Available online at www.sciencedirect.com

SCIENCE DIRECT®

Spectrochimica Acta Part A 63 (2006) 749–753

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Theoretical studies of the spin Hamiltonian parameters and local structures for Cs_3CoX_5 (X = Cl, Br)

Shao-Yi Wu [a,b,*], Hui-Ning Dong [b,c], Xiu-Ying Gao [a]

[a] Department of Applied Physics, University of Electronic Science and Technology of China, College of Physical Electronics, Chengdu 610054, PR China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, PR China
[c] College of Electronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, PR China

Received 7 December 2004; accepted 14 June 2005

Abstract

The spin Hamiltonian (SH) parameters (zero-field splitting D and anisotropic g factors $g_{||}$ and $g_{\perp}$) and local structures for Cs_3CoX_5 (X = Cl, Br) are theoretically studied from the perturbation formulas of the SH parameters for a $3d^7$ ion in tetragonally distorted tetrahedra based on the cluster approach. In these formulas, both the contributions from the crystal-field (CF) mechanism and those from the charge-transfer (CT) mechanism are taken into account. It is found that the $[CoX_4]^{2-}$ clusters are slightly elongated and the tetragonal distortion angles $\Delta\theta(=\theta-\theta_0$, where $\theta_0 \approx 54.74^\circ$ is the bonding angle related to the C_4-axis in regular tetrahedra) are about -1.68° and -1.71° for X = Cl and Br, respectively. The calculated SH parameters as well as the effective magnetic moments based on the above angles are in reasonable agreement with the observed values. From the studies, the importance of the contributions to the SH parameters from the CT mechanism increases with increasing the spin–orbit coupling coefficient of the ligand, i.e., $Cl^- < Br^-$. The results are compared with those obtained from the conventional crystal-field model in the previous works.

Keywords: Crystal-fields and spin Hamiltonians; Electron paramagnetic resonance (EPR); Co^{2+}; Cs_3CoX_5 (X = Cl; Br)

1. Introduction

Cs_3CoX_5 (X = Cl, Br) have attracted interest of workers due to their magnetic $[CoX_4]^{2-}$ clusters and were extensively investigated by polarized neutron diffraction (PND) technique [1–4]. The related magnetic structure and spin density were also systematically analyzed [5–13]. Obviously, the above behavious are sensitive to structure property of the $[CoX_4]^{2-}$ clusters. Since electron paramagnetic resonance (EPR) is a useful tool to investigate local structure of magnetic centers in crystals, EPR experiments have been carried out on these systems and the spin Hamiltonian (SH) parameters (zero-field splitting D, anisotropic g factors $g_{||}$ and $g_{\perp}$) were also measured by means of EPR and Zeeman effect techniques [14,15]. The SH parameters as well as the effective magnetic moment for the tetragonal (D_{2d}) $[CoX_4]^{2-}$ clusters were studied from the crystal-field model by some authors [14–17].

However, there seems to be some imperfectness in their studies. First, the spin–orbit (SO) coupling coefficient of the ligands Br^{2-}(or Cl^{2-}), which is much larger than (or comparable with) that of the central Co^{2+} ion was not considered. In addition, the p orbitals of the ligands and their contributions to the SH parameters were neglected as well. Moreover, only the crystal-field (CF) mechanism (related to the anti-bonding orbitals) were included in the conventional crystal-field model [15–17]. In fact, another mechanism, i.e., the charge-transfer (CT) mechanism (related to the bonding or non-bonding orbitals) can also influence the SH parameters, as mentioned in Refs. [18,19]. Particularly, since the energies of the CT bands lower with increasing atomic number of ligand ion in the same group of periodictable [20], the contributions from both the CF and CT mechanisms should be considered. Finally, local structures of the $[CoX_4]^{2-}$ clusters seem not satisfactorily related to the SH parameters,

---

[*] Corresponding author. Tel.: +86 2883206121; fax: +86 2883200056.
E-mail address: wushaoyi@netease.com (S.-Y. Wu).

1386-1425/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2005.06.029

although the tetragonal distortion angles $\Delta\theta$ (i.e., difference between the Co–X bonding angle θ related to the C_4-axis and the corresponding angle $\theta_0 \approx 54.74^\circ$ in regular tetrahedra) were estimated from the approximation formula of zero-field splitting D [$\approx 2\sqrt{2}\xi^2\Delta\theta/(15Dq)$] in Ref. [15]. Thus, the theoretical SH parameters or the tetragonal distortion angles in the previous works may be expected to be improved by considering the above factors.

In order to study the SH parameters and the local structures for Cs_3CoX_5 to a better extent, in this work, the perturbation formulas of the SH parameters are established for a $3d^7$ ion in tetragonally distorted tetrahedra, by including both the CF and CT mechanisms based on the cluster approach.

2. Calculation formulas

For a $3d^7$ (Co^{2+}) ion in a tetragonally (D_{2d}) distorted tetrahedron, the perturbation formulas of the SH parameters based on the CF mechanism were given from the conventional crystal-field model in Ref. [21] and the cluster model in our previous work [22]. Since the CT mechanism is considered here, the perturbation Hamiltonian containing both the CF and CT mechanisms may be expressed as

$$H' = H_b + H_{CF}^{tetr} + H_{SO}^{CF} + H_{SO}^{CT} + H_{Ze}^{CF} + H_{Ze}^{CT}, \tag{1}$$

where H_b, H_{CF}^{tetr}, H_{SO} and H_{Ze} are, respectively, the off-diagonal terms of the electrostatic Coulombic interaction, the tetragonal crystal-fields, the SO coupling and the Zeeman interactions. The superscripts CF and CT denote the related terms in the CF and CT mechanisms, with the corresponding SO coupling coefficients ζ_{CF}, ζ'_{CF} and ζ_{CT}, ζ'_{CT} and the orbital reduction factors k_{CF}, k'_{CF} and k_{CT}, k'_{CT}.

