The D_{2h} Distortion around the Cu^{2+} Center in $Cu_{0.5}Zr_2(PO_4)_3$ Single Crystals

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A formula for the calculation of the three g factors of $3d^9$ ions in an orthorhombic field D_{2h} has been derived. Using it to investigate the EPR g factors of the Cu^{2+} ions in single crystals of $Cu_{0.5}Zr_2(PO_4)_3$, the variation of the g factors on changing the angle α between the x- and y-axis has been explained. According to that, it can be confirmed that the angle α of the D_{2h} distortion is about 62.6°. PACS: 71.70C; 76.30F

Key words: $Cu_{0.5}Zr_2(PO_4)_3$ Crystal; Gyromagnetic Factor; D_{2h} Distortion.

1. Introduction

$Cu_{0.5}Zr_2(PO_4)_3$ crystals belong to the Nasicon-type family with a three-dimensional network built of PO_4 tetrahedra sharing corners with ZrO_6 octahedra [1]. The three-dimensional network can be considered as being made of infinite ribbons linked by PO_4 tetrahedra. They are used in chemistry and ceramic industry because of their catalytic and low thermal expansion properties, as well the ionic conductivity of their derivatives [2 – 8].

Taoufik et al. [9] have investigated the magnetic susceptibility and EPR of $Cu_{0.5}Zr_2(PO_4)_3$ crystals. They contain an important amount of paramagnetic Cu^{2+} ions, and EPR spectra give information about local paramagnetic environments. Their structure shows a monoclinic distortion compared to that of $NaZr_2(PO_4)_3$ [6]. It is suggested that the field surrounding the Cu^{2+} ions is orthorhombic (D_{2h}) rather than tetragonal (D_{4h}) [9, 10] from the observed optical spectrum of the Cu^{2+} ions. But these observations didn't confirm the distortion structure when the crystal field varies from D_{4h} to D_{2h}.

In this paper, using experimental EPR results, further studies have been done to observe the distortion tendency from D_{4h} to D_{2h}.

2. The g Factors of $3d^9$ in the Symmetry of D_{2h}

The Cu^{2+} ions lie in the interspace of the three-dimensional network and are surrounded by six oxygen atoms [2]. Taoufik et al. assumed that it is the D_{2h} symmetry [9] shown in Fig. 1, where the angle α between the x- and y-axis lies in the plane perpendicular to the z-axis. For the $Cu_{0.5}Zr_2(PO_4)_3$ crystal $R_1 = 1.95$ Å and $R_2 = 2.82$ Å have been given in [2], but the resulting angle α was not confirmed.

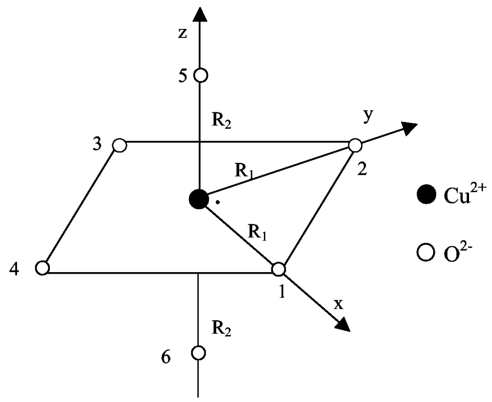

Fig. 1. Position of the six ligands in D_{2h}.

It is known that Cu^{2+} belongs to the electron system $3d^9$. Its energy level will be split into ^2E and $^2T_2$ in a cubic field. The ground state is ^2E in octahedral symmetry. In the orthorhombic field D_{2h} the energy levels will be split further. $^2T_2$ is split into $B_1(\zeta)$, $B_2(\eta)$, and $B_3(\xi)$. ^2E is split into $A_1(\varepsilon)$ and $A_1(\theta)$. A_1, B_1, B_2, and B_3 are the irreducible representation in D_{2h} symmetry. ε and θ indicate the components of ^2E. ζ, η, and ξ indicate the components of $^2T_2$. $A_1(\varepsilon)$ is the ground state in the $Cu_{0.5}Zr_2(PO_4)_3$ crystal [11].

