mathrm{CF}} + A_\parallel^{(2)\mathrm{CT}},$$

$$A_\parallel^{(1)} = P_{\mathrm{CF}}\left(-\kappa + \frac{4}{7}\right),$$

$$A_\parallel^{(2)\mathrm{CF}} = P'_{\mathrm{CF}}[(g_\parallel^{\mathrm{CF}} - g_{\mathrm{e}}) - \frac{1}{7}(g_\perp^{\mathrm{CF}} - g_{\mathrm{e}})],$$

$$A_\parallel^{(2)\mathrm{CT}} = P'_{\mathrm{CT}}\left(\frac{3\zeta_{\mathrm{CT}}^2 k'_{\mathrm{CT}}}{E_1^{\mathrm{CT}}E_2^{\mathrm{CT}}}\right),$$

$$A_\perp = A_\perp^{(1)} + A_\perp^{(2)\mathrm{CF}} + A_\perp^{(2)\mathrm{CT}},$$

$$A_\perp^{(1)} = P_{\mathrm{CF}}\left(-\kappa - \frac{2}{7}\right),$$

$$A_\perp^{(2)\mathrm{CF}} = P'_{\mathrm{CF}}\left[\frac{15}{14}(g_\perp^{\mathrm{CF}} - g_{\mathrm{e}})\right],$$

$$A_\perp^{(2)CT} = P'_{\mathrm{CT}}\left(\frac{6\zeta_{\mathrm{CT}}k_{\mathrm{CT}}}{E_1^{\mathrm{CT}}}\right) \qquad (2)$$

with the spin–orbit parameters ζ, $\zeta\prime$, the orbit reduction factors k, $k\prime$ and the dipolar hyperfine structure constants P, $P\prime$ in CF and CT mechanisms [17, 18]:

$$\zeta_{\mathrm{CF}} = (N_{\mathrm{t}}^{\mathrm{a}})^2\left[\zeta_d^0 + \left(\sqrt{2}\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{a}} - \frac{\lambda_\pi^{\mathrm{a}2}}{2}\right)\zeta_p^0\right],$$

$$\zeta'_{\mathrm{CF}} = N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{a}}\left[\zeta_d^0 + \left(\frac{\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{a}}}{\sqrt{2}} + \frac{\lambda_\pi^{\mathrm{a}2}}{2}\right)\zeta_p^0\right],$$

$$\zeta_{\mathrm{CT}} = N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{t}}^{\mathrm{b}}\left[\zeta_d^0 + \left(\frac{\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{b}} + \lambda_\pi^{\mathrm{b}}\lambda_\sigma^{\mathrm{a}}}{\sqrt{2}} - \frac{\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}}}{2}\right)\zeta_p^0\right],$$

$$\zeta'_{\mathrm{CT}} = N_{\mathrm{e}}^{\mathrm{b}}N_{\mathrm{t}}^{\mathrm{a}}\left[\zeta_d^0 + \left(\frac{\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{b}}}{\sqrt{2}} + \frac{\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}}}{2}\right)\zeta_p^0\right],$$

$$k_{\mathrm{CF}}=(N_{\mathrm{t}}^{\mathrm{a}})^2\left[1-\frac{\lambda_\pi^{\mathrm{a}2}}{2}+\sqrt{2}\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{a}}+2\lambda_\sigma^{\mathrm{a}}S_{dp}(\sigma)+2\lambda_\pi^{\mathrm{a}}S_{dp}(\pi)\right],$$

$$k'_{\mathrm{CF}} = N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{a}}\left[1 + \frac{\lambda_\pi^{\mathrm{a}2}}{2} + \frac{\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{a}}}{\sqrt{2}}\right.$$
$$\left. +4\lambda_\pi^{\mathrm{a}}S_{dp}(\pi) + 2\lambda_\sigma^{\mathrm{a}}S_{dp}(\sigma)\right],$$

