Energy Levels and g Factors of Cu^{2+}-Doped Bis(L-asparaginato)zinc(II)

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The formulas for the energy levels and g factors for $3d^9$ ions in an orthorhombic field with D_{2h} symmetry are obtained. They are used to investigate the energy levels and the g-anisotropy of Cu^{2+} ions in a bis(L-asparaginato)zinc(II) single crystal. The theoretically calculated values of the energy levels have agree well with the observed optical spectrum of the Cu^{2+} ions in the compound considered here, and also the calculated values of the g-anisotropy conform with the experimental values.

Key words: Bis(L-asparaginato)zinc(II) Crystal; Energy Levels; g-Anisotropy; D_{2h} Distortion.
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1. Introduction

The amino acid L-asparagine is known to an essential growth factor for a variety of tumours, in particular animal lymphomas [1]. Recently it has been shown that the activity of L-asparagine can be inhibited by a number of metal ions [2]. A L-asparagine acid easily forms easily additive compounds with a number of metals and inorganic salts. When a paramagnetic ion is placed in a crystalline surrounding in the presence of an external magnetic field, its behaviour will change from its free ion behaviour.

In [3] Kripal and Singh have presented an optical study on the single crystal of bis(L-asparaginato)zinc(II) with Cu^{2+} impurity at room temperature. They have given both observed and calculated optical absorption spectra in the wavelength range 195 – 1100 nm. But though their calculated values are near to the experimental values, they did not conform with the theory of energy level splitting. As for the g-anisotropy in [3], the calculated value δ_g ($\delta_g = g_y - g_x$) is negative, while the experimental value δ_g is positive. To confirm the optical absorption spectra of Cu^{2+}-doped bis(L-asparaginato)zinc(II), the calculated g-anisotropy and δ_g values are necessary.

2. Crystal Structure

The bis(L-asparaginato)zinc(II) crystal is monoclinic with space group $P21$ and unit cell dimensions $a = 12.323$ Å, $b = 5.027$ Å, $c = 9.702(2)$ Å, and $Z = 2$ [4]. The zinc atom is in a distorted octahedral environment. A carboxylic O atom and the α-amino N atom from each ligand coordinate to the Zn atom in a trans square planar configuration. The octahedral environment is completed by the carbonyl O atoms from neighbouring molecules, creating infinite chains linked in the [011] direction. So the crystal field around the centre Zn^{2+} ion is D_{2h} indeed. The D_{2h} structure is shown in Figure 1. The angle between the y-axis and N atom is denoted as α. In the bis(L-asparaginato)zinc(II) crystal, the structure has been determined with $R_1 = 2.094$ Å, $R_2 = 2.0815$ Å, $R_3 = 2.3795$ Å, $\alpha = (8.85 \pm 0.02)°$ [4].

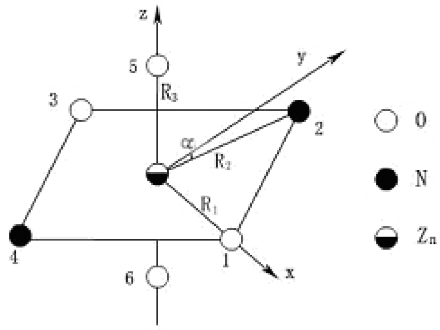

Fig. 1. Structure of the bis(L-asparaginato)zinc(II) crystal.

3. The Energy Levels and g Factors of the Bis(L-asparaginato)zinc(II) Crystal

3.1. *Formulas for the Energy Levels of a $3d^9$ System in the D_{2h} Symmetry*

The Cu^{2+} ion belongs to the electron system $3d^9$ [5]. Its energy level in a cubic field will split into ^2E and

$^2T_2$. The ground state in octahedral symmetry is ^2E. In an orthorhombic field with D_{2h} symmetry the energy level will split further. ^2T splits into $^2B_1(\xi)$, $^2B_2(\eta)$, and $^2B_3(\xi)$; ^2E splits into $^2A_1(\varepsilon)$ and $^2A_1(\theta)$. $^2A_1$, $^2B_1$, $^2B_2$, and $^2B_3$ are the irreducible representations in D_{2h} symmetry. ε and θ are the two components of ^2E; ζ, η and ξ are the components of $^2T_2$.

Using the crystal field theory, the crystal-field potential in D_{2h} symmetry can be described by the following expression:

$$\begin{aligned}V(D_{2h}) = \sum_i \big[&B_{20}(r_i)C_0^2(\theta_i\varphi_i) + B_{22}(r_i)C_2^2(\theta_i\varphi_i)\\ &+ B_{40}(r_i)C_0^4(\theta_i\varphi_i) + B_{42}(r_i)C_2^4(\theta_i\varphi_i)\\ &+ B_{44}(r_i)C_4^4(\theta_i\varphi_i) + B_{2-2}(r_i)C_{-2}^2(\theta_i\varphi_i)\\ &+ B_{4-2}(r_i)C_{-2}^4(\theta_i\varphi_i) + B_{4-4}(r_i)C_{-4}^4(\theta_i\varphi_i)\big],\end{aligned} \tag{1}$$

where $B_{22}(r_i) = B_{2-2}(r_i)$, $B_{44}(r_i) = B_{4-4}(r_i)$, $B_{42}(r_i) = B_{4-2}(r_i)$, $A_q^k = B_{kq}/\gamma^k$. From this, we can calculate the energy matrix

$$\langle \Gamma_\gamma | V(D_{2h}) | \Gamma'_\gamma \rangle, \tag{2}$$

where $|\Gamma'_{\gamma'}\rangle$ and $|\Gamma_\gamma\rangle$ are $|\zeta\rangle, |\eta\rangle, |\xi\rangle, |\varepsilon\rangle, |\theta\rangle$.