In an orthorhombic field, the spin Hamiltonian of the $3d^9$ ion can be described by the expression

$$H_s = g_x \mu_B H_x \hat{S}_x + g_y \mu_B H_y \hat{S}_y + g_z \mu_B H_z \hat{S}_z, \quad (1)$$

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 magnetic field along the x-, y- and z-axes.

Using the perturbation theory, the g factors can be obtained by the formula [12]

$$g_i = g_s - 2\lambda \Lambda_{ii}, \quad (2)$$

$$\Lambda_{ij} = \sum_{n\neq 0} \frac{\langle 0|\widehat{L_i}|n\rangle\langle n|\widehat{L_j}|0\rangle}{E_n^{(0)} - E_0^{(0)}}, \quad (i,j = x,y,z), \quad (3)$$

where $g_s = 2.0023$ is the value of free electron and λ is the spin-orbit coupling coefficient of the $3d^9$ 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 [13] to describe the covalency, the g factors of the $3d^9$ ion in D_{2h} symmetry can be obtained as

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

$$g_x = g_s - \frac{2\zeta_d N^4}{E(\xi) - E(\varepsilon)}, \quad (5)$$

$$g_y = g_s - \frac{2\zeta_d N^4}{E(\eta) - E(\varepsilon)}, \quad (6)$$

where the energy denominators are

$$E(\zeta) - E(\varepsilon) = -\frac{2}{3}\sqrt{\frac{10}{7}} B_{44}, \quad (7)$$

$$E(\eta) - E(\varepsilon) = -\frac{1}{3}\sqrt{\frac{10}{7}} B_{44} + \frac{2\sqrt{10}}{21} B_{42} - \frac{2}{21} B_{40} + \frac{\sqrt{6}}{7} B_{22} + \frac{2}{7} B_{20}, \quad (8)$$

$$E(\xi) - E(\varepsilon) = -\frac{1}{3}\sqrt{\frac{10}{7}} B_{44}, - \frac{2\sqrt{10}}{21} B_{42} - \frac{2}{21} B_{40} - \frac{\sqrt{6}}{7} B_{22} + \frac{2}{7} B_{20}. \quad (9)$$

The crystal-field parameter B_{kq} is related to the crystal structure parameter. In D_{2h} symmetry the crystal-field parameters B_{44}, B_{42}, B_{40}, B_{22}, and B_{20} are related to the band lengths R_1, R_2, and the angle α. They can be obtained from the expressions

$$B_{44} = B_{4-4} = \frac{-1}{4}\sqrt{\frac{25}{2}}(1+\cos 4\alpha)\frac{eq}{R_1^5}\langle r^4\rangle, \quad (10)$$

$$B_{42} = B_{4-2} = \frac{1}{2}\sqrt{\frac{5}{2}}(1+\cos 2\alpha)\frac{eq}{R_1^5}\langle r^4\rangle, \quad (11)$$

$$B_{40} = \frac{-1}{2}\left(\frac{3}{R_1^5} + \frac{4}{R_2^5}\right) eq\langle r^4\rangle, \quad (12)$$

$$B_{22} = B_{2-2} = -\sqrt{\frac{3}{2}}(1+\cos 2\alpha)\frac{eq}{R_1^3}\langle r^2\rangle, \quad (13)$$

$$B_{20} = -2\left(\frac{1}{R_2^3} + \frac{1}{R_2^3}\right) eq\langle r^2\rangle, \quad (14)$$

where q is the charge of the ligand, e the charge of the electron, and $\langle r^2\rangle$ and $\langle r^4\rangle$ are the expectation values in the crystal.