$$k_{\mathrm{CT}} = N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{t}}^{\mathrm{b}}\left[1 + \left(\frac{\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{b}} + \lambda_\pi^{\mathrm{b}}\lambda_\sigma^{\mathrm{a}}}{\sqrt{2}} - \frac{\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}}}{2}\right)\right.$$
$$\left. +(\lambda_\sigma^{\mathrm{a}} + \lambda_\sigma^{\mathrm{b}})S_{dp}(\sigma) + (\lambda_\pi^{\mathrm{a}} + \lambda_\pi^{\mathrm{b}})S_{dp}(\pi)\right],$$

$$k'_{\mathrm{CT}} = N_{\mathrm{e}}^{\mathrm{a}}N_{\mathrm{t}}^{\mathrm{b}}\left[1 + \left(\frac{\lambda_\pi^{\mathrm{a}}\lambda_\sigma^{\mathrm{b}}}{\sqrt{2}} - \frac{\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}}}{2}\right)\right.$$
$$\left. +\lambda_\sigma^{\mathrm{b}}S_{dp}(\sigma) + (3\lambda_\pi^{\mathrm{a}} + \lambda_\pi^{\mathrm{b}})S_{dp}(\pi)\right],$$

$$P_{\mathrm{CF}} = (N_{\mathrm{t}}^{\mathrm{a}})^2P_0, \quad P'_{\mathrm{CF}} = N_{\mathrm{t}}^{\mathrm{a}}N_{\mathrm{e}}^{\mathrm{a}}P_0,$$

$$P_{\mathrm{CT}} = N_{\mathrm{t}}^{\mathrm{b}}N_{\mathrm{t}}^{\mathrm{a}}P_0, \quad P'_{\mathrm{CT}} = N_{\mathrm{e}}^{\mathrm{a}}N_{\mathrm{t}}^{\mathrm{b}}P_0. \qquad (3)$$

In above formulae, the superscripts and subscripts CF and CT stand for the parameters in the CF and CT mechanisms. g_{e} (≈ 2.0023) is the free-electron g value. κ is the core polarization constant. E_1^{CF} and $E_{\mathrm{j}}^{\mathrm{CT}}$ are the CF and CT energy levels. ζ_d^0 and ζ_p^0 are the spin–orbit parameters of free d^n ion and free ligand. P_0 is the corresponding parameter of free d^n ion. For $(\mathrm{MoO_4})^{3-}$ clusters under study, we have $\zeta_d^0(Mo^{5+}) \approx 1030\ \mathrm{cm^{-1}}$ [14], $\zeta_p^0(\mathrm{O}^{2-}) \approx 150\ \mathrm{cm^{-1}}$ [20], $P_0(^{95}\mathrm{Mo}^{5+}) \approx -66.7 \times 10^{-4}\ \mathrm{cm^{-1}}$ and $P_0(^{97}\mathrm{Mo}^{5+}) \approx -68.2 \times 10^{-4}\ \mathrm{cm^{-1}}$ [21]. $S_{dp}(\beta)$ are the group overlap integrals which can be calculated from the Slater-type self-consistent field (SCF) functions [22, 23] with the metal–ligand distance R. Since the ionic radius r_{i} of impurity is unlike the radius r_{h} of the host ion it replaces, the metal–ligand distance R in the impurity center should differ from the corresponding distance R_{h} in the host crystal. As an approximation, we estimate the distance R by using the empirical formula $R \approx R_{\mathrm{h}} + \frac{1}{2}(r_{\mathrm{i}} - r_{\mathrm{h}})$ [24]. For Mo^{5+} at the W^{6+} site of $\mathrm{CaWO_4}$ crystal, from $r_{\mathrm{i}}(\mathrm{Mo}^{5+}) \approx 0.60$ Å, $r_{\mathrm{h}}(\mathrm{W}^{6+}) \approx 0.56$ Å [25] and $R_{\mathrm{h}} \approx 1.782$ Å [26], we obtain $R \approx 1.802$ Å. Thus, we have $S_{dp}(\pi) \approx 0.03320$ and $S_{dp}(\sigma) \approx -0.10744$.

