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Theoretical studies of spin-Hamiltonian parameters of Mo^{5+} ion doped in K_2SnCl_6 crystal



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ABSTRACT

The spin-Hamiltonian (SH) parameters (g factors g_{\parallel} , g_{\perp} and hyperfine structure constants A_{\parallel} , A_{\perp}) of $\text{K}_2\text{SnCl}_6: \text{Mo}^{5+}$ ($4d^1$) crystal are theoretically studied by the use of two microscopic spin-Hamiltonian (SH) methods, the high-order perturbation theory method (PTM) and the complete diagonalization (of energy matrix) method (CDM) within the molecular orbital (MO) scheme. The contributions arising both from the crystal field and charge transfer excitations are taken into account. The investigations show that the charge transfer mechanism plays a decisive role in the understanding of the spin-Hamiltonian (SH) parameters for $4d^1$ ions in crystals with the strong coordinate covalence, especially for $g_{\parallel} > g_{\perp}$ which cannot be explained in the frame work of traditional crystal field approximation (CFA). The local defect structure around Mo^{5+} impurity ion center is determined to be D_{4h} point group symmetry.

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1. Introduction

A_2XY_6 ($\text{A}=\text{K}, \text{Cs}, \text{Rb}, \text{Tl}$; $\text{X}=\text{tetravalent cation}$, $\text{Y}=\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$) crystals doped with transition metal or rare earth ions have attracted a great deal of attention [1–8] because of the applications in luminescence and, in particular, in upconversion luminescent materials [6–8], and of the merits of being doped easily with different impurities (especially at the 6-fold coordinated tetravalent cation site) [1]. When the pentavalent Mo^{5+} ion is doped into K_2SnCl_6 crystal (Fig. 1), it will substitute for the tetravalent Sn^{4+} ion and a vacancy with negative charge will be introduced along one of the C_4 axis at the interstitial site because of the charge compensation effect [9]. The experimental EPR results (g factors g_{\parallel} , g_{\perp} and hyperfine structure constants A_{\parallel} , A_{\perp}) show that $[\text{MoCl}_6]^{-1}$ clusters are in the compressed tetragonal symmetry and the ground state of Mo^{5+} ion is $B_{2g}(d_{xy})$ [9,10]. There are two possible defect models for the compressed tetragonal symmetry proposed in the investigation, one is C_{4v} symmetry caused by the repulsion of one Cl^- with the negative compensating hole along the C_4 axis, another is D_{4h} symmetry due to the static Jahn-Teller effect. To find which one is realistic, the calculations have been carried out by the use of those two defect models proposed, and the calculated results show that when D_{4h} defect model is used, the results from both PTM and CDM methods are in good agreement with the experimental data, while for C_{4v} defect model, no plausible results can be obtained in any case. So, we carry out the calculations by the use D_{4h} defect model in the following

section. In the calculation, the MO theory in the ligand-field (LF) scheme is used and the contributions from the CT excitation states are taken into account. The investigation show that this CT mechanism plays a decisive role in accounting for the SH parameters of $4d^n$ transition metal (TM) ions with Cl^- ligands.

2. Calculations

The ground state of Mo^{5+} ion in K_2SnCl_6 crystal is $B_{2g}(d_{xy})$ and the expressions of SH parameters g factors and hyperfine structure constants A factors for the single orbital term can be derived by the PTM which have been discussed in detail elsewhere [11–13].

The one-electron basis functions for antibonding orbitals belonging to t_{2g} and e_g state for $4d^n$ ions in octahedral field can be expressed as the linear combination of atomic orbitals (LCAO) [14],

$$\begin{aligned}\psi_t^a &= (N_t^a)^{-1/2}(\varphi_t - \lambda_{\pi}\chi_{\pi}), \\ \psi_e^a &= (N_e^a)^{-1/2}(\varphi_e - \lambda_s\chi_s - \lambda_{\sigma}\chi_{\sigma}),\end{aligned}\quad (1)$$

respectively, and the bonding orbital can be written as [14]

$$\begin{aligned}\psi_t^b &= (N_t^b)^{-1/2}(\chi_{\pi} + \gamma_{\pi}\varphi_t), \\ \psi_e^b &= (N_e^b)^{-1/2}(\chi_{\sigma} + \gamma_{\sigma}\varphi_e),\end{aligned}\quad (2)$$

where φ_t and φ_e denote the pure d orbital of the metal ion, χ_i ($i=\pi, s, \sigma$) are group orbitals of ligands, $(N_t^b)^{-1/2}$, $(N_e^b)^{-1/2}$ and $(N_t^a)^{-1/2}$, $(N_e^a)^{-1/2}$ are the normalization constants, and λ_i ($i=\pi, s, \sigma$) are covalency parameters. The third-order perturbation formulas of g factors g_{\parallel} , g_{\perp} and second-order hyperfine structure constants A factors A_{\parallel} , A_{\perp} based on CF mechanisms for $4d^1$ ion in tetragonal symmetry

