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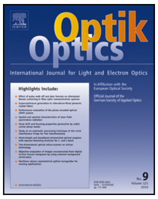

Research on the spin-Hamiltonian parameters for the approximately trigonal Mn^{5+} tetrahedral center in $Sr_5(PO_4)_3Cl$ crystal

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ABSTRACT

The spin-Hamiltonian parameters (*g* factors $g_{//}$, $g_\perp$ and zero-field splitting *D*) of the approximately trigonal Mn^{5+} tetrahedral cluster in $Sr_5(PO_4)_3Cl$ crystal are computed from the complete high-order perturbation formulas established on the two-mechanism model, in which in addition to the contributions due to the frequently-applied crystal-field (*CF*) mechanism in the *CF* theory, those due to the commonly-ignored charge-transfer (*CT*) mechanism are contained. The calculated results are in rational accordance with the experimented values. The calculations demonstrate that for the high valence state d^n clusters in crystals, the contributions to spin-Hamiltonian parameters from the *CT* mechanism should also be considered. The negative sign of zero-field splitting *D* and the defect structure of the approximately trigonal Mn^{5+} center in $Sr_5(PO_4)_3Cl$ are proposed from the calculations.

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1. Introduction

Since the infrared laser action was discovered for Cr^{4+} ion at the tetrahedral Si^{4+} site of forsterite Mg_2SiO_4 crystal [1,2], the tetrahedrally coordinated $3d^2$ (e.g., Cr^{4+}, Mn^{5+} and Fe^{6+}) ions doped in crystals and their spectroscopic properties have attracted significant attention because these materials have the potential applications in infrared tunable lasers [3–10] and the vivo fluorescence imaging [11]. Misra et al. [10] reported the EPR spectra of Mn^{5+}-doped $Sr_5(PO_4)_3Cl$ crystal. From the EPR experiment, an orthorhombic Mn^{5+} tetrahedral center attributed to Mn^{5+} occupying the tetrahedral P^{5+} site was found and its spin-Hamiltonian parameters (*g* factors $g_{//}$, $g_\perp$ and zero-field splittings *D*, *E*) were given [10]. Since the orthorhombic component *E* of zero-field splitting is very small and may be neglected, the Mn^{5+} center can be approximated as C_{3v} symmetry [10]. To date no theoretical explanations or calculations for the spin-Hamiltonian parameters $g_{//}$, $g_\perp$ and *D* of the approximately trigonal Mn^{5+} center in $Sr_5(PO_4)_3Cl$ crystal have been found in the literature. It is known that the reasonable calculations rely upon the suitable theoretical method or model. Mn^{5+} ion has high valence state which leads the charge-transfer (*CT*) energy levels to become lower, so, besides the contributions to spin- Hamiltonian parameters due to crystal-field (*CF*) mechanism related to the interactions of *CF* excited states with the ground state in the vastly-applied *CF* theory, the contributions due to *CT* mechanism concerning the interactions of *CT* excited states with the ground state are also considered. Thus, a two (*CF* and *CT*)-mechanism model [12,14] should be applied here. In the present paper, the high-order perturbation formulas established on the two-mechanism model are adopted to calculate the spin-Hamiltonian parameters $g_{//}$, $g_\perp$ and *D* for the approximately trigonal Mn^{5+} tetrahedral center in $Sr_5(PO_4)_3Cl$ crystal. The results are discussed.

