

SPIN-HAMILTONIAN PARAMETERS FOR CrLi^{3+} DOPED IN LiNbO_3

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Abstract

By using crystal field theory, the spin-Hamiltonian parameters [zero-field splitting D , the gyromagnetic factors g (g_{\parallel} and g_{\perp}) and the first excited state splitting $\delta(^2E)$] for the CrLi^{3+} doped in LiNbO_3 have been calculated from the higher-order perturbation formulas. The method used is based on the two-spin-orbit coupling parameter model, in a cluster approach. The g parameters were also calculated as a second derivative of the energy, method implemented into ORCA computer program. The results were discussed and good agreement with experimental data was demonstrated.

1. Introduction

Electron paramagnetic resonance (EPR) is a powerful technique to study the local structure and electronic properties of paramagnetic impurity ions in crystals and analyze the local structure around an impurity ion. The EPR spectra of $\text{Cr}^{3+}:\text{LiNbO}_3$ have been extensively studied and they show intense axial EPR spectra attributed to Cr^{3+} ions substituting for Li or Nb ions [1-9]. Up to now, however, these useful experimental results, especially those concerning the spin Hamiltonian parameters (zero-field splitting D and g factors g_{\parallel} and g_{\perp}) and the first excited state splitting $\delta(^2E)$ for the CrLi^{3+} doped LiNbO_3 have had no satisfactory theoretical interpretation.

In this paper we calculated the g factors, zero-field splitting D and $\delta(^2E)$ from the perturbation formulas based on the two-spin-orbit coupling parameter model in a cluster approach, in trigonal symmetry for $\text{CrLi}^{3+}:\text{LiNbO}_3$ crystal. In this model the contributions due to

the spin-orbit coupling coefficient of the central $\text{Cr}_{\text{Li}}^{3+}$ ion and that of O^{2-} ligands are both taken into account. The crystal field parameter Dq , the Racah parameters B , C , and the trigonal crystal field parameters ν and ν' are taken from optical spectra data. The Macfarlane's high order perturbation formulas were used.

2. Theory

It is well known that for Cr^{3+} ($3d^3$ configuration) ions the orbital singlet ground state 4A_2 (4F) splits, in trigonal symmetry, into two Kramers doublets, separated by an interval $2D = [{}^4A_2(2\bar{A}) - {}^4A_2(\bar{E})]$, whereas the first excited state 2E (2G) splits into two levels separated by an interval $\delta({}^2E) = 2E(\bar{E}) - {}^2E(2\bar{A})$.

We consider the full Hamiltonian of a $3d^3$ transition-metal ion in crystal as [10]

$$H = H_{ee}(B, C) + H_{SO}(\xi, \xi') + H_{tri}(\nu, \nu') + H_{CF}(B_{kq}) + H_z \quad (1)$$

where $H_{ee}(B, C)$, $H_{SO}(\xi, \xi')$, $H_{tri}(\nu, \nu')$ represent, respectively, the Coulomb interactions (expressed in terms of the Racah parameters B and C), the spin-orbit coupling (with the spin-orbit coupling parameter ξ for an impurity ion and ξ' for the ligands), the trigonal distortion of octahedral site of $3d^3$ ion (ν and ν' are the net trigonal crystal field parameters). H_z is the Zeeman Hamiltonian.

The crystal-field Hamiltonian H_{CF} depends on the crystal field parameters (CFP) B_{kq} , and in Wybourne notation, for a trigonal symmetry is given as [10]

$$H_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{43}C_3^{(4)} + B_{4-3}C_{-3}^{(4)} \quad (2)$$

where B_{kq} are the CFP and $C_q^{(k)} = [4\pi/(2k+1)]^{1/2} Y_{kq}$ are the spherical operators expressed in terms of the spherical harmonics Y_{kq} . For a C_3 symmetry the B_{20} and B_{40} parameters are always real, whereas the B_{43} and B_{4-3} parameters are complex. For $\text{Cr}_{\text{Li}}^{3+}$ sites with the C_3 site symmetry in $\text{LiNbO}_3:\text{Cr}_{\text{Li}}^{3+}$, we have [11] $|\text{Im}(B_{43})|/|\text{Re}(B_{43})| = \text{tg } 3\varphi \approx 0.18$, using $\varphi = 3^\circ 49'$ [12], where φ is the angle of rotation of the upper and lower oxygen triangles in the octahedron composed of six oxygen ions. In this case we approximately can neglect the imaginary part of B_{43} and take $|B_{43}| \approx |\text{Re}(B_{43})| = |\text{Re}(B_{4-3})|$, which justifies the assumption of nearly C_{3v} symmetry

for the octahedral CrLi^{3+} sites used below. The last term in the Hamiltonian (1) is the Zeeman term, and for the ${}^4\text{A}_2$ ground state of Cr^{3+} in trigonal symmetry is given as [13]

$$H_z = D \left(S_z^2 - \frac{1}{3} S(S+1) \right) + \beta g_{\parallel} H_z S_z + \beta g_{\perp} (H_x S_x + H_y S_y) \quad (3)$$

with the symbols appearing in Eq.(3) having their usual meaning .

