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Defect models of the low and high temperature centres of Cr^{3+} in $\alpha\text{-LiIO}_3\text{:Cr}^{3+}$ crystals

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Abstract. By analysing the EPR spectra of $\alpha\text{-LiIO}_3\text{:Cr}^{3+}$, the defect models of a low temperature centre Cr^{3+}L and two high temperature centres Cr^{3+}H_1 and Cr^{3+}H_2 are suggested. In centre Cr^{3+}L , the Cr^{3+} ion replaces the Li^+ ion and excess charge is compensated by two nearest Li^+ vacancies on the same axis. In centres Cr^{3+}H_1 and Cr^{3+}H_2 , the Li^+ vacancies below and above the Cr^{3+} ion are, respectively, dissociated from the low temperature centre Cr^{3+}L . The suggestions are supported by the theoretical calculations of EPR parameters D , g_{\parallel} and g_{\perp} for the three Cr^{3+} centres. The reasonableness of these models is discussed.

1. Introduction

$\alpha\text{-LiIO}_3$ crystals have a number of remarkable properties, such as electro-optical, nonlinear optical and photoelastic properties [1–3] and are used in electronic and electro-optical devices. In the applications the transition metal ($3d^n$) ion impurities in the materials play a major role because they can be responsible for the modification of the optical properties and the photorefractive effect [4] of the matrix. So, knowledge of the defect nature and substitutional sites of these impurities in $\alpha\text{-LiIO}_3$ is of importance. Progress has been made for the nature and substitutional sites of some $3d^n$ ions in $\alpha\text{-LiIO}_3$. It is recognized that these $3d^n$ ions, such as Fe^{3+} , Mn^{2+} and Co^{2+} , replace Li^+ ions in $\alpha\text{-LiIO}_3$ and the excess charge compensation is performed by two nearest Li^+ vacancies (V_{Li}) along the c -axis for trivalent ions, or by one nearest V_{Li} for divalent ions [5–7]. However, for Cr^{3+} in $\alpha\text{-LiIO}_3$, there are some controversies and problems:

(1) At room temperature (RT) and below RT, a trigonal symmetry Cr^{3+} centre (called the low temperature centre Cr^{3+}L) was found with zero-field splitting $D \approx -0.6099 \text{ cm}^{-1}$ at RT by EPR study [8]. From the hyperfine interaction tensors of Li nuclei with Cr^{3+} ions in $\alpha\text{-LiIO}_3$ obtained from the method of radiofrequency discrete saturation (RFDS), Brauer and Daraselia [7] suggested that in the centre, the Cr^{3+} ion replaces the Li^+ ion along the c -axis and the excess charge is compensated by two nearest V_{Li} on the same axis. Recently, by calculating the zero-field splittings D for Cr^{3+} at both cation Li^+ and I^{5+} sites in $\alpha\text{-LiIO}_3$ from the superposition model and Macfarlane's perturbation formula, Han and Kim [9] found that the calculated sign and magnitude of splitting D for Cr^{3+} at the Li^+ site are different from, but those for Cr^{3+} at the I^{5+} site are consistent with, the observed ones. They therefore thought Cr^{3+} to be at the I^{5+} site rather than at the Li^+ site in $\alpha\text{-LiIO}_3$. However, as they pointed out

[9], in the calculations the O^{2-} arrangement around the Cr^{3+} replacing Li^+ or I^{5+} is assumed to be unchanged. The assumption is not reasonable because the O^{2-} arrangement must be changed owing to charge compensation. In fact, as has been said before, when Cr^{3+} replaces Li^+ , two nearest V_{Li} are formed to compensate the excess charge. Since the effective charge of V_{Li} is negative, the O^{2-} ions in the nearest surroundings of the Cr^{3+} ion must be repulsed from the V_{Li} (and hence from the c -axis) by ΔX_i (see figure 1). So, the bonding angles β_i change from $\beta_i < \beta_0$ (where $\beta_0 \approx 54.74^\circ$, is the angle in the corresponding cubic case) to $\beta_i > \beta_0$ [10, 11], thus, the signs and magnitude of splitting D not only for the Cr^{3+} ion, but also for other $3d^n$ ions in α - $LiIO_3$, can be reasonably explained [12]. So, as pointed out by the majority of authors [7, 10–14], the model of the low temperature centre $Cr^{3+}L$ in α - $LiIO_3$ is Cr^{3+} at Li^+ site associated with two nearest V_{Li} (characterized by $V_{Li}-Cr^{3+}-V_{Li}$).

