Investigation of the EPR Parameters of an Orthorhombic Cu^{2+} Center in Cs_2ZnCl_4 Crystal

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Z. Naturforsch. **60a,** 373 – 375 (2005); received February 23, 2005

The electron paramagnetic resonance (EPR) anisotropic g-factors g_x, g_y and g_z and hyperfine structure constants A_x, A_y and A_z of Cu^{2+} in Cs_2ZnCl_4 crystal are theoretically investigated by the method of diagonalizing the full Hamiltonian matrix. The crystal-field parameters are obtained from the crystal structure by the superposition model. The results, agreeing reasonably with the observed values, are discussed.

Key words: Crystal-field Theory; Electron Paramagnetic Resonance; Cu^{2+}; Cs_2ZnCl_4.

1. Introduction

Cu^{2+} enters easily into a number of host lattices, and one gets an idea about various characteristics, such as the ground state of the ion, the type of distortions, delocalization of free electrons and also structural phase transitions. The optical and magnetic characteristics of Cu^{2+} coordinated complexes have been studied in [1 – 6]. The theoretical studies are usually related to Cu^{2+} complexes with six coordinated octahedra and axial symmetry. Those of low symmetry and four coordinated complexes are infrequent. For example, the EPR g-factors g_x, g_y and g_z and the hyperfine structure constants A_x, A_y and A_z for orthorhombic Cu^{2+} centers in Cs_2ZnCl_4 crystal were reported in 1965 [7]. But up to now no theoretical explanation has been made for these EPR parameters. In this paper, by diagonalizing the full energy matrix, we calculated the EPR anisotropic g-factors g_x, g_y and g_z and hyperfine structure constants A_x, A_y and A_z for Cu^{2+} in Cs_2ZnCl_4 crystal. The crystal-field parameters were obtained by the superposition model. The results are discussed.

2. Calculation

The Cs_2ZnCl_4 crystal has orthorhombic symmetry and belongs to the *Pnam* space group. The host Cs^+ ion is coordinated by four nearest-neighbour Cl^- ions. The tetrahedron $(CsCl_4)^{3-}$ has the D_2 point symmetry. The impurity Cu^{2+} replaces the Cs^+ site with approximate D_2 point group symmetry [8].

The Hamiltonian of a transition-metal ion in the crystal under an external magnetic field can be written as [6]

$$\hat{H}' = \hat{H}_\mathrm{e} + \hat{H}_\mathrm{CF} + \hat{H}_\mathrm{so} + \hat{H}_\mathrm{z}, \tag{1}$$

where $\hat{H}_\mathrm{e}$ is the electron-electron repulsion term, $\hat{H}_\mathrm{CF}$ the crystal-field Hamiltonian and $\hat{H}_\mathrm{so}$ the spin-orbit coupling interaction. For orthorhombic D_2 symmetry, the crystal-field interaction $\hat{H}_\mathrm{CF}$ can be expressed in terms of the irreducible tensor operators C_k^q:

$$\begin{aligned}\hat{H}_\mathrm{CF} = {} & B_{20}C_0^2 + B_{22}(C_2^2 + C_{-2}^2) + B_{40}C_0^4 \\ & + B_{42}(C_2^4 + C_{-2}^4) + B_{44}(C_4^4 + C_{-4}^4),\end{aligned} \tag{2}$$

where B_{kq} are crystal field parameters. $\hat{H}_\mathrm{so}$ can be written as:

$$\hat{H}_\mathrm{so} = \sum \zeta_\mathrm{d} \hat{l}_i \hat{s}_i \tag{3}$$

where ζ_d is the spin-orbit coupling coefficient for free Cu^{2+}, $\zeta_\mathrm{d} \approx 829\ \mathrm{cm}^{-1}$ [9]. The Zeeman interaction $\hat{H}_\mathrm{z}$ can be written as $\hat{H}_\mathrm{z} = g_J \mu_\beta \hat{H} \hat{J}$, with their original meanings [9, 10].