From a molecular orbital (MO) model for octahedral $3d^n$ cluster in crystals, the one-electron basis functions can be expressed as [14-16]

$$|\gamma\rangle = N_{\gamma}^{1/2} \left(|d_{\gamma}\rangle - \lambda_{\gamma} |p_{\gamma}\rangle \right) \quad (4)$$

where $\gamma = t_{2g}, e_g$ denotes the irreducible representations of the O_h point group. $|d_{\gamma}\rangle$ and $|p_{\gamma}\rangle$ are, respectively, the d orbitals of the central $3d^n$ ion and the p orbitals of the ligands. The MO coefficients N_{γ} and λ_{γ} are the normalization factors and the orbital mixing coefficients, which can be determined from the approximate relations [14-16]

$$f_{\gamma} = N_{\gamma}^2 \left[1 + \lambda_{\gamma}^2 S_{dp}(\gamma) - 2\lambda_{\gamma} S_{dp}(\gamma) \right], \quad (5)$$

and the normalization conditions

$$N_{\gamma} \left[1 - 2\lambda_{\gamma} S_{dp}(\gamma) + \lambda_{\gamma}^2 \right] = 1 \quad (6)$$

where $S_{dp}(\gamma)$ are the group overlap integrals. The covalence parameter $f_{\gamma} \approx \frac{1}{2} \left[\frac{B}{B_0} + \frac{C}{C_0} \right]$ is expressed in term of ratios of the Racah parameters for a $3d^n$ ion in a crystal to those (having the “0” subscript) of a free ion.

According to the cluster approach [14-16], the SO coupling coefficients ξ , ξ' , the orbital reduction factors k , k' for the octahedral $3d^n$ clusters can be expressed as

$$\begin{aligned} \xi &= N_i \left(\xi_d^0 + \lambda_i^2 \xi_p^0 / 2 \right) \\ \xi' &= (N_i N_l)^{1/2} \left(\xi_d^0 - \lambda_i \lambda_l \xi_p^0 / 2 \right) \\ k &= N_i \left(1 + \lambda_i^2 / 2 \right) \\ k' &= (N_i N_l)^{1/2} \left(1 - \lambda_i \lambda_l / 2 \right) \end{aligned} \quad (7)$$

where ξ_d^0 and ξ_p^0 are the SO coupling coefficient of d electrons of a free $3d^n$ ion and that of p electrons of a free ligand ion, respectively. From the basis function and by use of the Macfarlane’s perturbation – loop method [17, 18], the high-order perturbation formulas of EPR

parameters based on the two spin-orbit coupling parameter models for $3d^3$ ions in trigonal symmetry are as follows [14-16,19]

$$D = \frac{2}{9} \xi'^2 v \left(\frac{1}{D_1^2} - \frac{1}{D_3^2} \right) - \sqrt{2} \xi \xi' v' \left(\frac{2}{3D_1 D_4} + \frac{1}{D_2 D_3} + \frac{1}{3D_3 D_4} + \frac{1}{D_2 D_4} + \frac{4\sqrt{2}B}{D_1 D_4 D_5} \right) - \sqrt{2} \xi'^2 B v' \left(\frac{4B}{D_3 D_4 D_5} + \frac{9B}{2D_2^2 D_3} \right) \quad (8)$$

$$g_{\parallel} = g_s - \frac{8\xi'k'}{3D_1} - \frac{2\xi'}{9D_1^2} (2k'\xi - k\xi' + 2g_s\xi') + \frac{4\xi'^2}{9D_3^2} (k - 2g_s) - \frac{2\xi^2}{3D_2^2} (k + g_s) - \frac{4\xi\xi'k'}{3D_1 D_2} + \frac{4\xi\xi'k'}{9D_1 D_3} + \frac{4\xi\xi'k'}{3D_2 D_3} + \frac{8\xi'k'}{9D_1^2} v - \frac{4\sqrt{2}}{3D_1 D_4} (k'\xi + k\xi') v' \quad (9)$$

$$g_{\perp} = g_{\parallel} - \frac{4\xi'k'}{3D_1^2} v + \frac{4\sqrt{2}}{3D_1 D_4} (2k\xi' + k'\xi) v' \quad (10)$$