2. Calculations

By means of the one-electron basis functions (which consist of anti-bonding and bonding orbitals, corresponding to *CF* and *CT* mechanisms, respectively) and the perturbation method in the two-mechanism model [14], the high-order perturbation formulas of spin-Hamiltonian parameters $g_{//}$, $g_\perp$ and *D* for a trigonal d^2 tetrahedral cluster are deduced as [14]

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$$\begin{gathered}
g_{//} = g_s + \Delta g_{//}^{CF} + \Delta g_{//}^{CT} \\
\Delta g_{//}^{CF} = -4k'_{CF}\zeta'_{CF}/E_1 - [g_e\left(\zeta'_{CF}\right)^2 + k'_{CF}\zeta_{CF}\zeta'_{CF} - k_{CF}\left(\zeta'_{CF}\right)^2/2]/E_1^2 \\
-(g_e - k_{CF}/2)\left(\zeta'_{CF}\right)^2/E_2^2 - k'_{CF}\zeta_{CF}\zeta'_{CF}/(E_1E_2) - 6Bk'_{CF}\left(\zeta'_{CF}\right)^2 \\
\times[2/(E_1E_2E_5) + 1/(E_2^2E_5)] + 4k'_{CF}\zeta'_{CF}\upsilon/(3E_1^2) - 4\sqrt{2}\zeta'\upsilon' \\
\times[k_{CF}/(E_1E_3) + 12Bk'_{CF}/(E_1E_3E_4)] \\
\Delta g_{//}^{CT} = 4(k'_{CT}\zeta'_{CT}/E_n + k_{CT}\zeta_{CT}/E_a) - 8k_{CT}\zeta_{CT}\upsilon/(9E_a^2) \\
g_{\perp} = g_s + \Delta g_{\perp}^{CF} + \Delta g_{\perp}^{CT} \\
\Delta g_{\perp}^{CF} = \Delta g_{//}^{CF} - 2k'_{CF}\zeta'_{CF}\upsilon/E_1^2 + 6\sqrt{2}\zeta'_{CF}\upsilon'[k_{CF}/(E_1E_3) + 12Bk'_{CF}/(E_1E_3E_4)] \\
\Delta g_{\perp}^{CT} = \Delta g_{//}^{CT} + 4k_{CT}\zeta_{CT}\upsilon/(3E_a^2) \\
D = D^{CF} + D^{CT} \\
D^{CF} = \frac{\upsilon}{2}\left(\zeta'_{CF}\right)^2(1/E_1^2 - 1/E_2^2) + \frac{3\upsilon'}{\sqrt{2}}\{\zeta_{CF}\zeta'_{CF}[1/(E_2E_3) - 1/(E_1E_3)] + \\
4B\left(\zeta'_{CF}\right)^2[1/(E_2E_3E_5) + 1/(E_2^2E_5) - 3/(E_1E_3E_4) - 3/(E_2E_3E_4)]\} \\
D^{CT} = -\zeta_{CT}^2\upsilon/(3E_a^2)
\end{gathered} \tag{1}$$

with

$$\begin{gathered}
\zeta_{CF} = (N_t{}^a)^2\left\{\zeta_d^0 + \left[\sqrt{2}\lambda_\pi^a\lambda_\sigma^a - (\lambda_\pi^a)^2/2\right]\zeta_p^0\right\}, \\
\zeta'_{CF} = N_t{}^a \cdot N_e^a\left\{\zeta_d^0 + \left[\lambda_\pi^a\lambda_\sigma^a/\sqrt{2} + (\lambda_\pi^a)^2/2\right]\zeta_p^0\right\}, \\
\zeta_{CT} = N_t^a \cdot N_t^b\left\{\zeta_d^0 + \left[\frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a\lambda_\pi^b}{2}\right]\zeta_p^0\right\}, \\
\zeta'_{CT} = N_t^b \cdot N_e^a\left\{\zeta_d^0 + \left[\frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a\lambda_\pi^b}{2}\right]\zeta_p^0\right\}, \\
k_{CF} = (N_t^a)^2\left[1 - (\lambda_\pi^a)^2/2 + \sqrt{2}\lambda_\pi^a\lambda_\sigma^a + 2\lambda_\sigma^a S_{dp}(\sigma) + 2\lambda_\pi^a S_{dp}(\pi)\right], \\
k'_{CF} = N_t^a \cdot N_e^a\left[1 - (\lambda_\pi^a)^2/2 + \lambda_\pi^a\lambda_\sigma^a/\sqrt{2} + 4\lambda_\pi^a S_{dp}(\pi) + \lambda_\sigma^a S_{dp}(\sigma)\right], \\
k_{CT} = N_t^a N_t^b\left\{1 + \left[\frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a\lambda_\pi^b}{2}\right] + \left(\lambda_\sigma^a + \lambda_\sigma^b\right)S_{dp}(\sigma) + \left(\lambda_\pi^a + \lambda_\pi^b\right)S_{dp}(\pi)\right\}], \\
k'_{CT} = N_t^b N_e^a\left\{1 + \left[\frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}} - \frac{\lambda_\pi^a\lambda_\pi^b}{2}\right] + \lambda_\sigma^b S_{dp}(\sigma) + \left(3\lambda_\pi^a + \lambda_\pi^b\right)S_{dp}(\pi)\right\},
\end{gathered} \tag{2}$$

