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Superposition model and crystal-field analysis of the $^4A_2$ and ^2_aE states of Cr^{3+} ions at C_3 sites in $LiNbO_3$

Y M Chang†§, T H Yeom†‖, Y Y Yeung‡ and C Rudowicz†¶

† Department of Applied Science, City Polytechnic of Hong Kong, Hong Kong

‡ Department of Applied Physics, Hong Kong Polytechnic, Hong Kong

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Abstract. The energy levels and wavefunctions including the two lowest-lying levels, namely $^4A_2$ and ^2_aE, for which reliable experimental data exist for Cr^{3+} ions at C_3 symmetry sites in $LiNbO_3$, are calculated using the complete matrix diagonalization method within the $3d^3$ configuration. The Hamiltonian considered includes the electrostatic term, the Trees correction, the spin–orbit interaction and the crystal-field interaction. The role of the additional low-symmetry crystal-field term $B_4^{-3}O_4^{-3}$ (in the Stevens operator notation), neglected in the C_{3v} approximation used so far in the literature, is studied. The superposition model is developed for $3d^3$ ions at C_3 symmetry sites and applied to study the site occupancy of Cr^{3+} in $LiNbO_3$. Analysis of the optical data indicates that Cr^{3+} ions substitute at Nb sites and Li sites simultaneously. The present considerations offer an improvement over the earlier approximations using C_{3v} symmetry only. The zero-field splitting predicted by the crystal-field calculations for Cr^{3+} at the Nb site matches the experimental value from EPR studies very well. This is contrary to the earlier prediction by the superposition model analysis of the spin-Hamiltonian parameters indicating that the zero-field splitting for Cr^{3+} ions at Li sites matches the experimental zero-field splitting better than that for Cr^{3+} at Nb sites. Since the present calculations involve fitting not only the zero-field splitting but also the energies of the ^2_aE state, the present predictions may be more reliable than the previous predictions.

1. Introduction

Pure $LiNbO_3$ crystals as well as $LiNbO_3$ crystals co-doped with Mg and other transition ions are very important technological crystals because of their excellent electro-optic, non-linear and laser host properties, and also because large crystals of very good quality can be grown [1–3]. Since Cr^{3+} ions have been successfully used for laser emission in various crystal hosts, recently there has been renewed interest in the spectroscopic studies of Cr^{3+} ions in $LiNbO_3$. Earlier, Glass [4] conducted a comparative study of the absorption and fluorescence spectra of $LiNbO_3$:Cr^{3+} and concluded that Cr^{3+} substituted at the Nb site and not the Li site. Recently, evidence for compensating Cr^{3+} dimers, i.e. Cr^{3+} substituted at both Nb and Li sites, was obtained from axial EPR spectra [5, 6] and also from the spectroscopic studies of R lines of Cr^{3+} [7].

The identification of the site location of Cr^{3+} in $LiNbO_3$ is very difficult because of the very similar environments of the cation sites. The EPR spectra of Cr^{3+} in $LiNbO_3$ [8, 9] show strong axial symmetry about the c axis, suggesting that Cr^{3+} substitutes at the

§ On leave from Department of Physics, Nakai University, Tianjin 300071, People's Republic of China.

‖ On leave from Department of Physics, Korea University, Seoul 136-701, South Korea.

¶ Author to whom correspondence should be addressed.

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C_3 symmetry sites, leading to the three possible site assignments, namely the Li, Nb and structural vacancy site. There exists a contradiction concerning Cr^{3+} site occupancy in $LiNbO_3$ from EPR analysis (see e.g. table 1 of [10]). The results of our recent literature survey of the optical absorption and emission studies [4, 7, 11–13] are given in table 1.

Table 1. Survey of the optical absorption or emission data for Cr^{3+} in $LiNbO_3$ and/or in $LiNbO_3$:Mg.