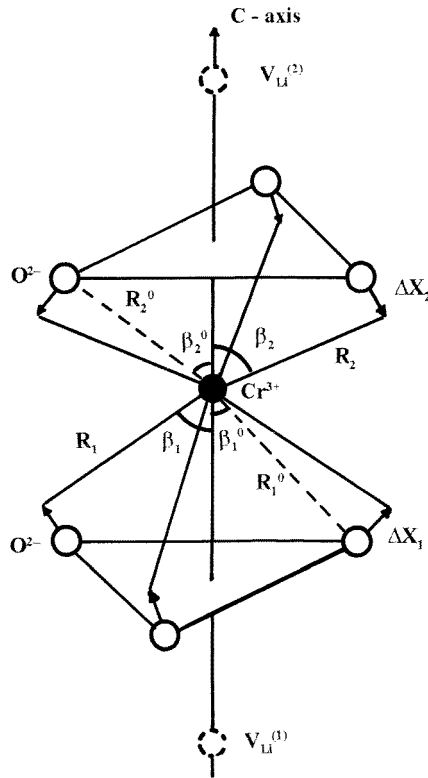


Figure 1. Vacancy-induced local lattice distortions for the $Cr^{3+}L$ centre in an α - $LiIO_3:Cr^{3+}$ crystal (note: in the $Cr^{3+}H_1$ centre, the $V_{Li}^{(2)}$ is dissociated, so $\Delta X_2 = 0$, and the Cr^{3+} shifts ΔZ_1 towards $V_{Li}^{(1)}$ along the c -axis. In the $Cr^{3+}H_2$ centre, $V_{Li}^{(1)}$ is dissociated, so $\Delta X_1 = 0$, and the Cr^{3+} shifts ΔZ_2 towards $V_{Li}^{(2)}$ along the c -axis).

(2) At $T > 300$ K, the concentration of the $Cr^{3+}L$ centre decreased and two new trigonal symmetry centres $Cr^{3+}H_1$ (at $T = 320$ K, $D \approx -0.3100$ cm^{-1}) and $Cr^{3+}H_2$ (at $T = 320$ K, $D \approx -0.3265$ cm^{-1}) were identified with the intensity of the former markedly exceeding the intensity of the latter by EPR experiments [14]. The transition between the above low and high temperature centres with temperature change is reversible. So, Sharoyan *et al* [14] suggested that the appearance of $Cr^{3+}H_1$ and $Cr^{3+}H_2$ centres in α - $LiIO_3$ can be interpreted on the basis of two possible models related to the low temperature centre $V_{Li}-Cr^{3+}-V_{Li}$ decay:

(A) $(V_{Li}-Cr^{3+}-V_{Li}) \rightleftharpoons (Cr^{3+}-V_{Li}) + V_{Li}$, i.e., one of the Cr³⁺H centres is formed owing to the dissociation of one V_{Li} from a Cr³⁺L centre. The model is similar to that of the divalent impurities associated with one V_{Li} in α -LiIO₃ [5, 6]. (B) $(Cr^{3+}-V_{Li}) \rightleftharpoons Cr^{3+}+V_{Li}$, i.e., another Cr³⁺H centre is formed owing to the dissociation of V_{Li} from the first Cr³⁺H centre and its defect model is Cr³⁺ at an Li⁺ site without V_{Li}. However, model B is doubtful because (i) in both models, only one V_{Li} is dissociated from the distinct centre; it is difficult to understand why the change of splitting D in model A is great (i.e., $-0.6099 \text{ cm}^{-1} \rightleftharpoons -0.3265 \text{ cm}^{-1}$ [14]) but in model B it is so small (i.e., $-0.3265 \text{ cm}^{-1} \rightleftharpoons -0.3100 \text{ cm}^{-1}$ [14]), and (ii) more importantly, in model B, since two V_{Li} are dissociated from the Cr³⁺ centre, the O²⁻ ions around Cr³⁺ ion are not repulsed from the c -axis by V_{Li} and so the angles $\beta_i < \beta_0$. Thus, the zero-field splitting D for this centre should be positive, as pointed out in [10–12]. The result is opposite to the observed value [8, 11]. So, model B is unreasonable.

Considering that in α -LiIO₃ the Li⁺ ion is arranged eccentrically in octahedral LiO₆, i.e., the Li⁺ ion is displaced by 0.02 Å along the c -axis from a plane half-way between those formed by the O²⁻ ions [15], the bonding length R_1 and angle β_1 in the LiO₆ group must be, respectively, different slightly from R_2 and β_2 (see figure 1). So, we can suggest that for the Cr³⁺H₁ centre, the model is $(V_{Li}^{(1)}-Cr^{3+}-V_{Li}^{(2)}) \rightleftharpoons (Cr^{3+}-V_{Li}^{(1)}) + V_{Li}^{(2)}$ and for the Cr³⁺H₂ centre, it is $(V_{Li}^{(1)}-Cr^{3+}-V_{Li}^{(2)}) \rightleftharpoons (Cr^{3+}-V_{Li}^{(2)}) + V_{Li}^{(1)}$, i.e., both Cr³⁺H centres are formed by a Cr³⁺ ion associated with one V_{Li} below and above the Cr³⁺ ion. Thus, the small difference of zero-field splittings D between Cr³⁺H₁ and Cr³⁺H₂ centres can be understood. In order to further check the models, in the following we calculate theoretically the zero-field splitting D and g factors g_{\parallel} , g_{\perp} for Cr³⁺L, Cr³⁺H₁ and Cr³⁺H₂ centres in α -LiIO₃ by considering suitable local lattice distortions arising from charge compensation. The calculated results are in reasonable agreement with the observed values. The reasonableness of the above defect models is discussed.

2. Calculations

For Cr³⁺(3d³) ion in trigonal symmetry, the high-order perturbation formulas of zero-field splitting D and g factors g_{\parallel} and g_{\perp} obtained from the perturbation-loop method can be written as [16, 17]

$$D = (2/9)\zeta^2\nu(1/D_1^2 - 1/D_3^2) - \sqrt{2}\zeta^2\nu'(2/3D_1D_4 + 1/D_2D_3 + 1/3D_3D_4 + 1/D_2D_4 + 4\sqrt{2}B/D_1D_4D_5 + 4B/D_3D_4D_5 + 9B/2D_2^2D_3) \quad (1)$$

$$g_{\parallel} = g_s - 8\zeta k/3D_1 - 2\zeta^2(k + g_s)/3D_2^2 + 4\zeta^2(k - 2g_s)/9D_3^2 + 8\zeta^2(k - 2g_s)/9D_1^2 - 4\zeta^2k/3D_1D_2 + 4\zeta^2k/9D_1D_3 + 4\zeta^2k/3D_2D_3 + 8\zeta k\nu/9D_1^2 - 8\sqrt{2}\zeta k\nu'/3D_1D_4 \quad (2)$$

$$g_{\perp} = g_{\parallel} - 4\zeta k\nu/3D_1^2 + 4\sqrt{2}\zeta k\nu'/D_1D_4 \quad (3)$$

where $g_s = 2.0023$, D_i are the zero-order energy denominators defined in [16] and [17]. ζ is the spin-orbit coupling coefficient, k is the orbital reduction factor. B (and C) are the Racah parameters. ν and ν' are the trigonal field parameters.

