Defect Structure of Co^{2+} Center in α-$LiIO_3$ Crystal

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In this paper we establish the formulas of EPR g factors $g_{\|}$, $g_{\perp}$ for $3d^7$ ions in trigonal octahedral crystals from a cluster approach. In these formulas, the contributions from configuration interaction- and covalency-effects are considered. The parameters related to both effects can be determined from the optical spectra and the structural parameters of the studied crystal. With these formulas, the defect structure of a Co^{2+} center in α-$LiIO_3$ crystal is studied. It is found that, to reach good fits between the calculated and observed $g_{\|}$, $g_{\perp}$, the O^{2-} ions between Co^{2+} and Li^+ vacancy (V_{Li}) should shift away from the V_{Li} by about 0.49 Å. The displacement direction is consistent with those obtained for Cr^{3+}, Fe^{3+}, and Mn^{2+} centers in α-$LiIO_3$ crystals as well as with the expectation based on the electrostatic interaction model.

Key words: Electron Paramagnetic Resonance (EPR); Crystal-field Theory; Defect Structure; Co^{2+}; α-$LiIO_3$ Crystal.

1. Introduction

α-$LiIO_3$ single crystals are of great practical importance in electronics, acoustooptics and nonlinear optics [1–4]. Transition metal (TM) impurities placed in the crystal can affect its optical properties and photorefractive effects [5]. In order to fully understand the role of TM impurity ions, knowledge of the nature and defect structure of these impurity centers is important. Radio-frequency discrete saturation (RFDS), ENDOR and EPR studies [6–11] suggest that TM ions replace Li^+ ions in α-$LiIO_3$ and the excess charge compensation is performed by two nearest Li^+ vacancies (V_{Li}) along the C_3-axis for trivalent TM ions, or by one nearest V_{Li} for divalent TM ions. Since the effective charge of V_{Li} is negative, the TM ions (only in the case of divalent ions), the Li^+ and O^{2-} ions in the vicinity of V_{Li} should be displaced owing to the electrostatic interactions between these ions and V_{Li}, and so the local (or defect) structure of the impurity center is considerably different from that in the pure crystal. The local structures of Cr^{3+}, Fe^{3+}, and Mn^{2+} centers in α-$LiIO_3$ were obtained by studying the RFDS, ENDOR and ERP data [6–10]. For a Co^{2+} center in α-$LiIO_3$, although the local shifts of Co^{2+} and those of the nearest and next-nearest Li^+ ions were obtained by studying the RFDS data [11], the local shifts of O^{2-} ions between Co^{2+} and V_{Li} have not been studied by analyzing the EPR g factors. The reason may be the lack of the effective calculation formulas of $g_{\|}$ and $g_{\perp}$ related to the structural parameters for $3d^7$ ions in trigonal octahedral crystals. In this paper, we first establish the perturbation formulas of $g_{\|}$ and $g_{\perp}$ for $3d^7$ ions in trigonal symmetry from a cluster approach. In these formulas, the role of configuration interaction (CI)- and covalency (CO)-effects is considered and the parameters related to both effects can be obtained from the optical spectra and the structural parameters of the studied system. Based on these formulas, the EPR parameters $g_{\|}$ and $g_{\perp}$ for a Co^{2+} center in α-$LiIO_3$ crystal are reasonable explained by considering suitable shifts of O^{2-} ions between the Co^{2+} and V_{Li}, and the local structure of the CoO_6 group in α-$LiIO_3$ is therefore determined.

