

Theoretical explanation of electron paramagnetic resonance and optical parameters for Cu^{2+} ion in LiNbO_3 crystal

S RAVI and P SUBRAMANIAN*

Department of Physics, Gandhigram Rural University, Gandhigram 624 302, India

*Corresponding author. E-mail: psmanian_gri@yahoo.com; sravi_phygri@yahoo.com

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Abstract. The EPR parameters, anisotropic g -factors g_x , g_y and g_z for Cu^{2+} ion and hyperfine structure constants A_x , A_y and A_z for Cu^{2+} in LiNbO_3 crystal are calculated by the method of diagonalizing the full Hamiltonian matrix. The crystal-field parameters contact with the crystal structure by the aid of the superposition model. The optical transition parameters are calculated using Zhao crystal-field model. The calculated results are in good agreement with the observed values. The results are discussed.

Keywords. Electron paramagnetic resonance; Cu^{2+} ; superposition model.

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1. Introduction

LiNbO_3 crystals have wide range of applications in non-linear optics, holograms, optical thin-film waveguides etc. [1–4]. LiNbO_3 doped with paramagnetic ions form interesting crystals for investigating ferroelectric behavior. Several workers reported electron paramagnetic resonance (EPR) studies on doped paramagnetic ions [5–10]. Optical absorption study of this type is important because of its application in optical devices. Kobayashi *et al* [11] reported EPR and optical studies of Cu^{2+} -doped LiNbO_3 crystal in 1979. The Cu^{2+} ion has the ability to take substitutionally the position of the lithium ion, niobium ion or at any interstitial site. The experimental report confirms that Cu^{2+} replaces Nb ion in LiNbO_3 . The hyperfine lines calculated for Nb site agreed well with the experimental values. In this paper, based on the superposition model, the anisotropic g -factors g_x , g_y and g_z for Cu^{2+} ion and the hyperfine structure constants A_x , A_y and A_z for $\text{Cu}^{2+} : \text{LiNbO}_3$ are calculated from the crystal-field theory. The results are discussed.

2. Calculations

LiNbO₃ belong to rhombohedral space group, with oxygen atoms arranged in planar sheets, forming octahedral network in ferroelectric phase [12]. Cu²⁺ ion replaces Nb⁵⁺ site in LiNbO₃ crystal, which was confirmed by Kobayashi *et al* [11]. Cu²⁺ has a 3d⁹ electronic configuration. The Hamiltonian for a transition-metal ion in the crystal under an external magnetic field can be written as

$$\bar{H} = \hat{H}_e + \hat{H}_{CF} + \hat{H}_{SO} + \hat{H}_z, \quad (1)$$

where \hat{H}_e is the electron–electron repulsion term, \hat{H}_{SO} is the spin-orbit coupling interaction and \hat{H}_{CF} is the crystal field Hamiltonian. \hat{H}_{SO} can be written as

$$\hat{H}_{SO} = \sum \zeta_d l_i s_i, \quad (2)$$

where ζ_d is the spin-orbit coupling constant. For free Cu²⁺, $\zeta_d = -830 \text{ cm}^{-1}$. For orthorhombic symmetry, the crystal-field interaction \hat{H}_{CF} can be expressed in the form of irreducible tensor operators C_k^q .

$$\begin{aligned} \hat{H}_{CF} = & B_{20}C_0^2 + B_{22}(C_2^2 + C_{-2}^2) + B_{40}C_0^4 + B_{42}(C_2^4 + C_{-2}^4) \\ & + B_{44}(C_4^4 + C_{-4}^4). \end{aligned} \quad (3)$$

The terms used in the above equation have their usual meaning [13], and finally \hat{H}_z can be written as $\hat{H}_z = g_J \mu_B \mathbf{H} \cdot \mathbf{J}$ [14]. The EPR spectra of Cu²⁺ in octahedral environment with spin S=1/2 can be expressed with the wave functions $|\varepsilon \pm \frac{1}{2}\rangle$ and the anisotropic g factor is written as

$$\begin{aligned} g_x &= 2 \left\langle \varepsilon, \frac{1}{2} \left| kL_x + g_e S_x \right| \varepsilon, -\frac{1}{2} \right\rangle, & g_y &= 2 \left\langle \varepsilon, \frac{1}{2} \left| kL_y + g_e S_y \right| \varepsilon, -\frac{1}{2} \right\rangle, \\ g_z &= 2 \left\langle \varepsilon, \frac{1}{2} \left| kL_z + g_e S_z \right| \varepsilon, -\frac{1}{2} \right\rangle, \end{aligned} \quad (4)$$

where $g_e = 2.0023$ (free electron g value), k is the orbital reduction factor and we take $k \approx 0.896$ here. The hyperfine constants A_x , A_y and A_z can be written as [15,16]