Ion(s)	T (K)	Cr site assignment	Remarks	Reference
Cr^{3+}	4.2	Nb	$Dq(T)$ analysis of C_{3v} CF	[4]
Cr^{3+}	300	Nb	O_h CF analysis	[11]
Cr^{3+}	10	Nb and Li	R line	[7]
Cr^{3+}/Mg^{2+}	100 20	Li and Nb	R line	[12]
Cr^{3+}/Mg^{2+}	20	Li and Nb	R line	[13]

However, to the best of our knowledge, the previous crystal-field (CF) calculations [4, 7, 14] for $LiNbO_3$:Cr^{3+} were always based on the approximated C_{3v} (or higher) symmetry rather than on the exact C_3 symmetry. This approximation cannot provide full understanding of the energy level structure of Cr^{3+} ions in $LiNbO_3$. The polarization character of the optical transitions indicates that the local symmetry departs from C_{3v} to C_3 [12]. The reason why many workers prefer to use the approximated C_{3v} symmetry is that an additional 'imaginary' CF term needs to be taken into account for C_3 symmetry [15], whereas the available CF computer programs can mostly handle only the real CF matrix.

In order to enable studies of low-symmetry CF terms to be made, an extension of the CF computer package [16, 17], which is applicable for orthorhombic or higher symmetry involving only real CF terms, has been worked out for $3d^N$ ions at arbitrary symmetry sites in crystals including trigonal symmetry cases involving 'imaginary' CF terms (point groups, C_3 and S_6). So it is now possible to diagonalize fully the complex CF Hamiltonian matrices and to analyse the fine structure of Cr^{3+} energy levels for C_3 symmetry. Moreover, the superposition model (SPM) [18] is used to analyse the relationships between the CF parameters and the structural parameters. The CF and SPM results for possible Cr^{3+} ion sites enable the Cr^{3+} site occupancy to be identified by comparing the CF calculated values of the lowest-lying energy levels with the site-sensitive zero-field splitting (ZFS) and the positions of R lines observed in EPR and optical experiments respectively.

2. Crystal structure

The structure of $LiNbO_3$ was investigated by Abraham *et al* [19–21] in 1966. Below the ferroelectric Curie temperature of 1190 °C, the crystal is rhombohedral with Nb and Li cations occupying an octahedral site with C_3 (nearly C_{3v}) symmetry. The departure from C_{3v} symmetry is measured by the angle α of the rotation of the upper (or equivalently the lower) oxygen triangle measured from one of the σ_v planes [4]. Since the angle α is not large, it has been neglected in most CF calculations for $LiNbO_3$ so far, leading to the C_{3v}

local symmetry [22]. The CF z axis has always been chosen along the [111] axis (see e.g. [23]). For C_{3v} symmetry, the CF x axis is always defined along the line joining the centre of the upper oxygen triangle to one of its vertices. After the x and z axes have been selected, the y axis is chosen such that the axis system is right handed. The positions of Li and Nb ions in $LiNbO_3$ as well as the distortion angle α [19–21] in this coordinate system are given in table 2.

Table 2. Nearest-neighbour O^{2-} positions in $LiNbO_3$.

	R_1 (Å)	R_2 (Å)	θ_1 (deg)	θ_2 (deg)	α (deg)
Nb [19–21]	1.889	2.112	61.65	132.01	0.68
Nb [25] (congruent)	1.8787	2.1264	61.887	132.11	0.68
Li [19–21]	2.238	2.068	44.57	110.262	3.82
Li [25] (congruent)	2.274	2.053	43.96	109.16	3.82

Li^+ and Nb^{5+} ions in $LiNbO_3$ have nearly identical ionic radii, namely 0.68 Å and 0.69 Å, respectively, unlike in other ABO_3 perovskites. Since the Nb^{5+}–O^{2-} bond is stronger than the Li^+–O^{2-} bond, $LiNbO_3$ crystals have a tendency to non-stoichiometry with [Li]/[Nb] < 1. Such crystals therefore have a very high concentration of intrinsic defects. The nominal congruent composition with [Li]/[Nb] = 48.6/51.4, at which a single crystal grows from the melt with uniform composition, was widely used. O'Bryan *et al* [24] reported this composition ratio to be 48.45/51.55. Abraham and Marsh [25] re-investigated the crystal structure of $LiNbO_3$ with both the near-stoichiometric and the new congruent composition. The crystal structure was found to be given by $[Li_{1-5x}Nb_{5x}]Nb_{1-4x}O_3$, with $x = 0.0118$ for congruent composition, indicating that there are 5.9% vacant Li sites. These Li sites are filled with Nb ions forming the so-called 'antisite' defects [26]. The structural data for Li and Nb sites with the new congruent composition are also given in table 2.