2. Relevant Formulas

From a molecular orbital model for $3d^n$ octahedral clusters in crystals, the one-electron basis functions can be expressed as [12, 13]

$$|\gamma> = N_\gamma^{1/2} (|d_\gamma> - \lambda_\gamma |p_\gamma>), \tag{1}$$

where $\gamma = t_{2g}$ and e_g are the irreducible representations of the O_h group. $|d_\gamma>$ and $|p_\gamma>$ are the d orbital of the $3d^n$ ion and the p orbital of ligands, respectively. N_γ and λ_γ are the normalization and mixing coefficients. From (1), the spin-orbit coupling coefficients ζ, ζ'

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and the orbital reduction factors k, k' can be written [12, 13]

$$\zeta = N_t\,(\zeta_d^0 + \lambda_t^2\,\zeta_p^0/2)\,, \quad \zeta' = (N_t\,N_e)^{1/2}\,(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2)\,,$$
$$k = N_t\,(1 + \lambda_t^2/2)\,, \qquad k = (N_t\,N_e)^{1/2}\,(1 - \lambda_t\lambda_e/2)\,, \quad (2)$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficient of the d electron of the $3d^n$ ion and that of the p electron of the ligand in free ions. N_γ and λ_γ can be determined by a semiempirical LCAO method [12, 13] which yields the approximate relation

$$f_\gamma = N_\gamma^2\,[1 + \lambda_\gamma^2\,S_{dp}^2(\gamma) - 2\lambda_\gamma\,S_{dp}(\gamma)] \qquad (3)$$

and the normalization correlation

$$N_\gamma\,(1 - 2\lambda_\gamma\,S_{dp}(\gamma) + \lambda_\gamma^2) = 1\,, \qquad (4)$$

where $S_{dp}(\gamma)$ are the group overlap integrals which can be calculated from Slater-type SCF functions. f_γ [$\approx (B/B_0 + C/C_0/2]$ is the ratio of the Racah parameters for a $3d^n$ ion in a crystal to those of a free ion. Thus, the parameters N_γ and λ_γ and hence those in (2) can be calculated from the optical spectrum of the studied crystal.

Similar to a $3d^7$ ion in tetragonal symmetry [14], the Hamiltonian for a $3d^7$ ion in trigonal octahedral symmetry can be written as

$$\begin{aligned} H &= H_0 + H'\,, \\ H_0 &= H_{Coul}\,(B, C) + V_{crys}{}^a(D_q, V, V')\,, \\ H' &= H_z(k, k', \alpha, \alpha') + H_{SO}(\zeta, \zeta') \\ &\quad + V_{crys}{}^b(D_q, V, V')\,, \end{aligned} \qquad (5)$$

where H_{Coul} is the Coulomb repulsion interaction. $V_{crys}{}^a$ and $V_{crys}{}^b$ are, respectively, diagonal and off-diagonal parts of crystal field with the cubic field parameter D_q and trigonal field parameters V and V'. H_z is the Zeeman term with the effective Landé factors α and α' in the axial and perpendicular directions. H_{SO} is the spin-orbit coupling term. Thus, the second-order perturbation formulas of $g_\parallel$ and $g_\perp$ for $3d^7$ ions in trigonal symmetry can be derived by the perturbation method as

$$g_\parallel = 2 + \frac{4(k\alpha + 2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right] + 2\left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right]\nu_1 + \left(\frac{\alpha}{\alpha'}\right)\left[\left(\frac{\alpha}{\alpha'}\right)\nu_2 - 2\left(\frac{3}{x} - \frac{4}{(x+2)^2}\right)\nu_3\right]}{\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right]}\,,$$

$$g_\perp = \frac{4\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{2k\alpha}{x+2} + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha'}\right)^2 \nu_4 + \frac{8}{(x+2)^2}\nu_5 + \frac{12}{x(x+2)}\nu_6 - \left(\frac{\alpha}{\alpha'}\right)\frac{4}{(x+2)}\nu_7}{\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right]}\,, \qquad (6)$$

where x can be calculated from the energy splitting $\Delta\,(= E\,\{^4A_2\,[^4T_1(F)]\} - E\,\{^4E\,[^4T_1(F)]\})$ of the $^4T_1$ ground orbital state in the trigonal crystal field by using the expression

$$\Delta = \frac{\zeta\alpha'^2}{3\alpha}\left[\frac{3}{x} + \frac{4}{x+2}\right] - \frac{\zeta\alpha}{6}(x+3)\,. \qquad (7)$$