where the superscripts and subscripts *CF* and *CT* stand for the parameters in *CF* and *CT* mechanisms. $g_s \approx 2.0023$, the g value of free electron. E_j ($j = 1$–5) are the zero-order energy denominations between the *CF* excited states and the ground state. They are the functions of Racah parameters B, C and the cubic field parameter Dq of the studied system and their expressions are given in Ref. [14]. E_a and E_n are the *CT* energy levels. For $(MnO_4)^{3-}$ clusters considered, $E_n \approx 31{,}600\ cm^{-1}$ and $E_a \approx 33{,}600\ cm^{-1}$ [15]. υ and υ' are the trigonal field parameters. ${\zeta_d}^0$ and ${\zeta_p}^0$ are the spin-orbit coupling parameters of free d^n ion and free ligand ion. For $(MnO_4)^{3-}$ cluster, we have ${\zeta_d}^0$ $(Mn^{5+}) \approx 503\ cm^{-1}$ [16] and ${\zeta_p}^0$ $(O^{2-}) \approx 150\ cm^{-1}$ [17]. The group overlap integrals S_{dp} (β) ($\beta = \sigma, \pi$) rely on the average metal-ligand distance $\bar{R}$ of the studied cluster. The metal-ligand distance R in an impurity center may be unlike the corresponding distance R_h in the host crystal because of the difference between the ionic radii r_i of impurity and r_h of the replaced host ion. An approximate formula $R \approx R_h + (r_i - r_h)/2$ [18] is often applied to estimate the distance R. From $R_{h1} \approx 1.540$ Å, $R_{h2} \approx 1.539$ Å [19], r_i $(Mn^{5+}) \approx 0.47$ Å and r_h $(P^{5+}) \approx 0.31$ Å [20], we have $R_1 \approx 1.62$ Å, $R_2 \approx 1.619$ Å and $\bar{R} \approx 1.639$ Å. Thus, we obtain S_{dp} $(\sigma) \approx -0.1151$ and S_{dp} $(\pi) \approx 0.0393$ from the Slater-type self-consistent field (*SCF*) functions [21,22] for the $(MnO_4)^{3-}$ cluster in $Sr_5(PO_4)_3Cl{:}Mn^{5+}$ crystal.

The molecular orbital (MO) coefficients ${N_\gamma}^X$ ($X = a, b$, $\gamma = t, e$) and ${\lambda_\beta}^X$ needed for calculations of the parameters in Eq. (2) follow the normalization correlations [14]

$$\begin{gathered}
N_e^X = \left[1 + 3\left(\lambda_\sigma^X\right)^2 + 6\lambda_\pi^X S_{dp}(\pi)\right]^{-1/2} \\
N_t^X = \left[1 + \left(\lambda_\sigma^X\right)^2 + \left(\lambda_\pi^X\right)^2 + 2\lambda_\sigma^X S_{dp}(\sigma) + 2\lambda_\pi^X S_{dp}(\pi)\right]^{-1/2},
\end{gathered} \tag{3}$$

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