3. The D_{2h} Distortion Structure

Considering the average covalent factor N, the relations between the expectation values $\langle r^k\rangle$ in the crystal and $\langle r^k\rangle 0$ in the free ion are

$$\langle r^2\rangle = N^2\langle r^2\rangle 0, \quad \langle r^4\rangle = N^2\langle r^4\rangle 0, \quad (15)$$

and the relation between the spin-orbit coupling coefficient ζ_d in the crystal and ${\zeta_d}^0$ in the free ion is

$$\zeta_d = N^2 {\zeta_d}^0. \quad (16)$$

The expectation values $\langle r^k\rangle 0$ in a free Cu^{2+} ion are [14]

$$\langle r^2\rangle 0 = 3.11\, {a_0}^2, \quad \langle r^4\rangle 0 = 44.80\, {a_0}^4, \quad (17)$$

where a_0 is the Bohr radius. The spin-orbit coupling coefficient ${\zeta_d}^0$ in the free Cu^{2+} is [15]

$${\zeta_d}^0 = 829\ \text{cm}^{-1}. \quad (18)$$

Then the g factors can be calculated. From (10)–(14), the g factors depend on the band lengths R_1, R_2, and the angle α. When α is 90°, g_x and g_y are equal. When α is not 90°, the difference between g_x and g_y is not zero. Moreover, we can get the varying tendency of the g factors with the angle α, when the crystal field around Cu^{2+} is distorted from D_{4h} to D_{2h}. The results are shown in Figure 2.

Table 1. Comparison of the theoretical and experimental results ($\alpha = 62.6°$, $N = 0.98$)

g Factor	Calculated	Experimental
g_x	2.0519	2.068
g_y	2.0594	2.071
g_z	2.3772	2.374

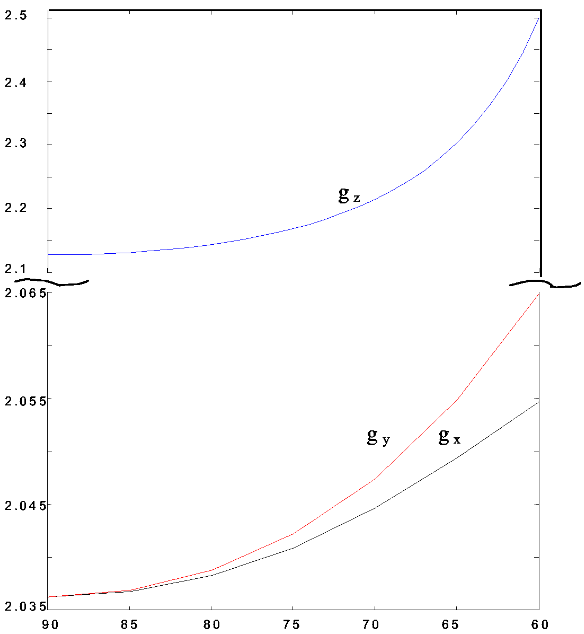

Fig. 2. Dependence of the components of the g factor on the angle α ($N = 0.98$).

As shown in Fig. 2, when the angle α decreases from 90°, g_z increases. At $\alpha = 90°$ i. e. when the field is D_{4h}, g_x and g_y are equal. When α decreases from 90°, g_x and g_y increase, whereby g_y increases more than g_x. According to the EPR experimental data, g_x and g_y are different. It shows that the crystal field around the center of the Cu^{2+} ion is D_{2h}. This confirms Taoufik's analysis [9]. From (4) – (6), the values of g_x, g_y, and g_z are related to the crystal structure data R_1, R_2, and α. Taking the angle α as the fitting parameter, we can fit the experimental values of the g factors ($g_z = 2.374$, $g_x = 2.068$, $g_y = 2.071$) [9]. The results are shown in Table 1. The theoretical values are very close to the experimental ones, when α is about 62.6°.

Thereby it is reasonable and satisfactory to explain the paramagnetic g factors of Cu^{2+} ions in $Cu_{0.5}Zr_2(PO_4)_3$ crystals. The crystal field around the central Cu^{2+} ion is D_{2h} indeed. From the EPR experiment, the angle α is about 62.6°.

4. Conclusion

In this paper, formulas for the calculation of the three g factors of $3d^9$ ions in an orthorhombic field D_{2h} have been given. They are related to the angle α and the band lengths R_1 and R_2 of the crystal structure. With these formulas, the tendency of the g factors to vary with the angle α has been explained for $Cu_{0.5}Zr_2(PO_4)_3$ crystal. The best fitting value of the angle α is 62.6°.

Acknowledgement

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