The parameters ν_i are defined as

$$\nu_1 = \frac{k'\zeta'}{3}\left[\frac{15 f_1^2}{2E_{1X}} + \frac{2q_1^2}{E_{2X}}\right], \quad \nu_2 = \frac{10\,k'\zeta'\,f_4^2}{3E_{2Z}}\,,$$
$$\nu_3 = \frac{k'\zeta'}{3}\left[\frac{5 f_1 f_2}{2E_{2X}} + \frac{5 f_3 f_4}{E_{2Z}} + \frac{2q_1 q_2}{E_{1X}}\right],$$
$$\nu_4 = \frac{k'\zeta'}{3}\left[\frac{5 f_2^2}{E_{2X}} + \frac{4q_2^2}{E_{1X}}\right],$$
$$\nu_5 = \frac{k'\zeta'}{3}\left[\frac{5 f_3^2}{E_{2Z}} + \frac{4q_3^2}{E_3} + \frac{4q_4^2}{E_{1Z}}\right],$$
$$\nu_6 = \frac{k'\zeta'}{3}\left[\frac{5 f_5^2}{E_{2X}} + \frac{5 f_3^2}{E_{2Z}} + \frac{2q_3^2}{E_3} + \frac{2q_4^2}{E_{1Z}}\right],$$
$$\nu_7 = \frac{k'\zeta'}{3}\left[\frac{5 f_1 f_2}{E_{2X}} + \frac{5 f_3 f_4}{E_{2Z}} + \frac{q_1 q_2}{E_{1X}}\right], \qquad (8)$$

where the energy denominators $E_{1X}, E_{1Z}, E_{2X}, E_{2Z}$ and E_3 and the separation Δ can be obtained from the d-d transition energy matrices of the $3d^7$ ion in trigonal symmetry.

The parameters f_i, q_i α and α' can be calculated by considering the admixture of the ground and excited states via the CI effect by means of Coulomb repulsion and crystal field interaction. Thus, from the perturbation method, we obtain

$$f_1 = -\,\varepsilon\varepsilon''\left[1 + \left(\frac{\varrho}{\varepsilon}\right)^2\right],$$

$$f_2 = \varepsilon''\varepsilon\left[-1 + \frac{4}{\sqrt{5}}\frac{\sigma}{\varepsilon'} - \frac{2}{\sqrt{5}}\frac{\tau'\tau''}{\varepsilon'\varepsilon''} + \frac{3}{\sqrt{5}}\frac{\varrho}{\varepsilon}\right],$$

$$f_3 = \varepsilon\left[-1+\frac{1}{\sqrt{5}}\frac{\varrho}{\varepsilon}\right],$$

$$f_4 = \varepsilon'\left[1+\frac{2}{\sqrt{5}}\frac{\sigma}{\varepsilon'}\right],$$

$$f_5 = -\varepsilon\varepsilon''\left[1+\frac{4}{\sqrt{5}}\frac{\varrho}{\varepsilon}-\frac{2}{\sqrt{5}}\frac{\tau'\tau''}{\varepsilon'\varepsilon''}-\left(\frac{\varrho}{\varepsilon}\right)^2\right],$$

$$q_1 = \varepsilon N_{1X}\left[-\frac{5}{2}\frac{\tau'}{\varepsilon'}+\frac{\sqrt{5}}{2}\frac{\varrho}{\varepsilon}\frac{\tau}{\varepsilon}\right],$$

$$q_2 = \varepsilon' N_{1X}\left[\frac{\tau'}{\varepsilon'}+\frac{3}{2}\frac{\tau}{\varepsilon}+\frac{2\sigma\tau''}{\varepsilon'\varepsilon''}+\frac{\sqrt{5}}{2}\frac{\tau''}{\varepsilon''}\right],$$

$$q_3 = \varepsilon N_2\left[\frac{2\varrho}{\varepsilon}+\frac{3\sigma}{2\varepsilon'}+\frac{\tau\sigma}{\varepsilon N_{1Z}}+\frac{\sqrt{5}}{2}\frac{\sigma\varrho}{\varepsilon\varepsilon'}\right],$$

