Theoretical Investigation of the g Factors for Copper (II) Ion in an Orthorhombic Crystal and its Application to $(CuCl_4)^{2-}$ Cluster

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On the basis of the crystal- and ligand-field theory, the high-order perturbation formulas of the g factors (g_x, g_y, g_z) are established for Cu^{2+} ions in an orthorhombic tetrahedral field with D_2 symmetry, including the central cationic and ligand anionic spin-orbital coupling interactions. By using these formulas, the anisotropic g factors of Cu^{2+} ion in $(CuCl_4)^{2-}$ cluster are calculated. The results are consistent with the experimental values. The calculations show that the contribution from covalency of the central ion and the 3p orbital ligand can not be neglected.

Key words: Crystal- and Ligand-Field; Electron Paramagnetic Resonance; Spin Hamiltonian; $(CuCl_4)^{2-}$ Cluster.

1. Introduction

There has been a great deal of interest in the theoretical investigation of the electronic structure and magnetic and optical properties of the transition metal ions in a covalent crystal [1 – 6]. Due to the large covalency and the large spin-orbit (s. o.) coupling constant of the ligand ions, however, the classical crystal-field calculations cannot agree with the experimental data of the g factors in some covalent crystals such as CdS, ZnSe, CdTe, etc. [4 – 5]. For the $(CuCl_4)^{2-}$ cluster, the g factors were investigated in literature [7, 8]. And the calculated g factors are unreasonable because the contribution from the s. o. coupling of the ligand ions were not considered. In the present work, a theoretical study of the g factors is made within the molecular orbital method. In this study, the ligand ionic s. o. coupling interactions are taken into account and the overlap integral is used which can be obtained from the Slater-type self-consistent field (SCF) functions. The calculated g factors agree well with the available experimental data and show that the contribution from covalency of the central ion and the 3p orbital ligand should be included.

2. Formulas

The Cu^{2+} ion has the $3d^9$ configuration and the ${}^2B_{2g}$ ground state in an orthorhombic tetrahedral symmetry. According to the two s. o. coupling parameter models [5, 6], the linear combination molecular orbitals (LCMO) have been adopted as the basis functions. Thus, the one-electron irreducible representation basis function in O_h symmetry can be given as [9, 10]

$$|\gamma\rangle = N_\gamma(|d_\gamma\rangle - \lambda_\gamma |p_\gamma\rangle), \tag{1}$$

where $\gamma = t_{2g}$ or e_g are the irreducible representations of the O_h group, N_γ and λ_γ are the normalization coefficients and the mixing coefficients of the atomic orbits, respectively. $|d_\gamma\rangle$ and $|p_\gamma\rangle$ are, respectively, the central metal orbitals and the ligand ones. Within the molecular orbitals scheme there are two s. o. coupling parameters ζ and ζ' as follows:

$$\begin{aligned} \zeta &= N_{t_{2g}}^2 \left[\zeta_d^0 + \left(\sqrt{2}\lambda_\pi\lambda_\sigma - \lambda_\pi^2/2\right)\zeta_p^0\right], \\ \zeta' &= N_{t_{2g}} N_{e_g} \left[\zeta_d^0 + \left(\lambda_\pi\lambda_\sigma/\sqrt{2} + \lambda_\pi^2/2\right)\zeta_p^0\right]. \end{aligned} \tag{2}$$

The LCMO coefficients N_γ and λ_γ can be determined from the normalization correlation

$$\begin{aligned} N_{t_{2g}} &= [1 + \lambda_\sigma{}^2 + \lambda_\pi{}^2 + 2\lambda_\sigma S_{dp}(\sigma) \\ &\quad + 2\lambda_\pi S_{dp}(\pi)]^{-1/2}, \\ N_{e_g} &= [1 + 3\lambda_\pi{}^2 + 6\lambda_\pi S_{dp}(\pi)]^{-1/2}, \end{aligned} \tag{3}$$

where $S_{dp}(\gamma)$ is the group overlap integral which can be calculated using the Slater-type SCF functions.