0932–0784 / 05 / 0500–0373 $ 06.00

By diagonalizing the complete energy matrix, one obtains the energy eigenvectors. For the orthorhombic $(CuCl_4)^{2-}$ cluster, the wave functions of ground Kramers doublets can be written as $|\varepsilon, \pm\frac{1}{2}\rangle$, which can be obtained by diagonalizing the energy matrix. Then the anisotropic g-factors g_x, g_y and g_z can be expressed as [10]

$$\begin{aligned} g_x &= 2\left\langle \varepsilon, \frac{1}{2} \middle| N^2 L_x + g_e S_x \middle| \varepsilon, -\frac{1}{2} \right\rangle, \\ g_y &= 2\left\langle \varepsilon, \frac{1}{2} \middle| N^2 L_y + g_e S_y \middle| \varepsilon, -\frac{1}{2} \right\rangle, \\ g_z &= 2\left\langle \varepsilon, \frac{1}{2} \middle| N^2 L_z + g_e S_z \middle| \varepsilon, \frac{1}{2} \right\rangle, \end{aligned} \tag{4}$$

where $g_e \approx 2.0023$ is the free spin g-value. N is the average covalent reduction factor due to the covalency reduction effect. We take it as an adjustable parameter here. L_i and S_i $(i = x, y, z)$ are, respectively, the orbital and spin angular momenta.

The hyperfine structure constants A_x, A_y and A_z are [11, 12]

$$\begin{aligned} A_x = P \Bigg[& -N^2\kappa + \frac{2}{7}N^2(\alpha^2 - \beta^2) + (g_x - g_e) \\ & - \frac{1}{14}\left(\frac{3\alpha + \sqrt{3}\beta}{\alpha - \sqrt{3}\beta}\right)(g_y - g_e) \\ & + \frac{\sqrt{3}\beta}{14\alpha}(g_z - g_e) - \frac{4\sqrt{3}k\alpha\beta}{7} \Bigg], \\ A_y = P \Bigg[& -N^2\kappa + \frac{2}{7}N^2(\alpha^2 - \beta^2) + (g_y - g_e) \\ & - \frac{1}{14}\left(\frac{3\alpha - \sqrt{3}\beta}{\alpha + \sqrt{3}\beta}\right)(g_x - g_e) \\ & - \frac{\sqrt{3}\beta}{14\alpha}(g_z - g_e) + \frac{4\sqrt{3}k\alpha\beta}{7} \Bigg], \\ A_z = P \Bigg[& -N^2\kappa - \frac{4}{7}N^2(\alpha^2 - \beta^2) + (g_z - g_e) \\ & + \frac{1}{14}\left(\frac{3\alpha - \sqrt{3}\beta}{\alpha + \sqrt{3}\beta}\right)(g_x - g_e) \\ & + \frac{1}{14}\left(\frac{3\alpha + \sqrt{3}\beta}{\alpha - \sqrt{3}\beta}\right)(g_y - g_e) \Bigg], \end{aligned} \tag{5}$$

where κ is the core polarization constant, which is about 0.3 for $3d^n$ ions in crystals [13]. Here we take $\kappa \approx 0.288$. P is the dipolar hyperfine parameter for Cu^{2+} in the crystal, $P = N^2 P_0$ (where P_0 is the free-ion value, i. e., $P_0 \approx 388 \times 10^{-4}$ cm^{-1} for $^{63}Cu^{2+}$ and $P_0 \approx 416 \times 10^{-4}$ cm^{-1} for $^{65}Cu^{2+}$ [13]). α and β are mixing coefficients for the $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ orbitals. They can be determined from the normalization condition $\alpha^2 + \beta^2 = 1$ [11, 12].