$$q_4 = \varepsilon N_{1Z}\left[\frac{\tau}{\varepsilon}+\frac{3\tau'}{2\varepsilon'}-\frac{2\varrho\sigma}{\varepsilon N_{1Z}}+\frac{\sqrt{5}}{2}\frac{\varrho\tau'}{\varepsilon\varepsilon'}\right],$$

$$\alpha = \frac{3}{2}\varepsilon^2-\sqrt{5}\,\varepsilon\varrho+\frac{1}{2}\varrho^2-\tau^2,$$

$$\alpha' = \frac{3}{2}\varepsilon\varepsilon'-\frac{\sqrt{5}}{2}\varepsilon'\varrho+2\varrho\sigma-\tau\tau', \tag{9}$$

where ε^i, τ^i, σ^i, ϱ and N_{ij} are the above admixture (or CI) coefficients. Thus, we have the normalization relationships

$$\begin{aligned}
&\varepsilon^2+\tau^2+\varrho^2 = 1,\\
&\varepsilon'\,[1+(\tau'/\varepsilon')^2+(\sigma/\varepsilon')^2]^{1/2} = 1,\\
&\varepsilon''\,[1+(\tau''/\varepsilon'')^2+(\varrho/\varepsilon)^2]^{1/2} = 1,\\
&N_{1X}\,[1+(\tau''/\varepsilon'')^2+(\tau/\varepsilon)^2]^{1/2} = 1,\\
&N_{1Z}\,[1+(\tau'/\varepsilon')^2+(\sigma/N_{1Z})^2]^{1/2} = 1,\\
&N_2\,[1+(\sigma'/N_{1Z})^2+(\sigma/\varepsilon')^2]^{1/2} = 1.
\end{aligned} \tag{10}$$

From a modified perturbation procedure [15] and the d-d transition energy matrices of the $3d^7$ ion in trigonal symmetry we obtain

$$\frac{\tau}{\varepsilon} \approx \frac{-40\,D_q+(2V-\sqrt{2}\,V')}{-60\,D_q+(150\,B+3V+11\sqrt{2}\,V')},$$

$$\frac{\varrho}{\varepsilon} \approx \frac{\sqrt{5}\,V+2\sqrt{10}\,V'}{-80\,D_q+4V+8\sqrt{2}\,V'},$$

$$\frac{\tau'}{\varepsilon'} \approx \frac{-40\,D_q+8\sqrt{2}\,V'}{-60\,D_q+150\,B-13\sqrt{2}\,V'},$$

$$\frac{\tau''}{\varepsilon''} \approx \frac{2\sqrt{5}\,V'-\sqrt{10}\,V'}{-20\,D_q+150\,B-V+3\sqrt{2}\,V'},$$

$$\frac{\sigma}{\varepsilon'} \approx \frac{2\sqrt{10}\,V'}{-180\,D_q+\sqrt{2}\,V'},$$

$$\frac{\sigma'}{N_{1Z}} \approx \frac{4\sqrt{10}\,V'}{-120\,D_q+150\,B+14\sqrt{2}\,V'}, \tag{11}$$

Thus, if the optical spectral parameters B, C, D_q, V and V' (note: the trigonal field parameters V and V' are often estimated from the structural parameters because it is difficult to measure them exactly) are obtained for the studied crystal, all of the parameters in the formulas of $g_{\parallel}$ and $g_{\perp}$ can be determined, and so the parameters $g_{\parallel}$ and $g_{\perp}$ can be calculated.