3. Superposition model analysis of CF parameters

The CF Hamiltonian for C_3 symmetry within the ^{2S+1}L multiplet of $3d^N$ ions can be written in terms of the extended Stevens operators [27] as (for references, see e.g. [28, 29])

$$\mathcal{H}_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_4^{-3} O_4^{-3} \tag{1}$$

and

$$B_k^q = A_k^q(r^k)\theta_k \equiv C_k^q \theta_k$$

where θ_k are the Stevens operator equivalent factors and, for the ground-state multiplet ^4F of the Cr^{3+} ion, these are $\alpha_J = 2/105$ and $\beta_J = 2/315$ for $k = 2$ and 4, respectively. The last term in (1) accounts for the departure from C_{3v} to C_3 symmetry.

The superposition model [30, 31] provides an expansion of the Stevens CF parameters C_k^q in terms of the intrinsic parameters $\bar{A}_k$ and the coordination factors K_k^q:

$$C_k^q = \sum_{j=1}^{n} \bar{A}_k(R_j) K_k^q(\theta_j, \phi_j) \tag{2}$$

where (R_j, θ_j, ϕ_j) are the polar coordinates of the jth ligand. The conversion between the CF parameters in Wybourne's [32] notation B_{kq}, which is used for the CF calculations within the whole $3d^3$ configuration, and those in the Stevens notation C_k^q are as follows:

$$C_k^0 = d_0^k \operatorname{Re} B_{kq} \qquad C_k^{+q} = d_q^k(-1)^q \operatorname{Re} B_{kq} \qquad C_k^{-q} = d_q^k(-1)^{q+1} \operatorname{Im} B_{kq} \tag{3}$$

where the numerical coefficients d_q^k are given in table 3 of [27] (see also [33]). For C_3 symmetry, we need $d_0^2 = \frac{1}{2}$, $d_0^4 = \frac{1}{8}$ and $d_3^4 = \sqrt{35}/2$.

The parameters B_k^q are all real, while the matrix elements of the O_k^{-q} operators are imaginary, whereas the parameters B_{kq} may be complex in general [28,29]. On the assumption of the power law for the intrinsic parameters,

$$\bar{A}_k(R_j) = \bar{A}_k(R_0)(R_0/R_j)^{t_k} \equiv \bar{A}_k(R_0/R_j)^{t_k} \tag{4}$$

where R_0 is the reference distance, which is always chosen as the mean metal-ion–ligand distance. Explicit expressions for the ground-state ^4F term of $3d^3$ ions in C_3 local symmetry using the coordinate system defined above are derived as follows:

$$\begin{aligned}
B_2^0 &= \tfrac{1}{35}\{\bar{A}_2[(R_0/R_1)^{t_2}(3\cos^2\theta_1 - 1) + (R_0/R_2)^{t_2}(3\cos^2\theta_2 - 1)]\} \\
B_4^0 &= \tfrac{1}{140}\{\bar{A}_4[(R_0/R_1)^{t_4}(35\cos^4\theta_1 - 30\cos^2\theta_1 + 3) \\
&\qquad + (R_0/R_2)^{t_4}(35\cos^4\theta_2 - 30\cos^2\theta_2 + 3)]\} \\
B_4^3 &= \tfrac{2}{105}\{\bar{A}_4[(R_0/R_2)^{t_4}(35\cos\theta_2\sin^3\theta_2) - (R_0/R_1)^{t_4}(35\cos\theta_1\sin^3\theta_1)]\cos(3\alpha)\} \\
B_4^{-3} &= \tfrac{-2}{105}\{\bar{A}_4[(R_0/R_1)^{t_4}(35\cos\theta_1\sin^3\theta_1) + (R_0/R_2)^{t_4}(35\cos\theta_2\sin^3\theta_2)]\sin(3\alpha)\}.
\end{aligned} \tag{5}$$

The SPM parameters $\bar{A}_2$, t_2, $\bar{A}_4$ and t_4 are treated as adjustable. Using the crystallographic data [19–21,25] the CF parameters C_k^q (and B_k^q) can be calculated and used for fitting the energy levels arising from CF calculations within the whole $3d^3$ configuration in the next section.