$$\delta(^2E) = -\frac{4\xi v}{3D_7} - \frac{16B\xi'v}{D_7 D_{12}} + \frac{4Bv\xi'}{D_7 D_{13}} - \frac{16Bv\xi'}{D_{10} D_{12}} + \frac{4Bv\xi'}{D_{10} D_{13}} + \frac{8\sqrt{6}B\xi v'}{D_7 D_{12}} - \frac{2\sqrt{6}B\xi v'}{D_7 D_{13}} + \frac{8\sqrt{2}B\xi v'}{D_8 D_{12}} - \frac{2\sqrt{2}B\xi v'}{D_8 D_{13}} \quad (11)$$

where D_i ($i=1-13$) are the zero order energy denominators defined in [17,18]. v and v' are the trigonal field parameters and B and C are the Racah parameters, g_s (≈ 2.0023) is the g factor of a free $3d$ ion.

3. Results

3.1 Perturbation Theory

Now we apply the above formulas to estimate the D , g and $\delta(^2E)$ values for CrLi^{3+} in LiNbO_3 crystals. The group overlap integral $S_{ap}(\gamma)$ can be calculated from the Slater – type SCF functions [20] and the impurity – ligand distance R . Since the masses, charges, and ionic radii of the impurity ion and replaced host ion are different, the mutual interaction between the impurity ion and surrounding O^{2-} ions in doped crystals must differ from that between the replaced ion and surrounding ions in host crystals. Also, the impurity-ligand distances R in the doped crystal would be unlike the host values R_H in the pure host. Usually, strictly theoretical determination of impurity-ligand distance in crystals may be difficult. However, the studies based on the experimental super-hyperfine constant, EXAFS measurements and crystal-field analysis have suggested that the empirical formula [21-23] $R \approx R_H + (r_i - r_h)/2$, where R_H is the metal – ligand

distance in the host matrix, r_i is the ionic radius for the impurity Cr^{3+} , and r_h is the radius of the replaced ion in host crystal, is approximately valid for impurity ions in crystals. For $\text{LiNbO}_3:\text{Cr}_{\text{Li}}^{3+}$ we have [12] two different distances between Li ion and two triangles of oxygen ions: upper and lower triangles [11]. The distance between Li and upper oxygen triangle ions R_{H1} is 2.238 Å and the same distance for the lower oxygen triangle R_{H2} is 2.068 Å [24]. Also, $r(\text{Cr}^{3+}) = 0.63\text{Å}$ [25] and $r(\text{Li}^{1+}) = 0.68\text{Å}$ [25], so that we have $R_1 = 2.188\text{Å}$, $R_2 = 2.018\text{Å}$. From the Slater – type SCF wave function and the distances R , the group overlap integrals $S_{dp}(\gamma)$ for the considered system are calculated and shown above.

The Racah parameters B , C , the cubic field parameter Dq and the trigonal parameters ν and ν' , obtained from optical spectra of the crystal under study [6] are given below: $Dq = 1532\text{ cm}^{-1}$, $B = 550\text{ cm}^{-1}$, $C = 2910\text{ cm}^{-1}$, $\nu = -1400\text{ cm}^{-1}$, $\nu' = 700\text{ cm}^{-1}$. By using the free ion values $B_0 = 1030\text{ cm}^{-1}$, $C_0 = 3850\text{ cm}^{-1}$ [26] for Cr^{3+} , the covalence parameter is estimated to be $f_\gamma \approx 0.6449$. The MO coefficients N_γ and λ_γ are obtained from (5-6) and given in Table 1.

Table1. Group overlap integrals, MO coefficients, orbital reduction factors, SO coupling coefficients (in cm^{-1}) for $\text{Cr}_{\text{Li}}^{3+}:\text{LiNbO}_3$ crystal

$S_{dp}(e_g)$	$S_{dp}(t_{2g})$	N_t	N_e	λ_t	λ_e	k	k'	ξ	ξ'
0.0985	0.0336	0.8170	0.8476	0.5080	0.5337	0.9224	0.9449	255	210

From the free ion values $\xi_d^0(\text{Cr}^{3+}) \approx 273\text{ cm}^{-1}$ [26] and $\xi'(\text{O}^{2-}) \approx 151\text{ cm}^{-1}$ [25], the parameters k , k' , ξ , ξ' , are calculated from Eqs. (7); they are also shown in Table 2. Using the Eqs.(8)-(11) and the above-given results we obtain the EPR parameters (zero-field splitting D , g - factors g_{\parallel} , g_{\perp}) and first excited state splitting of $\text{Cr}_{\text{Li}}^{3+}$ doped in LiNbO_3 . The obtained in these way EPR parameters are shown in Table 2.