3. Calculations for α-$LiIO_3$:Co^{2+}

From the optical spectra of α-$LiIO_3$:Co^{2+} [16], we obtain the optical spectral parameters

$$D_q \approx -797\ \mathrm{cm}^{-1},\ B \approx 800\ \mathrm{cm}^{-1},\ C \approx 3550\ \mathrm{cm}^{-1}. \tag{12}$$

For a free Co^{2+} ion, $B_0 \approx 1115\ \mathrm{cm}^{-1}$ and $C_0 \approx 4366\ \mathrm{cm}^{-1}$ [17], so we have $f_\gamma \approx 0.7653$. From the Slater-type SCF functions [18, 19] and the average metal-ligand distance R (≈ 2.12 Å [20]) in α-$LiIO_3$, we obtain the group overlap integrals $S_{dp}(t_{2g}) \approx 0.0094$ and $S_{dp}(e_g) \approx 0.0322$. For free Co^{2+} and O^{2-} ions we have $\zeta_d^0 \approx 533\ \mathrm{cm}^{-1}$ [17], $\zeta_p^0 \approx 136\ \mathrm{cm}^{-1}$ [21]. Thus, from (2)–(4), we obtain

$$\zeta \approx 504\ \mathrm{cm}^{-1},\quad \zeta' \approx 425\ \mathrm{cm}^{-1},\qquad k = 0.938,\quad k' = 0.804. \tag{13}$$

According to the superposition model [22], the trigonal field parameters can be expressed as

$$\begin{aligned}
V = \sum_{i=1}^{2}\,&[(9/7)\,\bar{A}_2\,(R_0)\,(R_0/R_i)^{t_2}\,(3\cos^2\theta_i-1)\\
&+(20/21)\,\bar{A}_4\,(R_0)\,(R_0/R_i)^{t_4}\\
&\cdot(35\cos^4\theta_i-30\cos^2\theta_i+3)\\
&+(20\sqrt{2}/3)\,\bar{A}_4\,(R_0)\,(R_0/R_i)^{t_4}\sin^3\theta_i\,\cos\theta_i],\\
V' = \sum_{i=1}^{2}\,&[(-3\sqrt{2}/7)\,\bar{A}_2\,(R_0)\,(R_0/R_i)^{t_2}\,(3\cos^2\theta_i-1)\\
&+(5\sqrt{2}/21)\,\bar{A}_4\,(R_0)\,(R_0/R_i)^{t_4}\\
&\cdot(35\cos^4\theta_i-30\cos^2\theta_i+3)\\
&+(10/3)\,\bar{A}_4\,(R_0)\,(R_0/R_i)^{t_4}\sin^3\theta_i\,\cos\theta_i],
\end{aligned} \tag{14}$$

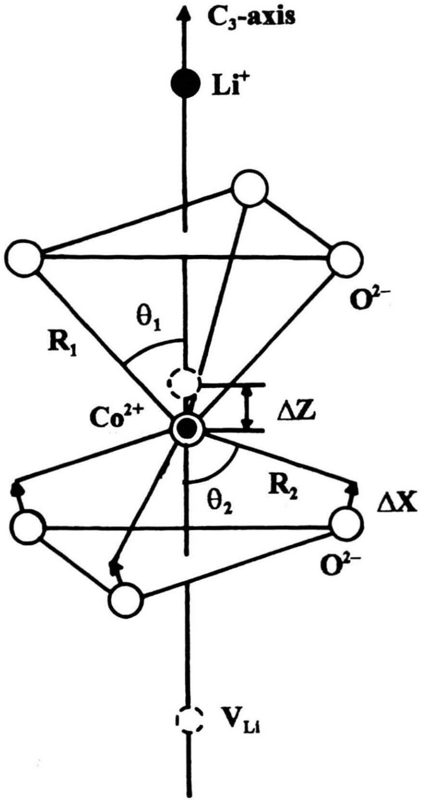

Fig. 1. Local geometry of Co^{2+} center for α-$LiIO_3$:Co^{2+} crystal.

Table 1. EPR parameters $g_{\parallel}$ and $g_{\perp}$ for Co^{2+} in α-$LiIO_3$.