4. The fine structure of the $^4A_2$ and ^2_aE states

For a $3d^3$ ion at an arbitrary symmetry site within the whole $3d^N$ configuration, the Hamiltonian can be written as [16,32,34]

$$\mathcal{H} = \mathcal{H}_{es}(B, C) + \mathcal{H}_{Trees}(\alpha) + \mathcal{H}_{CF}(B_{kq}) + \mathcal{H}_{so}(\xi) \tag{6}$$

where B and C are the Racah electrostatic parameters, α is the Trees correction parameter and ξ is the spin–orbit coupling coefficient. For details of the CF computer package for full diagonalization of the Hamiltonian (6), applicable to orthorhombic or higher symmetry involving only real CF terms, the files organization and the input–output specifications we refer the reader to [16, 17]. An extension of the program to lower-symmetry cases (involving 'imaginary' CF terms) for any $3d^N$ ions in crystals has recently been worked out.

For the input data, we choose $B = 554$ cm^{-1}, $C = 3224$ cm^{-1} [13] and $\xi = 195$ cm^{-1} [4]. Since no value for the Trees correction α is reported for Cr^{3+} in $LiNbO_3$, we use $\alpha = 70$ cm^{-1} suitable for MgO:Cr^{3+} [35]. It is reasonable to assume that the parameters B, C, ξ and α are less sensitive to the changes in the crystalline environment and do not

change with the different cation sites in $LiNbO_3$. There are no superposition model data for Cr^{3+} in $LiNbO_3$ available in the literature. Since the trigonally distorted Li^+ and Nb^{5+} sites are similar to the substitutional Al^{3+} sites in ruby and to the Mg^{2+} and Ti^{4+} sites in $MgTiO_3$, we use the SPM parameters [36, 37] for Cr^{3+} in these two crystals as initial input data.

The CF calculations are carried out within the free-ion basis functions $|^{2S+1}L,\ J,\ M_J\rangle$ [38] as well as $|^{2S+1}L,\ M_S,\ M_L\rangle$ [16]. The free-ion ^4F ground-state term of Cr^{3+} splits in octahedral symmetry into $^4A_2$, $^4T_2$ and $^4T_1$ states, whereas the other ^4P and ^2X terms split into various levels, of which $^2_aE(^2G)$ is the lowest. When the octahedral site is trigonally distorted, $^4A_2$ is the ground state, while $^2_aE(^2G)$ is the first excited state. According to the Kramers theorem, the $^4A_2(M_S)$ level splits into two sublevels with different spin components $M_S = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$, with $^4A_2(\pm\frac{3}{2})$ lying lower. The energy difference between $^4A_2(\pm\frac{3}{2})$ and $^4A_2(\pm\frac{1}{2})$ is actually the ZFS [27], which can be detected by EPR spectroscopy. The ^2_aE state splits into $^2_aE(\pm\frac{1}{2})$ and $^2_aE(\pm\frac{3}{2})$ corresponding to the $\bar{E}(^2E)$ and $2\bar{A}(^2E)$ states, respectively, (see e.g. [13]) in the E irreducible representation of the C_{3v} group [23]. The transitions from the ground-state $^4A_2$ level to $^2_aE(\pm\frac{1}{2})$ and $^2_aE(\pm\frac{3}{2})$, which give rise to the two R lines detected in optical spectroscopy, are sensitive to the local variations in the CF. In general, the CF and spin–orbit coupling introduce a mixing of the free-ion states. For illustration the wavefunctions of the ground state $^4A_2$ for the Cr^{3+} ion at the Nb site in $LiNbO_3$ are given in the appendix. It is easily seen that the wavefunction of the spin-quartet ground state $^4A_2(^4F)$ involves admixtures due to the spin-quartet ^4P and other spin-doublet states. In addition, the low-symmetry effects due to C_3 symmetry are evident in the small imaginary parts of the mixing coefficients.