For Cr³⁺ in α -LiIO₃, $B \approx 670 \text{ cm}^{-1}$, $C \approx 2550 \text{ cm}^{-1}$ and $Dq \approx 1430 \text{ cm}^{-1}$ obtained from the optical spectra [13, 18]. Defining the average covalency reduction factor $N^2 \approx \frac{1}{2}(\sqrt{B/B_0} + \sqrt{C/C_0})$ [19], where $B_0 \approx 1030 \text{ cm}^{-1}$ and $C_0 \approx 3850 \text{ cm}^{-1}$ are the Racah parameters of free Cr³⁺ ion [20], thus, we have $N^2 \approx 0.81$; $\zeta \approx N^2\zeta_d^0 \approx 221 \text{ cm}^{-1}$ (where $\zeta_d^0 \approx 273 \text{ cm}^{-1}$ [20] is the spin-orbit coupling coefficient of the free Cr³⁺ ion) and $k \approx N^2$ [19]. The crystal field parameters can be calculated from the superposition model [21] or the point-charge model. The relationship between both models is shown in [21]. We apply the

superposition model here because it is effective for interpreting the optical and EPR spectra of $3d^n$ ions in crystals [22–25]. From this model, the trigonal field parameters ν and ν' can be written as [21–23]

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

where t_2 and t_4 are the power-law exponents; we take $t_2 \approx 3$ and $t_4 \approx 5$ here because of the ionic nature of the bonds [21–23]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance $R_0 \approx (R_1 + R_2)/2$. According to the relationship between the electrostatic and superposition models [21], $\bar{A}_4(R_0) \approx (3/4)Dq$ (in passing, since $Dq(R) \approx (4/3)\bar{A}_4(R) \approx (4/3)\bar{A}_4(R_0)(R_0/R)^{t_4}$ [21], we have $Dq \propto R^{-t_4}$. The pressure experiment for NiO [26] and the theoretical studies based on molecular orbital calculations for $3d^n$ ions in many crystals [27, 28] show that $Dq \propto R^{-5}$ is approximately valid. So the above $t_4 \approx 5$ is reasonable here). The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range of 9–12 for $3d^n$ ions in crystals [24, 25]; we take $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ here. The structural parameters R_i and β_i can be calculated from the bonding lengths $R_1^0 (\approx 2.13 \text{ \AA})$, $R_2^0 (\approx 2.11 \text{ \AA})$, $\beta_1^0 (\approx 52.05^\circ)$ and $\beta_2^0 (\approx 52.90^\circ)$ of the LiO_6 group in $\alpha\text{-LiIO}_3$ [15] and the displacements ΔX_1 and ΔX_2 (see figure 1). Thus, in equations (1)–(4), there are only two adjustable parameters ΔX_1 and ΔX_2 . By fitting the calculated EPR parameters D , g_{\parallel} and g_{\perp} to the observed values, we obtain $\Delta X_1 \approx 0.155 \text{ \AA}$ and $\Delta X_2 \approx 0.152 \text{ \AA}$ (thus, $\beta_1 \approx 56.02^\circ$ and $\beta_2 \approx 56.79^\circ$ and so $\beta_i > \beta_0$ as expected above). The comparisons between the calculated and observed EPR parameters are shown in table 1.

Table 1. EPR parameters of low temperature centre Cr^{3+}L and high temperature centres Cr^{3+}H_1 and Cr^{3+}H_2 in $\alpha\text{-LiIO}_3:\text{Cr}^{3+}$ crystal.

| | T (K) | D (cm^{-1}) | | g_{\parallel} | | g_{\perp} | |
|----------------------------|---------|--------------------------|--------------|-----------------|------------|-------------|------------|
| | | Calc. | Expt | Calc. | Expt | Calc. | Expt |
| Cr^{3+}L | 297 | −0.6040 | −0.6099 [8] | 1.965 | 1.965 [8] | 1.970 | 1.971 [8] |
| Cr^{3+}H_1 | 320 | −0.3101 | −0.3100 [14] | 1.967 | 1.964 [14] | 1.969 | 1.979 [14] |
| Cr^{3+}H_2 | 320 | −0.3262 | −0.3265 [14] | 1.967 | 1.964 [14] | 1.969 | 1.979 [14] |