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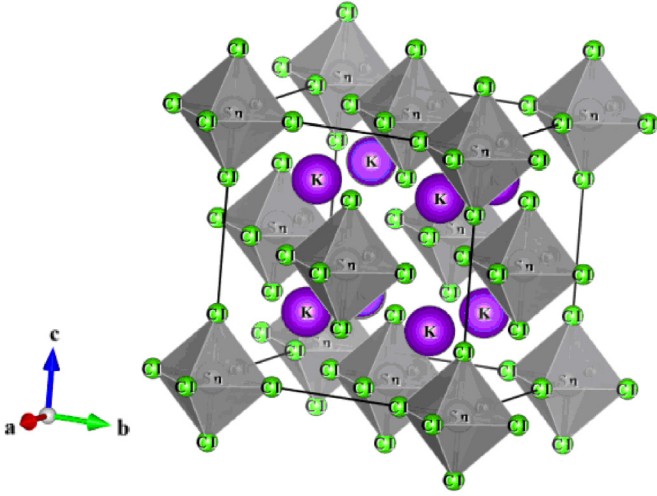


Fig. 1. One unit cell of K_2SnCl_6 crystal.

are derived as ($g_s=2.0023$)

$$g_z = g_s + \Delta g_z^{CF},$$

$$\Delta g_z^{CF} = -\frac{8k_{CF}'\zeta_{CF}'}{E_1} - \frac{4k_{CF}'\zeta_{CF}\zeta_{CF}'}{E_1E_2} - \frac{k_{CF}\zeta_{CF}^2}{E_2^2} - \frac{\zeta_{CF}^2g_s}{E_2^2},$$

$$g_x = g_s + \Delta g_x^{CF},$$

$$\Delta g_x^{CF} = -\frac{2k_{CF}\zeta_{CF}}{E_2} + \frac{k_{CF}\zeta_{CF}^2}{E_2^2} + \frac{2k_{CF}'\zeta_{CF}\zeta_{CF}'}{E_1E_2} - \frac{2\zeta_{CF}'^2g_s}{E_1^2} - \frac{\zeta_{CF}^2g_s}{2E_2^2}, \quad (3)$$

$$A_z = A_z^{CF}(1) + A_z^{CF}(2),$$

$$A_z^{CF}(1) = P \left(-\kappa - \frac{4}{7} \right) / N_t^a,$$

$$A_z^{CF}(2) = -P \left(\frac{8\zeta_{CF}'}{N_t^a E_1} + \frac{6\zeta_{CF}}{7\sqrt{N_t^a N_e^a} E_2} \right),$$

$$A_x = A_x^{CF}(1) + A_x^{CF}(2), \quad (4)$$

$$A_x^{CF}(1) = P \left(-\kappa + \frac{2}{7} \right) / N_t^a,$$

$$A_x^{CF}(2) = -P \left(\frac{11\zeta_{CF}}{7\sqrt{N_t^a N_e^a} E_2} \right),$$

in which

$$E_1 = 10Dq, \quad E_2 = -3Ds + 5Dt. \quad (5)$$

Dq is cubic crystal field parameter and estimated to be 2350 cm^{-1} [15], Ds and Dt represent the tetragonal crystal field parameter and have the following form using the superposition model

$$Ds = \frac{4}{7} \bar{A}_2(R_0) \left[\left(\frac{R_0}{R_{\perp}} \right)^3 - \left(\frac{R_0}{R_{//}} \right)^3 \right],$$

$$Dt = \frac{16}{21} \bar{A}_4(R_0) \left[\left(\frac{R_0}{R_{\perp}} \right)^5 - \left(\frac{R_0}{R_{//}} \right)^5 \right], \quad (6)$$

and $\bar{A}_2(R_0)$, $\bar{A}_4(R_0)$ are intrinsic parameters with reference distance R_0 , $\bar{A}_4(R_0) \approx 3/4Dq$ for d^n ions in cubic field [16,17]. The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ for md^n ions in clusters decreases with the increasing m value, for $3d^n$, $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9-12$ are found for many ions in crystals [18,19] and $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8.3$ is taken here in the calculations. The spin-orbit coupling (SOC) parameters ζ , ζ' and the orbital

reduction factors k , k' related to CF mechanisms in Eq. (3) are [14]

$$\zeta_{CF} = (N_t^a)^{-1} [\zeta_d + (\lambda_{\pi})^2 \zeta_p / 2],$$

$$\zeta_{CF}' = (N_t^a N_e^a)^{-1/2} [\zeta_d - \lambda_{\pi} \lambda_{\sigma} \zeta_p / 2],$$

$$k_{CF} = (N_t^a)^{-1} [1 - 2\lambda_t S_{\pi} + (\lambda_{\pi})^2 / 2] \quad (7)$$

$$k_{CF}' = (N_t^a N_e^a)^{-1/2} [1 - \lambda_s S_s - \lambda_{\sigma} S_{\sigma} - \lambda_{\pi} S_{\pi} - \lambda_{\pi} (\lambda_{\sigma} + A\lambda_s) / 2],$$