In order to gain insight into the site locations of Cr^{3+} ions in $LiNbO_3$, a careful fitting by a trial-and-error method of the calculated $^4A_2$ and ^2_aE energy levels to the experimental data, similar to that discussed for Fe^{2+} and Fe^{4+} in YBCO [39], has been performed. In order to ensure the reliability of the fitting, we also take into account the experimental energy levels corresponding to other transitions, namely $^4T_2$ related to the experimental Dq-value and $^4T_1$ (see below). Using the structure data obtained by Abraham *et al* [19–21] in 1966 as well as the structure data obtained by them [25] in 1986 (the values in parentheses), the intrinsic parameters [36, 37] are obtained as follows: $\bar{A}_2 = 11\,384\,(14\,184)$ cm^{-1}, $t_2 = 1.29$, $\bar{A}_4 = 1404\,(1450)$ cm^{-1} and $t_4 = 2.9$ for Li sites and $\bar{A}_2 = 9387\,(7063)$ cm^{-1}, $t_2 = 3$, $\bar{A}_4 = 1003\,(989)$ cm^{-1} and $t_4 = 8.1$ for Nb sites. Satisfactory fitting cannot be obtained using identical power-law exponents for both Li and Nb sites, possibly because of the different local environments [11, 40, 41] (e.g. local distortion and strength of covalent bond). The CF parameters obtained in this way are given in table 3. They are comparable with the experimental values for Cr^{3+} in YAG (S_6 symmetry) [42], where $B = 783$ cm^{-1}, $C = 3088$ cm^{-1}, $B_2^0 = 26.97$ cm^{-1}, $B_4^0 = -20.13$ cm^{-1} and $B_4^3 = 535.53$ cm^{-1}.

Table 3. The calculated CF parameters B_k^q for Cr^{3+} in $LiNbO_3$ using the SPM parameters given in text.

Site	B_2^0 (cm^{-1})	B_4^0 (cm^{-1})	B_4^3 (cm^{-1})	B_4^{-3} (cm^{-1})	$\sqrt{(B_4^3)^2 + (B_4^{-3})^2}$ (cm^{-2})
Li [19–21]	−57.76	−9.95	496.67	18.84	497.03
Nb [19–21]	−24.71	−12.8	462.41	8.06	462.48
Li [25] (congruent)	−82.77	−10.69	502.53	21.84	503.00
Nb [25] (congruent)	−22.78	−12.59	468.27	8.77	468.35

The values of the splitting of the $^4A_2$ as well as the ^2_aE level for Cr^{3+} occupying Nb and Li sites, calculated using the B_k^q-values in table 3, are listed in table 4 and table 5, respectively. The ground-state splitting $\Delta E(^4A_2)$ is to be compared with the ZFS given by $2D$, where D is the axial ZFS parameter measured by EPR [10, 43, 44]. The energy levels $^2_aE(\pm\frac{1}{2})$ and $^2_aE(\pm\frac{3}{2})$ were fitted with the two sets of R lines observed from the absorption spectra for Cr^{3+} [12], which were also confirmed by fluorescence spectra studies [7, 12, 13]. The structural vacancy site is not considered since no optical data can be fitted and its possibility has been excluded earlier (see e.g. [1, 45]). The analysis of the optical data shows that either option, i.e. Cr^{3+} occupying the Li site or Cr^{3+} occupying the Nb site, can explain the experimental data on Cr^{3+} in $LiNbO_3$. For Cr^{3+} at both Li and Nb sites our calculated energies for the $^4T_2$ level (which corresponds to $10Dq$) and the $^4T_1$ level are centred at approximately 15 000 cm^{-1} and 20 700 cm^{-1}, respectively. These values are comparable with the experimental centre values [13] of 15 300 cm^{-1} and 20 830 cm^{-1}, respectively. Because of the broadness of these two lines, no distinct experimental splittings corresponding to different Cr^{3+} centres are reported from these two transitions. However, there is sufficient evidence [7, 12, 13] from the full investigation of the very sharp R lines of Cr^{3+} to show that there are two Cr^{3+} centres present in $LiNbO_3$. Thus our results support the conclusion that Cr^{3+} substitutes at both Li and Nb sites.