Then we obtain the energy formulas as follows:

$$E(\zeta) = -\frac{2}{7}B_{20} + \frac{1}{21}B_{40} - \frac{1}{3}\sqrt{\frac{10}{7}}B_{44}, \tag{3a}$$

$$E(\eta) = \frac{1}{7}B_{20} + \frac{\sqrt{6}}{7}B_{22} - \frac{4}{21}B_{40} + \frac{2\sqrt{10}}{21}B_{42}, \tag{3b}$$

$$E(\xi) = \frac{1}{7}B_{20} + \frac{\sqrt{6}}{7}B_{22} - \frac{4}{21}B_{40} - \frac{2\sqrt{10}}{21}B_{42}, \tag{3c}$$

$$E(a) = \begin{bmatrix} -\frac{2}{7}B_{20} + \frac{1}{21}B_{40} + \frac{1}{3}\sqrt{\frac{10}{7}}B_{44} & -\frac{2\sqrt{2}}{7}B_{22} + \frac{\sqrt{30}}{21}B_{42} \\ -\frac{2\sqrt{2}}{7}B_{22} + \frac{\sqrt{30}}{21}B_{42} & \frac{2}{7}B_{20} + \frac{2}{7}B_{40} \end{bmatrix}. \tag{3d}$$

Here B_{kq} is the crystal-field parameter, which is related to the crystal-structure parameter. In a point-charge model it can be defined as

$$B_{kq} = A_q^k \langle r^k \rangle, \tag{4}$$

$$A_q^k = \sum_m \frac{eq_m}{R_m^{k+1}}(-1)^{q+1}C_{-q}^k(\Theta_m, \Phi_m). \tag{5}$$

In D_{2h} symmetry the non-zero crystal-field parameters are B_{44}, B_{42}, B_{40}, B_{22}, and B_{20}, which are related to the band lengths R_1 and R_2, and the angle α, and the charges of the ligands q_1 and q_2. They can be obtained from the following expressions:

$$B_{44} = B_{4-4} = \sqrt{\frac{35}{32}}\left(\frac{q_1}{R_1^5} + \frac{q_2}{R_2^5}\cos 4\alpha\right)e\langle r^4\rangle, \tag{6a}$$

$$B_{42} = B_{4-2} = \sqrt{\frac{5}{8}}\left(\frac{q_1}{R_1^5} - \frac{q_2}{R_2^5}\cos 2\alpha\right)e\langle r^4\rangle, \tag{6b}$$

$$B_{40} = -\frac{1}{4}\left(\frac{3q_1}{R_1^5} + \frac{3q_2}{R_2^5} + \frac{8q_1}{R_3^5}\right)e\langle r^4\rangle, \tag{6c}$$

$$B_{22} = B_{2-2} = -\sqrt{\frac{3}{2}}\left(\frac{q_1}{R_1^3} - \frac{q_2}{R_2^3}\cos 2\alpha\right)e\langle r^2\rangle, \tag{6d}$$

$$B_{20} = \left(\frac{q_1}{R_1^3} + \frac{q_2}{R_2^3} - \frac{2q_1}{R_3^3}\right)e\langle r^2\rangle, \tag{6e}$$

where q_1 is the charge of the O ligand, q_2 is the charge of the N ligand, and e is the electron charge; $\langle r^2\rangle$ and $\langle r^4\rangle$ are the expectation values for the respective powers of the distances of the Cu^{2+} ion in the crystal.

3.2. *Formulas for the g Factors of a 3d^9 System in the D_{2h} Symmetry*

In an orthorhombic field the spin Hamilton of a 3d^9 ion can be described by

$$H_s = g_x\mu_B H_x\hat{S}_x + g_y\mu_B H_y\hat{S}_y + g_z\mu_B H_z\hat{S}_z, \tag{7}$$

where g_i $(i = x,y,z)$ indicates the components of the g factor; μ_B is the Bohr magneton, $\hat{S}_i$ $(i = x,y,z)$ is the spin operator, and H_i $(i = x,y,z)$ indicates the components of the magnet field along the x-, y-, and z-axes.