The MO coefficients N_γ^χ and λ_β^χ needed for the calculations of the parameters in Eq. (3) can be related by the normalization correlations

$$N_{\mathrm{e}}^{\chi} = [1 + 3(\lambda_\sigma^\chi)^2 + 6\lambda_\pi^\chi S_{dp}(\pi)]^{-\frac{1}{2}},$$

$$N_{\mathrm{t}}^{\chi}=[1+(\lambda_\sigma^\chi)^2+(\lambda_\pi^\chi)^2+2\lambda_\sigma^\chi S_{dp}(\sigma)+2\lambda_\pi^\chi S_{dp}(\pi)]^{-\frac{1}{2}} \qquad (4)$$

and the orthonormal relations [11]:

$$\lambda_\pi^{\mathrm{b}} = -\frac{1+3\lambda_\pi^{\mathrm{a}} S_{dp}(\pi)}{3[\lambda_\pi^{\mathrm{a}} + S_{dp}(\pi)]},$$

$$\lambda_\sigma^{\mathrm{b}} = -\frac{1+\lambda_\pi^{\mathrm{a}}\lambda_\pi^{\mathrm{b}} + (\lambda_\pi^{\mathrm{a}}+\lambda_\pi^{\mathrm{b}})S_{dp}(\pi) + \lambda_\sigma^{\mathrm{a}} S_{dp}(\sigma)}{\lambda_\sigma^{\mathrm{a}} + S_{dp}(\sigma)} \quad (5)$$

and the approximate relationships

$$f_{\mathrm{e}} = (N_{\mathrm{e}}^{\mathrm{a}})^4[1+6\lambda_\pi^{\mathrm{a}} S_{dp}(\pi) + 9(\lambda_\pi^{\mathrm{a}})^2 S_{dp}^2(\pi)]$$

$$f_{\mathrm{t}} = (N_{\mathrm{t}}^{\mathrm{a}})^4[1+2\lambda_\sigma^{\mathrm{a}} S_{dp}(\sigma) + 2\lambda_\pi^{\mathrm{a}} S_{dp}(\pi)$$

$$+2\lambda_\sigma^{\mathrm{a}} S_{dp}(\sigma)\lambda_\pi^{\mathrm{a}} S_{dp}(\pi) + (\lambda_\sigma^{\mathrm{a}})^2 S_{dp}^2(\sigma) + (\lambda_\sigma^{\mathrm{a}})^2 S_{dp}^2(\sigma)], \quad (6)$$

in which we assume the covalence factor $f_{\mathrm{t}} \approx f_{\mathrm{e}} \approx f_\gamma$ for decreasing the number of adjustable parameter and take f_γ as an adjustable parameter.

The CT energy levels of $(\mathrm{MoO_4})^{3-}$ clusters have not been reported. Since the CT energy levels of the $(\mathrm{CuCl_4})^{2-}$ tetrahedral clusters are near to those of the $(\mathrm{CuCl_6})^{4-}$ octahedral clusters [27, 28], for $(\mathrm{MoO_4})^{3-}$ tetrahedral clusters, we approximately take $E_1^{\mathrm{CT}} \approx 32400\ \mathrm{cm}^{-1}$ and $E_2^{\mathrm{CT}} \approx 36400\ \mathrm{cm}^{-1}$, the values of $(\mathrm{MoO_6})^{7-}$ octahedral clusters [29].