Considering the contributions of the CT bands to the SH parameters, one can write the many-electron wave-functions of the CT configurations in terms of seven-electron wave-functions out of t_2^a, t_2^b and e^n. Here the superscripts 'a', 'b' and 'n' denote the anti-bonding orbitals (corresponding to the CF mechanism), bonding orbitals (corresponding to the CT mechanism) and non-bonding orbitals, respectively. So, the ground state $^4A_2$ can be written as follows:

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

In the above square bracket, the letters on the left column are e^n and t_2^a orbitals and those on the right column are t_2^b orbitals. Since only one excited configuration $(e^n)^4(t_2^a)^4(t_2^b)^5$ (labeled as $^4T_2^n$) has non-zero SO coupling interaction with the ground $^4A_2$ state, the ζ-component of $^4T_2^n$ state with $M_S = 3/2$ can be given as

$$\left|^4T_2^n \tfrac{3}{2}\zeta \geq \frac{\{[\theta^+\theta^-\varepsilon^+\varepsilon^-\xi^+\eta^+\eta^-\zeta^+|\xi^+\xi^-\eta^+\eta^-\zeta^+] + [\theta^+\theta^-\varepsilon^+\varepsilon^-\xi^+\xi^-\eta^+\zeta^+|\xi^+\xi^-\eta^+\eta^-\zeta^+]\}}{\sqrt{2}}.\right. \tag{3}$$

According to the LCAO-MO model, the one-electron basic functions for the tetrahedral $3d^7$ cluster may be established, i.e.:

$$\psi_t^x = N_t^x(\phi_{dt} - \lambda_\sigma^x\chi_{p\sigma} - \lambda_s^x\chi_s - \lambda_\pi^x\chi_{p\pi t}),$$
$$\psi_e^x = N_e^x(\phi_{de} - \sqrt{3}\lambda_\pi^x\chi_{p\pi e}). \tag{4}$$

Here the superscript x (=a or b) denotes the anti-bonding or bonding orbitals. ϕ_{dt} and ϕ_{de} are the d orbitals of the $3d^7$ ion, and $\chi_{p\sigma}$, $\chi_{p\pi t}$, $\chi_{p\pi e}$, and χ_s are the p and s orbitals of ligands. N_t^x and N_e^x are the normalization coefficients, and χ_σ, λ_π and λ_s are the orbital mixing coefficients. From Eq. (4), we have the normalization relation:

$$(N_t^x)^2[1 + (\lambda_\sigma^x)^2 + (\lambda_\pi^x)^2 - 2\lambda_\sigma^x S_\sigma - 2\lambda_s^x S_s - 2\lambda_\pi^x S_\pi] = 1,$$
$$(N_e^x)^2[1 + 3(\lambda_\pi^x)^2 + 6\lambda_\pi^x S_\pi] = 1 \tag{5}$$

and the orthogonality relationship:

$$1 + 3\lambda_\pi^a\lambda_\pi^b - 3(\lambda_\pi^a + \lambda_\pi^b)S_\pi = 0,$$
$$1 + \lambda_\pi^a + \lambda_\pi^b + \lambda_\sigma^a\lambda_\sigma^b + \lambda_s^a\lambda_s^b - (\lambda_\pi^a + \lambda_\pi^b)S_\pi$$
$$- (\lambda_\sigma^a\lambda_\sigma^a)S_\sigma - (\lambda_s^a + \lambda_s^b)S_s = 0,$$
$$\lambda_\pi^a\lambda_\pi^b + \lambda_s^a\lambda_s^b = 0 \tag{6}$$

for the 'e' or 't' irreducible representation and the p orbitals of the 't' representation, respectively. Here S_π, S_σ and S_s are the overlap integrals between the d-orbitals of the $3d^7$ ion and p or s orbitals of the ligands.

From the Macfarlane's perturbation-loop method [21], by applying the perturbation Hamiltonian in Eq. (1) to the wavefunction of the ground state $^4A_2$, the perturbation formulas of the zero-field splitting D, g factors $g_{||}$ and $g_\perp$ [and also anisotropy $\Delta g = (g_{||} - g_\perp)$] including both the CF and CT mechanisms for a $3d^7$ ion in tetragonally distorted tetrahedra can be derived. Thus, we have

$$D = D^{CF} + D^{CT},$$

$$D^{CF} = \frac{35}{9}D_t\zeta'^2_{CF}\left[\frac{1}{E_1^2} - \frac{1}{E_3^2}\right] - \frac{35B_4D_t\zeta_{CF}\zeta'_{CF}}{E_2E_3^2},$$

$$D^{CT} = \frac{8(5D_t - 3D_s)\zeta'^2_{CT}}{E_n^2},$$

$$g_{||} = g_{||}^{CF} + g_{||}^{CT},$$

$$g_{||}^{CF} = \frac{g_s + 8k'_{CF}\zeta'_{CF}}{3E_1} - \frac{2\zeta'_{CF}(2k'_{CF}\zeta_{CF} - k_{CF}\zeta'_{CF} + 2g_sk_{CF})}{9E_1^2}$$
$$+ \frac{4\zeta'^2_{CF}(k_{CF} - 2g_s)}{9E_3^2} - \frac{2\zeta^2_{CF}(k_{CF} + g_s)}{3E_2^2}$$
$$+ k'_{CF}\zeta_{CF}\zeta'_{CF}\left[\frac{4}{9E_1E_3} - \frac{4}{3E_1E_3} + \frac{4}{3E_2E_3}\right]$$
$$- \frac{140k'_{CF}\zeta'_{CF}D_t}{9E_1^2},$$