The departure from C_{3v} to C_3 symmetry is described by the CF parameter B_4^{-3}. From a consideration of the algebraic symmetry of the characteristic equation of the CF Hamiltonian [29] for C_3 symmetry, it follows that the energy levels depend on the combination $|v_3|^2 \equiv (B_4^3)^2 + (B_4^{-3})^2$ only and that the optical data cannot provide separate values of the parameters B_4^{-3} and B_4^3. Thus the 'length' of the v_3 vector [29] is also calculated and included in table 3 for comparison. In fact, B_4^{-3} can be made zero in a transformed axis system rotated by an angle ϕ about the z axis [29], where the angle ϕ is determined by the relation $\tan(3\phi) = B_4^{-3}/B_4^3$. In general, our CF program yields a smaller ZFS and higher ^2_aE energy with a smaller B_4^{-3}-value, which corresponds to a smaller distortion angle α and the impurity ions positioned near the centre of the octahedron. By considering the structural data, a smaller ZFS for the Nb environment can be expected. Maintaining ^2_aE levels (R line) and $^4T_2$ levels ($\Delta = 10Dq$) of a reasonable order of magnitude, e.g. 12 000–14 000 cm^{-1} and 14 000–16 000 cm^{-1}, respectively, yields splitting of the $^4A_2$ level, i.e. the ZFS value $2D$, in the ranges 0.4–0.9 cm^{-1} and 1.1–1.9 cm^{-1} for the Nb and Li sites, respectively. The reported experimental 2D values are 0.78 cm^{-1} [5], 0.79 cm^{-1} [10], 0.82 cm^{-1} [43] and 0.84 cm^{-1} [44]. This suggests that the theoretical ZFS for Cr^{3+} substituting at the Nb site matches the ZFS obtained from the main EPR spectra [5, 10, 43, 44] well, indicating that Cr^{3+} occupying the Nb site is responsible for the main spectra. This result is similar to that of [46] from the SPM analysis of the D-value, but Martin *et al* seemingly have used the data of Abraham *et al* [19–21] obtained in 1966 although they have cited the paper of Abraham *et al* [25] published in 1986. There exists a slight difference between the two sets of structural data (those in [19–21] and those in [25]), in particular for the Li site, indicating a stronger distortion for the Li environment than for the Nb environment.

Our present results from the complete matrix diagonalization of the CF Hamiltonian can be compared with the values of $\Delta E(^4A_2)$ and $\Delta E(^2_aE)$ calculated from the perturbation theory (PT) approach [46] using Macfarlane's [47] formulae. Using the values of the trigonal field parameters ν and ν' (table 4 of [14]) recalculated from the CF parameters B_k^q in table 3, the PT calculated values of the splittings are given in tables 4 and 5. It is found that the perturbation values for $\Delta E(^2_aE)$ are rather unreliable, possibly owing to the mixing with nearby states induced by the non-cubic CF components. However, as pointed out earlier [35], the fact that the traditional second-order PT approach is inaccurate, especially for the

excited states, has been overlooked by several workers (see e.g. [7,46]). Therefore, we stress again that the PT results may be unreliable for some Cr^{3+} systems and must be verified by complete CF matrix diagonalization.

Table 4. The calculated (by CF matrix diagonalization and PT) and experimental (from [12]) values of the energy levels with respect to the ground state $^4A_2(\pm\frac{3}{2})$ and relative splittings for Cr^{3+} at the Nb site.