	Cal.a)	Cal.b)	Experiment [11]
$g_{\parallel}$	6.345	3.690	3.687 (2)
$g_{\perp}$	3.172	4.654	4.656 (3)

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of the bonds [22, 23]. $\bar{A}_2$ (R_0) and $\bar{A}_4$ (R_0) are the intrinsic parameters with the reference distance R_0 [$\approx (R_1 + R_2)/2$]. For the $3d^n$ ion in octahedra we have $\bar{A}_4 (R_0) \approx (3/4)\, D_q$ [22, 23]. The ratio $\bar{A}_2 (R_0)/ \bar{A}_4 (R_0)$ is in the range of 9 ~ 12 for $3d^n$ ions in many crystals [23–25], we take $\bar{A}_2 (R_0) \approx 12\, \bar{A}_4 (R_0)$ here. R_i are the metal-ligand distances and θ_i the angles between the R_i and C_3 axis. Since Li^+ is arranged eccentrically in the LiO_6 group in α-$LiIO_3$, we obtain $R_1^0 \approx 2.11$ Å, $R_2^0 \approx 2.13$ Å, $\theta_1^0 \approx 52.90°$ and $\theta_1^0 \approx 52.15°$ from the crystallographic data [20]. When Co^{2+} replaces Li^+ in α-$LiIO_3$, RFDS measurement showed that the Co^{2+} ion should shift by $\Delta Z \approx 0.19$ (1) Å [11] towards V_{Li} (see Fig. 1) because of the electrostatic interaction. Thus we obtain for the CoO_6 group in α-$LiIO_3$:Co^{2+}, $R_1 \approx 2.22$ Å, $R_2 \approx 2.02$ Å, $\theta_1 \approx 49.20°$, and $\theta_2 \approx 56.07°$. Substituting these parameters into the above formulas, the trigonal field parameters V and V' and hence the $g_{\parallel}$ and $g_{\perp}$ for α-$LiIO_3$:Co^{2+} are calculated. The results of $g_{\parallel}$ and $g_{\perp}$ are in disagreement with the observed values (see Table 1). So, the O^{2-} arrangement in Co^{2+} centers in α-$LiIO_3$ should be changed. In fact, because the effective charge of V_{Li} is negative, it can be expected that not only the Co^{2+} is attracted towards V_{Li}, but also the three O^{2-} ions between V_{Li} and Co^{2+} can be repulsed from V_{Li} by ΔX (see Figure 1) owing to the electrostatic interaction. The displacement $\Delta X \approx 0.49$ Å (note: from ΔX we obtain for the CoO_6 group, $R_1 \approx 2.22$ Å, $R_2 \approx 2.23$ Å, $\theta_1 \approx 49.20°$, and $\theta_2 \approx 68.26°$) is obtained by fitting the calculated $g_{\parallel}$ and $g_{\perp}$ to the observed values. The comparison between the calculated and observed $g_{\parallel}$ and $g_{\perp}$ is shown in Table 1.

4. Discussion

From the above studies it can be seen that the O^{2-} ions between Co^{2+} and V_{Li} in α-$LiIO_3$:Co^{2+} are indeed displaced away from V_{Li}. The displacement direction is consistent with the expectation based on the electrostatic interaction. Similar displacements of O^{2-} ions away from V_{Li} were also found for Mn^{2+}, Fe^{3+}, and Cr^{3+} centers in α-$LiIO_3$ crystals by analyzing the EPR zero-field splittings [8–10]. So, the above O^{2-} displacement is reasonable physically. It appears that the above formulas of $g_{\parallel}$ and $g_{\perp}$ can be used to explain reasonably the g factors of $3d^7$ ions in trigonal symmetry, or, conversely, to determine the local structure of a paramagnetic center by studying the EPR data.

It is worth noticing that for divalent TM ions in α-$LiIO_3$, two TM impurity centers are formed because the V_{Li} on the C_3 axis can be above (center A) and below (center B) the TM ion [7, 11]. The studies in this paper are only made for the Co^{2+} (B) center. The Co^{2+} (A) center was also observed by EPR measurements [11], however, since the intensity of the EPR spectrum of this center at 4 K was about 20 times smaller than that of the Co^{2+} (B) center, the EPR parameters $g_{\parallel}$ and $g_{\perp}$ of the Co^{2+} (A) center were not given [11], and so the displacement of the O^{2-} ion for this center could not be studied here.

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