Using the perturbation theory, the g factors can be obtained by the formula

$$g_i = g_s - 2\lambda\Lambda_{ii}, \tag{8}$$

$$\Lambda_{ij} = \sum_{n\neq 0}\frac{\langle 0|\hat{L}_i|n\rangle\langle n|\hat{L}_j|0\rangle}{E_n^{(0)} - E_0^{(0)}} \quad (i,j = x,y,z). \tag{9}$$

Here $g_s = 2.0023$ is the value of the free electron and λ is the spin-orbit coupling coefficient for the 3d^9 ion. For a Cu^{2+} ion the relation between λ and the one-electron spin-orbit coupling coefficient ζ_d is $\lambda = -\zeta_d$. Using (2) and introducing the average covalent factor N [6] to describe the covalency, the g factors expressions of a 3d^9 ion in D_{2h} symmetry can be obtained as

$$g_z = g_s - \frac{8\zeta_d N^4}{E(\zeta) - E(\varepsilon)}, \tag{10a}$$

Table 1. Comparison of the theoretical calculations of the energy levels in this work and experimental results.

Transition	Band positions (cm^{-1})			
	Calculated	Experimental [3]		
${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{A}_1(\theta)$	10938	11299	12180	
${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{B}_1(\zeta)$	14288	14727	15576	
${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{B}_2(\eta)$	19184	19193	19920	20790
${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{B}_3(\xi)$	37397	32786	37878	42372

Table 2. Comparison of the theoretical calculations of the g factors in this work and experimental results.

g-Anisotropy	Principal g values	
	Calculated	Experimental [3]
g_x	2.040	2.034
g_y	2.101	2.064
g_z	2.296	2.239
δ_g	0.061	0.031

$$g_x = g_\mathrm{s} - \frac{2\zeta_\mathrm{d} N^4}{E(\xi) - E(\varepsilon)}, \qquad (10b)$$

$$g_y = g_\mathrm{s} - \frac{2\zeta_\mathrm{d} N^4}{E(\eta) - E(\varepsilon)}. \qquad (10c)$$

3.3. Results for Energy Levels and g Factors

According to (3), (6), and (10) the values of $E(\zeta)$, $E(\eta)$, $E(\xi)$, $E(\alpha)$, g_x, g_y, g_z, and δ_g are related to the crystal structure data R_1, R_2, and α. Also $q_1 = 2e$ for the O^{2-} ion and $q_2 = 1e$ for the N^{1-} ion. In error scope, taking $\alpha = 8.83°$, we can calculate the energy levels and g factors. An attempt has also been made to obtain $\delta_g = g_y - g_x$. The results for the energy levels are shown in Table 1; the three principal g and δ_g values are shown in Table 2. They both can be compared with the experimental values.

4. Discussion and Conclusion

The Cu^{2+} ion belongs to the electron system $3\mathrm{d}^9$. In an orthorhombic field its energy level will split into ${}^2\mathrm{A}_1(\varepsilon)$ and ${}^2\mathrm{A}_1(\theta)$, which come from ${}^2\mathrm{E}$, and into ${}^2\mathrm{B}_1(\zeta)$, ${}^2\mathrm{B}_2(\eta)$, ${}^2\mathrm{B}_3(\xi)$, which come from ${}^2\mathrm{T}_2$. It is known that ${}^2\mathrm{E}$ is the ground state in octahedral symmetry, which means that the ${}^2\mathrm{E}$ components ${}^2\mathrm{A}_1(\varepsilon)$ and ${}^2\mathrm{A}_1(\theta)$ should be in general lower than the ${}^2\mathrm{T}_2$ components ${}^2\mathrm{B}_1(\zeta)$, ${}^2\mathrm{B}_2(\eta)$, and ${}^2\mathrm{B}_3(\xi)$. But in [3], its calculated result ${}^2\mathrm{A}_1(\theta)$ is higher than ${}^2\mathrm{B}_1(\zeta)$, ${}^2\mathrm{B}_2(\eta)$, and ${}^2\mathrm{B}_3(\xi)$; it therefore did not conform with theory and seemed unreasonable. According to our calculation, the energy levels of the Cu^{2+} ion in the bis(L-asparaginato)zinc(II) single crystal are as follows: ${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{A}_1(\theta)$, 10938 cm^{-1}; ${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{B}_1(\zeta)$, 14288 cm^{-1}; ${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{B}_2(\eta)$, 19184 cm^{-1}; ${}^2\mathrm{A}_1(\varepsilon) \rightarrow {}^2\mathrm{B}_3(\xi)$, 37397 cm^{-1}. Note that the ${}^2\mathrm{E}$ components ${}^2\mathrm{A}_1(\varepsilon)$ and ${}^2\mathrm{A}_1(\theta)$ are both lower than the ${}^2\mathrm{T}_2$ components ${}^2\mathrm{B}_1(\zeta)$, ${}^2\mathrm{B}_2(\eta)$, and ${}^2\mathrm{B}_3(\xi)$. So these theoretical values of the present work not only rather well agree with the experimental result in [3] but also more reasonably and satisfactorily explain the optical absorption spectrum of Cu^{2+} in a bis(L-asparaginato)zinc(II) crystal of [3].

In [3] the experimental value δ_g is positive $(g_y > g_x)$, but the previously calculated value is $\delta_g = -0.007$ $(g_x > g_y)$, which obviously does not conform with the structure. In this paper the calculated δ_g value is not only positive but also matches with the experimental value; so our results can explain the structure of the bis(L-asparaginato)zinc(II) crystal more reasonably and satisfactorily.

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