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

Cu²⁺ ion in LiNbO₃ crystal

$$A_z = P \left[-\kappa + \frac{2}{7}k(\alpha^2 - \beta^2) + (g_z - g_e) + \frac{1}{14} \left(\frac{3\alpha - \sqrt{3}\beta}{\alpha + \sqrt{3}\beta} \right) (g_x - g_e) + \frac{1}{14} \left(\frac{3\alpha + \sqrt{3}\beta}{\alpha - \sqrt{3}\beta} \right) (g_x - g_e) \right], \quad (5)$$

where κ is the core polarization constant. We take $\kappa \approx 0.29$, which is very close for $3d^n$ ion (0.3) in crystals [17]. P is the dipolar hyperfine parameter for Cu^{2+} in the crystal and $P_0 = 0.036 \text{ cm}^{-1}$ for free Cu^{2+} . ($P = kP_0 = 0.032256$), α and β are mixing coefficients for $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ orbitals and can be determined using normalizing condition $\alpha^2 + \beta^2 = 1$ [15,16] and $\alpha = 0.7317$, $\beta = 0.2683$ for this system. The crystal-field parameter B_{kq} in eq. (3) can be expressed as

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

where t_k is the power-law exponent and $\bar{A}_k(R_0)$ is the intrinsic parameter with reference distance R_0 . Usually, $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of the bonds [18]. The coordination factor $K_k^q(\theta_j, \phi_j)$ can be obtained from the local structural parameters of the studied system [19].

Substituting all the parameters in the above formulas and diagonalizing the complete energy matrix using Fortran language, the anisotropic g factor for Cu^{2+} ion and hyperfine structure constants A in LiNbO_3 are obtained. The comparisons between experimental and calculated values are presented in table 1.

Following the point charge-dipole model containing an average covalence, the crystal-field parameter is given by [20,21].

$$D_q = -\frac{eq}{42} \left[3 \left(1 + \frac{5\mu_{\perp}}{qR_{\perp}} \right) / R_{\perp}^5 + 4 \left(1 + \frac{5\mu_{\parallel}}{qR_{\parallel}} \right) / R_{\parallel}^5 \right] \langle r^4 \rangle_0 N^2, \quad (7)$$

where q and μ denote the effective charge and electric dipole moment of ligand ion. Here we consider $q \approx e$. N is the average covalent reduction factor (as k in eq. (4)), R is the bond length of $\text{Cu}^{2+}-\text{O}^{2-}$ and $\langle r^n \rangle_0$ is the expectation value of r^n . $\mu_{\perp}, \mu_{\parallel}$ and R_{\perp}, R_{\parallel} are dipole and metal ligand distances respectively (0° or 180° for \parallel and 90° for \perp). Here we use $R_{\parallel} = 1.98 \text{ \AA}$ and $R_{\perp} = 1.9485 \text{ \AA}$ [22]. We take $\mu_{\parallel} = \mu_{\perp} \approx 0.0322$ for calculation. Using the above values, D_q is calculated as 650 cm^{-1} which is very close to the experimental value 600 cm^{-1} .

Table 1. EPR g factor and hyperfine tensor A for $\text{Cu}^{2+} : \text{LiNbO}_3$.

	g_x	g_y	g_z	A_x (10^{-4} cm)	A_y (10^{-4} cm)	A_z (10^{-4} cm)	D_q (cm^{-1})
Cal.	2.0775 (± 0.005)	2.1058 (± 0.005)	2.3807 (± 0.005)	51.22 (± 5)	32.11 (± 5)	78.12 (± 5)	650 (± 25)
Exp. [11]	2.076	2.106	2.381	50.53	30.24	77.97	600

3. Discussions

From table 1, one can observe that the calculated EPR parameters, g factors g_x , g_y , g_z and hyperfine constants A_x , A_y , A_z are in very close agreement with the experimental values as in ref. [11]. This suggests that full Hamiltonian matrix diagonalization is very suitable for determining EPR parameters for Cu^{2+} ion in LiNbO_3 crystals. The minor discrepancy occurred in A factor may be due to the mixing coefficients and polarization constant values. Zhao crystal-field model suits the calculation of the crystal-field parameter D_q with a difference of only 50 cm^{-1} between the experimental and calculated values.

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