In the CF theory, the CF energy level

$$E_1^{\mathrm{CF}} = E(|d_{xy,yz}\rangle) - E(|d_z\rangle) \approx 10Dq - Ds - 10Dt, \quad (7)$$

where the tetragonal field parameters Ds and Dt can be calculated from the superposition model [30]. In the model, they can be written as

$$Ds = -\frac{1}{7}B_{20} = -\frac{4}{7}\bar{A}_2(R)(3\cos^2\theta - 1)$$

$$Dt = -\frac{1}{21}\left(B_{40} - \frac{\sqrt{70}}{5}B_{44}\right) =$$

$$-\frac{4}{21}\bar{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3 + 7\sin^4\theta), \quad (8)$$

where B_{kl} are the CF parameters in Wybourne notation [31, 32]. $\bar{A}_k(R)$ $(k = 2, 4)$ are the intrinsic parameters. For $4d^n$ ions in crystals, the ratio $\bar{A}_2(R)/\bar{A}_4(R) \approx 6 \pm 2$ was found [29, 33–35], we take the average value $\bar{A}_2(R)/\bar{A}_4(R) \approx 6$ here. The parameter $\bar{A}_4(R)$ for d^n tetrahedral cluster can take the form $\bar{A}_4(R) \approx -\frac{27}{16}Dq$ [36], where Dq is the cubic field parameter. The value of Dq for $(\mathrm{MoO_4})^{3-}$ cluster in crystals has not been reported and is estimated approximately as follows.

The optical spectral data for various d^n ions in crystals suggest that the value of Dq for $4d^n$ clusters is about 1.5(1) times that of the isoelectronic $3d^n$ clusters [19]. So, from $Dq \approx 1350(50)\ \mathrm{cm}^{-1}$ of the $3d^1(\mathrm{CrO_4})^{3-}$ tetrahedral clusters [37], we obtain for the corresponding $4d^1(\mathrm{MoO_4})^{3-}$ tetrahedral cluster, $Dq \approx 1900\ \mathrm{cm}^{-1}$. θ refers to the angle between the metal–ligand distance R and C_4 axis. Analogous to the bonding length R, the bonding angle θ in the impurity center may be different from the corresponding angle θ_{h} in the host crystal. We assume $\theta \approx \theta_{\mathrm{h}} + \Delta\theta$, where $\theta_{\mathrm{h}} \approx 56.89°$ [26] in the host $\mathrm{CaWO_4}$ crystal and $\Delta\theta$ represents the impurity-induced angular distortion. $\Delta\theta$ is also treated as an adjustable parameter. Thus, in the above formulae, we have three parameters f_γ, $\Delta\theta$ and κ left as the adjustable parameters. From the calculated (with the above high-order perturbation formulae)-to-experimental fitting of spin-Hamiltonian parameters for $\mathrm{CaWO_4}$: Mo^{5+}, we obtain

$$f_\gamma \approx 0.525, \quad \Delta\theta \approx 0.4°, \quad \kappa \approx 0.41. \quad (9)$$

The MO coefficients based on the value of f_γ are given in Table I. The parameters in Eq. (3) calculated from these MO coefficients are listed in Table II. The calculated spin-Hamiltonian parameters are compared with the experimental values in Table III.

TABLE I

The molecular orbital (MO) coefficients for $(\mathrm{MoO_4})^{3-}$ tetrahedral clusters in $\mathrm{CaWO_4}$: Mo^{5+} crystal.

$N_{\mathrm{t}}^{\mathrm{a}}$	$N_{\mathrm{e}}^{\mathrm{a}}$	$N_{\mathrm{t}}^{\mathrm{b}}$	$N_{\mathrm{e}}^{\mathrm{b}}$	$\lambda_\sigma^{\mathrm{a}}$	λ_π^{a}	$\lambda_\sigma^{\mathrm{b}}$	λ_π^{b}
0.8767	0.8745	0.3622	0.2350	0.3709	−0.5274	−2.3792	0.6391

TABLE II

The spin-orbit parameters ζ, ζ' (cm^{-1}), the orbital reduction factors k, k' and the dipolar hyperfine structure constants P, P' (in $10^{-4}\ \mathrm{cm}^{-1}$) in CF and CT mechanisms for $(\mathrm{MoO_4})^{3-}$ tetrahedral clusters in $\mathrm{CaWO_4}$: Mo^{5+} crystal.