where ζ_d and ζ_p are the SOC parameters of free $3d^n$ ion and that of ligand ions in free state, respectively. For Mo^{5+} , $\zeta_d \approx 1013 \text{ cm}^{-1}$ [20] and for Cl^{-} , $\zeta_p \approx 587 \text{ cm}^{-1}$ [21], $S_s = \langle \varphi_e | \chi_s \rangle$, $S_{\sigma} = \langle \varphi_e | \chi_{\sigma} \rangle$, $S_{\pi} = \langle \varphi_t | \chi_{\pi} \rangle$ are the group overlap integrals, which can be calculated using the Clementi's SCF functions [22,23] and impurity-ligand distance R in crystal. Considering that the ionic radius r_i ($\approx 0.061 \text{ nm}$ [24]) of impurity Mo^{5+} is unlike the radius r_h ($\approx 0.069 \text{ nm}$ [24]) for the replaced host ion Sn^{4+} , the impurity-ligand distance R for Mo^{5+} ion in K_2SnCl_6 should be different from the corresponding R_h ($\approx 0.2448 \text{ nm}$ [25]) in the host K_2SnCl_6 crystal, we estimate approximately the distance R from the empirical formula $R_0 \approx R^h + 1/2(r_i - r_h)$ [26,27] and obtain $R_0 = 0.2408 \text{ nm}$. Thus, the group overlap are calculated to be

$$S_s \approx 0.1028, S_{\sigma} \approx 0.1848, \text{ and } S_{\pi} \approx 0.0746. \quad (8)$$

In Eq. (6) R_{\perp} represents equatorial metal-ligand distance and equal to R_0 , $R_{//}$ represents axial metal-ligand distance and taken to be $(R_0 - \Delta R)$ in which ΔR is the inward displacement of Cl^{-} along the C_4 axis. In Eq. (4), P is dipolar hyperfine structure constants and has the value of $-66.7 \times 10^{-4} \text{ cm}^{-1}$ for Mo^{5+} [28] and κ is the Fermi-contact term which is taken to be 1.05 [9], $A = R_0 \langle \varphi_x | \partial / \partial x | \chi_s \rangle$, for Cl^{-} ion $\langle \varphi_x | \partial / \partial x | \chi_s \rangle = -0.409$ [29].

The contributions to the SH parameters from the CT levels come from the excitation procedure of promoting an electron from the occupied π bonding orbitals e_g^* (d_{xz} and d_{yz}) or b_{1g}^* ($d_{x^2-y^2}$) to d_{xy} ground state, and the high-order perturbation formulas of the SH parameters due to this CT mechanism have the follow form

$$\Delta g_z^{CT} = \frac{8k_{CT}'\zeta_{CT}'}{E_{1c}},$$

$$\Delta g_x^{CT} = \frac{2k_{CT}\zeta_{CT}}{E_{2c}}, \quad (9)$$

$$A_z^{CT} = -P \left(\frac{8\gamma_e \zeta_{CT}'}{\sqrt{N_t^a N_e^b} E_{1c}} + \frac{6\gamma_t \zeta_{CT}}{7\sqrt{N_t^a N_e^b} E_{2c}} \right),$$

$$A_x^{CT} = -P \left(\frac{11\gamma_t \zeta_{CT}}{7\sqrt{N_t^a N_e^b} E_{2c}} \right), \quad (10)$$

where

$$\zeta_{CT} = (N_t^b N_e^a)^{-1/2} [\gamma_{\pi} \zeta_d - \lambda_{\pi} \zeta_p / 2],$$

$$\zeta_{CT}' = (N_t^b N_e^a)^{-1/2} [\gamma_{\sigma} \zeta_d + \lambda_{\pi} \zeta_p / 2], \quad (11)$$

$$k_{CT} = (N_t^b N_e^a)^{-1/2} [\gamma_{\pi} + (1 - \lambda_{\pi} \gamma_{\pi}) S_{\pi} - \lambda_{\pi} / 2],$$

$$k_{CT}' = (N_t^b N_e^a)^{-1/2} [\gamma_{\sigma} - \gamma_{\sigma} \lambda_{\pi} S_t - S_{\sigma} + \lambda_t / 2],$$

and E_{1c} , E_{2c} are CT energies of e_g^* (d_{xz} and d_{yz}) and b_{1g}^* ($d_{x^2-y^2}$), respectively. We estimate $E_{1c} = 41150$ and $E_{2c} = 28250 \text{ cm}^{-1}$ [15]. The g factors $g_{//}$, g_{\perp} and hyperfine structure constants $A_{//}$, A_{\perp} from both the CF and CT mechanisms are expressed as

$$g_{//} = g_z + g_z^{CT}, \quad g_{\perp} = g_x + g_x^{CT},$$

$$A_{//} = A_z + A_z^{CT}(2), \quad A_{\perp} = A_x + A_x^{CT}(2). \quad (12)$$

All the normalization relationship and the relations between the LCAO coefficients and the group overlap used in the calculations can be found in reference [14].

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