Table 1. Matrix of the two s. o. coupling parameters for a $3d^9$ ion with D_2 symmetry.

$\hat{H}_{SO}$	$\zeta^{\pm}$ ($\lvert d_{xy}\rangle$)	$\theta^{\pm}$ ($\lvert d_{z^2}\rangle$)	$\varepsilon^{\pm}$ ($\lvert d_{x^2-y^2}\rangle$)	$\xi^{\pm}$ ($\lvert d_{yz}\rangle$)	$\eta^{\pm}$ ($\lvert d_{xz}\rangle$)
$\zeta^{\pm}$	0	0	$\pm i\zeta'$	$\pm\zeta/2$	$-i\zeta/2$
$\theta^{\pm}$	0	0	0	$i\sqrt{3}\zeta'/2$	$\mp\sqrt{3}\zeta'/2$
$\varepsilon^{\pm}$	$\mp i\zeta'$	0	0	$i\zeta'/2$	$\pm\zeta'/2$
$\xi^{\mp}$	$\pm\zeta/2$	$-i\sqrt{3}\zeta'/2$	$-i\zeta'/2$	0	$\mp i\zeta/2$
$\eta^{\mp}$	$i\zeta/2$	$\mp\sqrt{3}\zeta'/2$	$\pm\zeta'/2$	$\pm i\zeta/2$	0

The matrix of the two s. o. coupling parameters can be calculated from the formula $\langle\Gamma(\alpha),m_s|\hat{H}_{SO}|\Gamma(\alpha'),m_s\rangle$ and is given in Table 1. In the formula, $|\Gamma(\alpha),m_s\rangle$ and $|\Gamma(\alpha'),m_s\rangle$ are the bases of the irreduced representations. $\hat{H}_{SO}$ is the s. o. Hamiltonian operator.

In the orthorhombic crystal-field, the anisotropic g factors can be expressed as

$$\begin{aligned} g_x &= \frac{1}{\mu_B H_x}\left[\left\langle\Gamma(0),\frac{1}{2}\middle|\hat{H}_{eff}\middle|\Gamma(0),-\frac{1}{2}\right\rangle + \left\langle\Gamma(0),-\frac{1}{2}\middle|\hat{H}_{eff}\middle|\Gamma(0),\frac{1}{2}\right\rangle\right],\\ g_y &= \frac{1}{\mu_B H_y}\left[\left\langle\Gamma(0),\frac{1}{2}\middle|\hat{H}_{eff}\middle|\Gamma(0),-\frac{1}{2}\right\rangle - \left\langle\Gamma(0),-\frac{1}{2}\middle|\hat{H}_{eff}\middle|\Gamma(0),\frac{1}{2}\right\rangle\right],\\ g_z &= \frac{1}{\mu_B H_z}\left[\left\langle\Gamma(0),\frac{1}{2}\middle|\hat{H}_{eff}\middle|\Gamma(0),\frac{1}{2}\right\rangle - \left\langle\Gamma(0),-\frac{1}{2}\middle|\hat{H}_{eff}\middle|\Gamma(0),-\frac{1}{2}\right\rangle\right], \end{aligned} \tag{4}$$

where g_i $(i = x,y,z)$ indicates the components of the g factors. μ_B is the Bohr magneton. H_i $(i = x,y,z)$ denotes the magnetic field along the x-, y-, and z-axes. $|\Gamma(0)\rangle$ denotes the ground state basis of the $3d^9$ electronic configuration. $\pm1/2$ denote the spin quantum numbers. $\hat{H}_{eff}$ denotes the effective Hamiltonian operator. Thus, the first-, second-, and third-order perturbation can be expressed as