ζ_{CF}	ζ'_{CF}	ζ_{CT}	ζ'_{CT}	k_{CF}	k'_{CF}	k_{CT}	k'_{CT}
743.8	789.8	250.0	360.3	0.3610	0.4698	0.7757	0.7222
$P_{\mathrm{CF}}(\mathrm{A})^a$	$P'_{\mathrm{CF}}(\mathrm{A})^a$	$P_{\mathrm{CT}}(\mathrm{A})^a$	$P'_{\mathrm{CT}}(\mathrm{A})^a$	$P_{\mathrm{CF}}(\mathrm{B})^a$	$P'_{\mathrm{CF}}(\mathrm{B})^a$	$P_{\mathrm{CT}}(\mathrm{B})^a$	$P'_{\mathrm{CT}}(\mathrm{B})^a$
−51.3	−51.1	−21.2	−21.1	−52.4	−52.3	−21.7	−21.6

[a] $P(\mathrm{A})$ and $P(\mathrm{B})$ belong to isotopes $^{95}\mathrm{Mo}^{5+}$ and $^{97}\mathrm{Mo}^{5+}$.

TABLE III

The spin-Hamiltonian parameters (g factor$g_{\parallel}$, $g_{\perp}$ and hyperfine structure constants $A_{\parallel}(\mathrm{A})$, $A_{\perp}(\mathrm{A})$, $A_{\parallel}(\mathrm{B})$ and $A_{\perp}(\mathrm{B})$, $A(\mathrm{A})$ and $A(\mathrm{B})$ belong to isotopes $^{95}\mathrm{Mo}^{5+}$ and $^{97}\mathrm{Mo}^{5+}$, constants A are in units of 10^{-4} cm^{-1}) for the tetragonal $(\mathrm{MoO_4})^{3-}$ clusters in $\mathrm{CaWO_4}$ crystals.

$\Delta g_{\parallel}^{\mathrm{CF}}$	$\Delta g_{\parallel}^{\mathrm{CT}}$	$g_{\parallel}$(calc.)	$g_{\parallel}$(expt. [12])	
-0.0175	0.0001	1.9849	1.987	
$\Delta g_{\perp}^{\mathrm{CF}}$	$\Delta g_{\perp}^{\mathrm{CT}}$	$g_{\perp}$(calc.)	$g_{\perp}$(expt. [12])	
-0.1508	0.0359	1.8874	1.887	
$A_{\parallel}^{(1)}(\mathrm{A})$	$A_{\parallel}^{(2)\mathrm{CF}}(\mathrm{A})$	$A_{\parallel}^{(2)\mathrm{CT}}(\mathrm{A})$	$A_{\parallel}(\mathrm{A})$(calc.)	$A_{\parallel}(\mathrm{A})$(expt.[12])
-8.27	-0.21	-0.002	-8.48	8.39^{a}
$A_{\perp}^{(1)}(\mathrm{A})$	$A_{\perp}^{(2)\mathrm{CF}}(\mathrm{A})$	$A_{\perp}^{(2)\mathrm{CT}}(\mathrm{A})$	$A_{\perp}(\mathrm{A})$(calc.)	$A_{\perp}(\mathrm{A})$(expt.[12])
35.66	8.26	-0.76	43.16	41.18^{a}
$A_{\parallel}^{(1)}(\mathrm{B})$	$A_{\parallel}^{(2)\mathrm{CF}}(\mathrm{B})$	$A_{\parallel}^{(2)\mathrm{CT}}(\mathrm{B})$	$A_{\parallel}(\mathrm{B})$(calc.)	$A_{\parallel}(\mathrm{B})$(expt.[12])
-8.45	-0.21	-0.002	-8.66	8.64^{a}
$A_{\perp}^{(1)}(\mathrm{B})$	$A_{\perp}^{(2)CF}(\mathrm{B})$	$A_{\perp}^{(2)CT}(\mathrm{B})$	$A_{\perp}(\mathrm{B})$(calc.)	$A_{\perp}(\mathrm{B})$(expt.[12])
36.46	8.44	-0.78	44.12	42.52^{a}

^{a}The values are actually the absolute values.