For Cr^{3+}H_1 centre in $\alpha\text{-LiIO}_3$, $V_{Li}^{(2)}$ is dissociated and so $\Delta X_2 = 0$, the displacement ΔX_1 can be assumed unchanged and the Cr^{3+} ion should shift towards the $V_{Li}^{(1)}$ by an amount ΔZ_1 as the divalent ions [5, 6] because of the electrostatic interaction between Cr^{3+} and $V_{Li}^{(1)}$ (see figure 1). By fitting the observed EPR parameters D , g_{\parallel} and g_{\perp} of Cr^{3+}H_1 centre, we obtain $\Delta Z_1 \approx 0.22 \text{ \AA}$. The comparisons between the calculated and observed EPR parameters are also shown in table 1.

Similar calculations can also be made for Cr^{3+}H_2 centre in $\alpha\text{-LiIO}_3$, where $\Delta X_1 = 0$ and ΔX_2 remains unchanged. The displacement ΔZ_2 of Cr^{3+} towards $V_{Li}^{(2)}$ is about 0.19 \AA by

fitting the EPR parameters of $Cr^{3+}H_2$ centre. The calculated EPR parameters are compared with the observed values in table 1.

3. Discussions

From table 1, one can find that on the basis of our defect models the EPR parameters D , g_{\parallel} and g_{\perp} of $Cr^{3+}L$, $Cr^{3+}H_1$ and $Cr^{3+}H_2$ centres in α - $LiIO_3$ crystals can be reasonably explained by considering the suitable local lattice distortion caused by charge compensation. Although in the calculations, there may be some errors arising from the approximations of the theoretical methods and the applied parameters, the satisfactory explanations of EPR parameters suggest that these defect models can be regarded as reasonable.

Noteworthy, for divalent $3d^n$ ions in α - $LiIO_3$, two nonequivalent defect centres A and B were found from EPR experiments [5, 6, 29]. The following properties of $Cr^{3+}H_1$ and $Cr^{3+}H_2$ are very similar to those of centres A and B of divalent ions in α - $LiIO_3$: (i) as in the $Cr^{3+}H_1$ and $Cr^{3+}H_2$ centres of α - $LiIO_3:Cr^{3+}$ [14], the EPR studies showed that the intensity of centre A is quite different from that of centre B for divalent ions in α - $LiIO_3$. For example, in α - $LiIO_3 : Mn^{2+}$ [24], the intensity ratio of centre B to centre A is about 4 and in α - $LiIO_3:Co^{2+}$ [6], the ratio is about 20. (ii) The RFDS method showed that in α - $LiIO_3:Mn^{2+}$ [5], the displacements of Mn^{2+} towards the distinct V_{Li} for centres A and B are about 0.16 and 0.31 Å, respectively. In α - $LiIO_3:Co^{2+}$ [6], the displacement of Co^{2+} towards V_{Li} for centre B is about 0.19 Å (note: the displacement for centre A was not given, maybe because of the very weak intensity). These displacements are close to those of Cr^{3+} in $Cr^{3+}H_1$ and $Cr^{3+}H_2$ centres in α - $LiIO_3:Cr^{3+}$ estimated in this work. Since the divalent M^{2+} centres are M^{2+} ions at Li^+ sites associated with only one V_{Li} along the c -axis above or below the M^{2+} ion [5, 6, 24], the above analogy between trivalent Cr^{3+} and divalent M^{2+} suggests that our defect models for $Cr^{3+}H_1$ and $Cr^{3+}H_2$ centres in α - $LiIO_3:Cr^{3+}$ are reasonable in physics.

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