$$\begin{aligned} &\hat{H}^{(1)}_{eff} = \hat{H}', \quad \hat{H}^{(2)}_{eff} = \sum_{\alpha}\frac{\hat{H}'|\Gamma(\alpha),m_s\rangle\langle\Gamma(\alpha),m_s|\hat{H}'}{\Delta E(\alpha)},\\ &\hat{H}^{(3)}_{eff} = \sum_{\alpha\beta}\frac{1}{\Delta E(\alpha)\Delta E(\alpha')}\hat{H}'|\Gamma(\alpha),m_s\rangle\langle\Gamma(\alpha),\\ &\qquad m_s|\hat{H}'|\Gamma(\alpha'),m_s\rangle\langle\Gamma(\alpha'),m_s|\hat{H}'\\ &\qquad -\sum_{\alpha}\frac{1}{[\Delta E(\alpha)]^2}\hat{H}'|\Gamma(\alpha),m_s\rangle\langle\Gamma(\alpha),\\ &\qquad m_s|\hat{H}'|\Gamma(0),m_s\rangle\langle\Gamma(0),m_s|\hat{H}', \end{aligned} \tag{5}$$

in which $\Delta E(\alpha)$ and $\Delta E(\alpha')$ are the energy differences between the excited states and the ground state. From (5) and Macfarlane's perturbation-loop method [11, 12], the third-order perturbation formulas of the g factors in an orthorhombic crystal are obtained as

$$\begin{aligned} g_x &= g_e + \frac{2k\zeta k}{\Delta E_2} + \frac{-2k\zeta'^2}{\Delta E_1\Delta E_2} + \frac{k\zeta^2}{\Delta E_2\Delta E_3}\\ &\quad + \frac{2k'\zeta\zeta'}{\Delta E_1\Delta E_3} + \frac{-2g_e\zeta'^2}{\Delta E_1^2} + \frac{(-1/2)g_e\zeta^2}{\Delta E_3^2},\\ g_y &= g_e + \frac{2k\zeta}{\Delta E_3} + \frac{2k'\zeta\zeta'}{\Delta E_1\Delta E_2} + \frac{k\zeta^2}{\Delta E_2\Delta E_3}\\ &\quad + \frac{-2k\zeta'^2}{\Delta E_1\Delta E_3} + \frac{-2g_e\zeta'^2}{\Delta E_1^2} + \frac{(-1/2)g_e\zeta^2}{\Delta E_3^2},\\ g_z &= g_e + \frac{8k'\zeta'}{\Delta E_1} + \frac{-2k'\zeta\zeta'}{\Delta E_1\Delta E_2} - \frac{k\zeta^2}{\Delta E_2\Delta E_3}\\ &\quad + \frac{-2k'\zeta\zeta'}{\Delta E_1\Delta E_3} + \frac{(-1/2)g_e\zeta^2}{\Delta E_2^2} + \frac{(-1/2)g_e\zeta^2}{\Delta E_3^2}, \end{aligned} \tag{6}$$

where $g_e = 2.0023$. The energy denominators ΔE_i $(i = 1,2,3)$ are defined as the energy differences between the ground state $^2B_{2g}$ and the excited levels $^2B_{1g}$, $^2E_{1g}$, and $^2E_{2g}$, respectively. k and k' are the two orbital reduction factors and can be obtained by

$$\begin{aligned} k &= N^2_{t_{2g}}\left[1 + \sqrt{2}\lambda_\pi\lambda_\sigma - \lambda_\pi{}^2/2 + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi)\right],\\ k' &= N_{t_{2g}}N_{e_g}\left[1 + \lambda_\pi\lambda_\sigma/\sqrt{2} + \lambda_\pi{}^2/2 + \lambda_\sigma S_{dp}(\sigma) + 4\lambda_\pi S_{dp}(\pi)\right]. \end{aligned} \tag{7}$$

Obviously, according to the classical crystal-field theory, the admixture of the s. o. coupling constants between the central metal ion and its ligands via the covalency effects is not considered, i. e., $\lambda_\pi = \lambda_\sigma = 0$, $N = (N_{e_g}N_{t_{2g}})^{1/2}$, and so $\zeta = \zeta'$, $k = k'$. Then (6) becomes the classical perturbation formulas which are based on the single s. o. coupling parameter model.