3. Discussion

The signs of hyperfine structure constants A_i are hard to be determined solely by EPR experiment [14, 21, 38]. So, even though the values of A_i are frequently written as positive in EPR experiment, they are actually the absolute values. For Mo^{5+} ions in $\mathrm{CaWO_4}$ crystal, our calculations suggest that $A_{\parallel}$ is negative and $A_{\perp}$ is positive (see Table III).

The angular distortion $\Delta\theta \neq 0$ confirms the expectation that the bonding angle θ in the Mo^{5+} impurity center in $\mathrm{CaWO_4}$ is different from the corresponding angle θ_h in the host crystal because of the impurity-induced local lattice relaxation. So, the local structure of a paramagnetic impurity center in crystals can be acquired by studying its EPR data.

Table III shows that by using three adjustable parameters, the calculated spin-Hamiltonian parameters $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}(\mathrm{A})$, $A_{\perp}(\mathrm{A})$, $A_{\parallel}(\mathrm{B})$ and $A_{\perp}(\mathrm{B})$ are in reasonable agreement with the experimental values. This suggests that the high-order perturbation formulae based on the two-mechanism model are effective here. To characterize the relative importance of CT mechanism, we introduce the ratio $|Q^{\mathrm{CT}}/Q^{\mathrm{CF}}|$. From Table III, we obtain $|Q^{\mathrm{CT}}/Q^{\mathrm{CF}}| \approx 0.6\%, 24\%, 1\%$ and 9% for $Q = \Delta g_{\parallel}, \Delta g_{\perp}, A_{\parallel}^{(2)}$ and $A_{\perp}^{(2)}$. It can be seen that the values $|Q^{\mathrm{CT}}/Q^{\mathrm{CF}}|$ of relative importance of CT mechanism for $\Delta g_{\parallel}$ and $A_{\parallel}^{(2)}$ are much smaller than those for $\Delta g_{\perp}$ and $A_{\perp}^{(2)}$. The main reason of the above great difference in $|Q^{\mathrm{CT}}/Q^{\mathrm{CF}}|$ may be due to the contributions to $\Delta g_{\parallel}$ and $A_{\parallel}^{(2)}$ in both the CF and CT mechanisms depending upon the third-order perturbation terms [note: the second-order terms are absent according to the derivation, see Eq. (2)], whereas those to $\Delta g_{\perp}$ and $A_{\perp}^{(2)}$ mainly from the second-order perturbation terms. This leads the ratios $|Q^{\mathrm{CT}}/Q^{\mathrm{CF}}|$ for $\Delta g_{\parallel}$ and $A_{\parallel}^{(2)}$ to be connected roughly with $(E^{\mathrm{CT}}/E^{\mathrm{CF}})^2$, but those for $\Delta g_{\perp}$ and $A_{\perp}^{(2)}$ roughly with $E^{\mathrm{CT}}/E^{\mathrm{CF}}$ [see Eq. (2)]. Since $E^{\mathrm{CT}}/E^{\mathrm{CF}} < 0.5$ (note: the calculated $E_1^{\mathrm{CF}} \approx 13240$ cm^{-1} here), the above large difference in the relative importance can be understood. In consideration of the great relative importance of CT mechanism to $\Delta g_{\perp}$ and $A_{\perp}^{(2)}$, in the rational and precise calculations of spin-Hamiltonian parameters and the estimations of the local structure of impurity centers (by analyzing the spin-Hamiltonian parameters) for the high-valence state d^n ions in crystals, one should apply the method based on the two-mechanism model.

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