3.2 *Ab initio* calculation of g factors

It is well known [27] that the EPR g -tensor is a property that can be calculated as a second derivative of the energy and it is implemented as such into ORCA [28] for the SCF methods such as Hartree - Fock (HF) and Differential Functional Theory (DFT). At the SCF level four contributions arise:

$$\begin{aligned}
g_{\mu\nu}^{(SZ)} &= \delta_{\mu\nu} g_s \\
g_{\mu\nu}^{(RMC)} &= -\frac{\alpha^2}{S} \sum_{h,l} P_{hl}^{\alpha-\beta} \langle \Phi_h | \hat{T} | \Phi_l \rangle \\
g_{\mu\nu}^{(DSO)} &= \frac{1}{2S} \sum_{h,l} P_{hl}^{\alpha-\beta} \langle \Phi_k | \sum_A \xi(r_A) [r_A r_O - r_{A,\mu} r_{O,\nu}] | \Phi_l \rangle \\
g_{\mu\nu}^{(PSO)} &= \sum_{h,l} \frac{\partial P_{kl}^{\alpha-\beta}}{\partial B_\mu} \langle \Phi_k | h_\nu^{SOC} | \Phi_h \rangle
\end{aligned} \tag{12}$$

Here, g_e is the free e -electron g_s -value ($=2.002319..$), S is the total spin, α is the fine structure constant, $P^{\alpha-\beta}$ is the spin density matrix, $\{\Phi\}$ is the basis set, \hat{T} is the kinetic energy operator, $\xi(r_A)$ an approximate radial operator, h^{SOC} the spatial part of an effective one-electron spin-orbit operator and B_μ is a component of the magnetic field. The derivative of the spin-density matrix is calculated from coupled π -perturbed SCF theory with respect to a magnetic field perturbation (orbital Zeeman term). Our calculation utilizes the Ahlrichs - VDZ basis [29] and the Ahlrichs auxiliary basis sets obtained from the TurboMole [30, 31]. The results, obtained with ORCA 2.8 computer program are also, given in Table 2.

Table 2. EPR parameters (zero-field splitting D , g - factors g_{\parallel} , g_{\perp} , Δg and $\delta^2(E)$) of $\text{Cr}_{\text{Li}}^{3+}$ doped LiNbO_3 crystal

	$D(\text{cm}^{-1})$	g_{\parallel}	g_{\perp}	Δg	g	$\delta^2(E)(\text{cm}^{-1})$
Calculated <i>a</i>	-0.356	1.9687	1.9721	-0.003450	1.970	59.53
Calculated <i>b</i>	-0.388	1.9644	1.9686	-0.004048	1.967	64.96
Calculated <i>c</i>	-	1.9887	1.9644	-0.024347	1.972	-

a- calculated by taking into account the spin-orbit for interaction of chromium ion and neglecting the spin-orbit interaction for ligands. It was done by using the above given equations with dropping the ligand' spin-orbit interaction.

b- calculated by taking into account the spin-orbit interactions for both chromium ion and ligands;

c- calculated by using DF method implemented in ORCA computer program.

Comparison these results with the experimental ones, $|D| = 0.393$ and $g = 1.957$ [32] and $D = 0.396$ and $g = 1.969$, [33] shows satisfactory agreement between the experimental values and theoretical calculations including the spin-orbit interaction for both chromium ion and

oxygen ligands in $\text{Cr}_{\text{Li}}^{3+}:\text{LiNbO}_3$, and DFT method. The negative sign in front of the zero-field splitting D means that trigonal deformation of the oxygen ions around chromium impurity is a contraction of the octahedron along the C_3 axis.

4. Conclusions

In the present work we reported on the detailed calculations of the spin Hamiltonian parameters for $\text{Cr}_{\text{Li}}^{3+}$ in LiNbO_3 . In addition, we have applied the two spin-orbit coupling model (the admixture of the spin-orbit coupling parameters between the d electrons of the central $3d^n$ ion and the p electrons of the ligands), via the covalence effects, to calculate the EPR parameters D , g_{\parallel} , g_{\perp} , and first excited state splitting of $\text{Cr}_{\text{Li}}^{3+}$ doped in LiNbO_3 . From the above calculations, it was demonstrated that this model gives satisfactory agreement with experimental data. The two-spin-orbit coupling coefficient formulas are more accurate than the conventional single-spin-orbit coupling coefficient formulas in theoretical studies of the EPR parameters. The small shift of g and quasi-isotropic g factors reveal the quasi-octahedral symmetry of the Cr^{3+} center in the title crystal. The EPR experimental data, are satisfactory explain using two-spin model of spin-orbit coupling.

DFT based calculations of g -factors, using ORCA computer program, gave the results according that from perturbation theory and close to experimental data.

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