3. Application

The Cs_2CuCl_4 crystal is orthorhombic with space group P_{nam} and unit cell dimensions $a = 9.7599(12)$ Å, $b = 7.6091(9)$ Å, $c = 12.3967(12)$ Å, and $Z = 4$ [13]. The crystal field around the centre Cu^{2+} ion by the chlorine ions is D_{2d} indeed. The Cu^{2+} ion belongs to the $3d^9$ electronic configuration. Its energy level in a

Table 2. g factors of the $(CuCl_4)^{2-}$ cluster.

	Calculations a	 b	Experiment [18]
g_x	2.256	2.082	2.083(1)
g_y	2.312	2.102	2.105(6)
g_z	2.696	2.392	2.384(6)

[a] Calculated from high-order perturbation formulas based on one single s. o. coupling parameter. [b] Calculated from high-order perturbation formulas based on two s. o. coupling parameters.

cubic field will split into $^2T_{2g}$ and ^2E_g, the ground state is ^2E_g. In an orthorhombic field with D_{2d} symmetry the energy level will split further. $^2T_{2g}$ splits into $^2B_{1g}$, $^2B_{2g}$, and $^2A_{1g}$; ^2E_g splits into $^2E_{1g}$, and $^2E_{2g}$. $^2B_{2g}$ is the ground state for the z-axis compression in the D_{2d} symmetry crystal.

Ferguson [14] has presented an optical study on the single crystal of Cs_2CuCl_4 with the Cu^{2+} ion at 20 K. He has given the observed optical absorption spectra at 4800 cm^{-1} ($^2B_{2g} \to {}^2E_{1g}$), 5550 cm^{-1} ($^2B_{2g} \to {}^2E_{2g}$), 7900 cm^{-1} ($^2B_{2g} \to {}^2B_{1g}$), and 9050 cm^{-1} ($^2B_{2g} \to {}^2A_{1g}$). The spin-orbit coupling parameter is $\zeta_d^0 \approx$ 829 cm^{-1} for the Cu^{2+} ion [15] and $\zeta_p^0 \approx 587$ cm^{-1} for the Cl^- ion [16, 17]. From the structure data [13], we have for the $(CuCl_4)^{2-}$ cluster $R \approx 2.2333$ Å. Thus, we obtain $S_{dp}(\pi) \approx 0.00625$, $S_{dp}(\sigma) \approx -0.02338$, and so $N_{t_{2g}} \approx 0.8902$, $N_{e_g} \approx 0.8421$. As a good approximation, we take λ_π and λ_σ as the adjustable parameters. By fitting the calculated g factors to the observed values, we obtain

$$\lambda_\pi \approx -0.376 \quad \text{and} \quad \lambda_\sigma \approx 0.378.$$

The comparison between calculation and experiment is shown in Table 2.

4. Conclusions

(1) Obviously, from the high-order perturbation formulas based on the two s. o. coupling parameters model, the g_x, g_y, and g_z of the $(CuCl_4)^{2-}$ cluster can be reasonably explained by using the above formulas.

(2) For comparison, we calculate g_x, g_y, and g_z from the single s. o. coupling parameter model, where $\lambda_\pi = \lambda_\sigma = 0$ and $N = (N_{e_g} N_{t_{2g}})^{1/2}$. The calculated results are also shown in Table 2. From Table 2, it can be seen that g_x, g_y, and g_z are in poor agreement with those of observed values from the single s. o. coupling parameter model. So, the neglecting of the contribution from covalency of the central ion and the ligand 3p orbital causes the unusual phenomenon related to the g factors.

(3) The theoretical methods in this paper are also effective for $3d^9$ ions in other isostructural covalent crystals.

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