According to Newman's superposition model [14, 15], the crystal field parameters B_{kq} in (3) can be expressed as

$$B_{kq} = \sum_{j=1}^{n} \bar{A}_k(R_0)(R_0/R_j)^{t_k} K_k^q(\theta_j, \phi_j), \tag{6}$$

where t_k is the power-law exponent and $\bar{A}_k(R_0)$ is the intrinsic parameter with the reference distance R_0 (here we take $R_0 \approx 2.399$ Å). Usually, the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of $9 \sim 12$ for $3d^n$ ions in many crystals [15, 16]. We take $\bar{A}_4(R_0)$ as adjustable parameter and $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$. $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of the bonds [15]. The coordination factor $K_k^q(\theta_j, \phi_j)$ can be obtained from the local structural parameters of the studied system.

As far as we know, no structure data of Cs_2ZnCl_4 crystal are reported. So we use those of the similar Cs_2CuCl_4 crystal, which for Cs^+ are [17]

$$R \approx 2.2345 \text{ Å}, \quad \theta \approx 64.4355^\circ, \quad \varepsilon \approx -1^\circ. \tag{7}$$

Here ε is the small departure from the 45° angle. Substituting these parameters into the above formulas and diagonalizing the complete energy matrix, the anisotropic g-factors for Cu^{2+} and the hyperfine structure constants A for the $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$ isotopes in Cs_2ZnCl_4 are obtained. Thus, from the above formulas and parameters, we find that to reach good fits between the calculated and experimental EPR parameters for the Cu^{2+} center, these parameters are

$$\bar{A}_4(R_0) \approx 467 \text{ cm}^{-1}, \quad N \approx 0.834. \tag{8}$$

The comparisons between the calculated and experimental EPR parameters are shown in Table 1.

3. Discussion

By diagonalizing the Hamiltonian matrix, we calculated the EPR anisotropic g-factors g_x, g_y and g_z and hyperfine structure constants A_x, A_y and A_z for Cu^{2+} in Cs_2ZnCl_4 crystal. From the Table 1 one finds that the calculated EPR parameters g_i factors and the hyperfine

Table 1. EPR g-factors and hyperfine structure parameters for Cu^{2+} in Cs_2ZnCl_4 crystal.

				$^{63}Cu^{2+}$ (10^{-4} cm^{-1})			$^{65}Cu^{2+}$ (10^{-4} cm^{-1})		
	g_x	g_y	g_z	$\lvert A_x\rvert$	$\lvert A_y\rvert$	$\lvert A_z\rvert$	$\lvert A_x\rvert$	$\lvert A_y\rvert$	$\lvert A_z\rvert$
Cal.	2.089	2.100	2.487	56.7	46.4	28.3	60.8	50.7	30.3
Expt. [7]	2.083(5)	2.101(5)	2.446(5)	51(5)	46(5)	25(5)	–	–	–

structure constants A_i of ion in Cs_2ZnCl_4:Cu^{2+} crystal agree reasonably with the observed values.

The structural data are not those of the Cs_2ZnCl_4 host crystal but those of the similar Cs_2CuCl_4 crystal, which would result in some errors of the calculated EPR parameters. Considering that Cu^{2+} and Zn^{2+} have the same charges and about the same ion radii ($r \approx 0.72$ Å for Cu^{2+} and $r \approx 0.74$ Å for Zn^{2+} [18]), the discrepancy of the EPR parameters originating from the host structural data can be neglected.

On the other hand, because of the difference of the charge and ion radii between the impurity Cu^{2+} and host Cs^+ ions, the local structural parameters in the vicinity of Cu^{2+} should be different from those of the host Cs^+ ion. Disregarding the charge compensation and the lattice relaxation caused by the substitution of an impurity for the host ion in crystals may result in some calculating errors. As the calculated EPR parameters are consistent with the observed values, this approximation and the results can be regarded as valid.

Considering that the spin-orbit interaction of ligand Cl^- ions is far smaller than that of Cu^{2+} ions, in our calculation, the effects of the ligand spin-orbit coupling coefficient to g_i and A_i factors are omitted. The approximate calculation is used by other authors and testified to be reliable [4, 5].

Acknowledgement

This work was supported by the Science Foundation of the Science and Education Committee of Chongqing.

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