	Nb [19–21], calculated			Nb [25] (congruent), calculated			Experimental	
	Energy levels (cm^{-1})	Splitting (cm^{-1}) Matrix diagonalization	PT	Energy levels (cm^{-1})	Splitting (cm^{-1}) Matrix diagonalization	PT	Energy levels (cm^{-1})	Splitting (cm^{-1})
$^2_aE(\pm\frac{1}{2})$	13 810	46	31	13 821	58	42	13 812	50
$^2_aE(\pm\frac{3}{2})$	13 764			13 763			13 762	
$^4A_2(\pm\frac{1}{2})$	0.79	0.79	0.63	0.78	0.78	0.64		

Table 5. The calculated (by CF matrix diagonalization and PT) and experimental (from [12]) values of the energy levels with respect to the ground state $^4A_2(\pm\frac{3}{2})$ and relative splittings for Cr^{3+} at the Li site.

	Li [19–21], calculated			Li [25] (congruent), calculated			Experimental	
	Energy levels (cm^{-1})	Splitting (cm^{-1}) Matrix diagonalization	PT	Energy levels (cm^{-1})	Splitting (cm^{-1}) Matrix diagonalization	PT	Energy levels (cm^{-1})	Splitting (cm^{-1})
$^2_aE(\pm\frac{1}{2})$	13 760	74	55	13 737	56	40	13 762	75
$^2_aE(\pm\frac{3}{2})$	13 686			13 681			13 687	
$^4A_2(\pm\frac{1}{2})$	1.57	1.57	1.41	1.69	1.69	1.87		

5. Conclusions and discussion

The energy levels and wavefunctions of the ground state $^4A_2$ and the first excited state ^2_aE for Cr^{3+} at Li and Nb sites in $LiNbO_3$ are calculated using the SPM and the complete CF matrix diagonalization within the $3d^3$ configuration. Our results support the finding [5,7,12] that the Cr^{3+} ions occupy both Nb and Li sites simultaneously, whereas Cr^{3+} ions substituted at Nb sites give rise to the main EPR spectra observed. This is contrary to our earlier finding that the ZFS predicted by the SPM analysis of the spin Hamiltonian for Cr^{3+} ions at Li sites matches the experimental ZFS better than that predicted for Cr^{3+} at Nb sites [10]. Since the present calculations involve fitting not only the ZFS but also the energies of the ^2_aE state, the present predictions may be more reliable than the previous predictions. In view of the present results it seems that it may be necessary to take explicitly into account in the consideration [10] the distortions introduced in the $LiNbO_3$ structure by doping with Cr^{3+} ions (see below) in order to achieve better agreement with the present predictions.

Let us consider the implications of the different electronegativities [4] of the cations in $LiNbO_3$, being 0.95 and 1.7 for Li^+ and Nb^{5+}, respectively, while it is 1.6 for Cr^{3+}.

The difference between the Li and Nb positions is that Nb^{5+} is closer to the centre of the octahedron than Li^+ is. The strong Nb–O bond is also confirmed by the structural studies of $LiNbO_3$ in the paraelectric phase, where Li^+ is situated at the centre of the oxygen triangle, while Nb^{5+} is at the centre of the oxygen octahedron. It is well known that Cr^{3+} and other transition-metal ions prefer the octahedral oxygen positions, forming CrO_6 clusters. We can therefore conclude, as Glass [4], that Cr^{3+} prefers Nb^{5+} sites [8,44]. There are two kinds of Nb site in $LiNbO_3$, namely the normal Nb sites and the Nb/Li 'antisites', i.e. Nb ions occupying vacant Li sites. Keeping in mind the large concentration (5.9%) of the antisites and their importance for the mechanism of the resistance to photorefraction [48], we maintain that Cr^{3+} ions substitute for Nb ions at the two kinds of Nb site. Since chromium is introduced during growth, we cannot determine whether, if chromium was not there, the site would be occupied by Li or Nb. However, when a Cr^{3+} ion enters an Nb site or an Nb/Li 'antisite', it is reasonable to expect that an additional distortion due to charge disparity of the environment will appear since the less positively charged Cr^{3+} ion will tend to interact with the nearby O^{2-} ligands differently from the way in which Nb^{5+} ions do. This may result in increased values of R_2 and θ_2 (see table 2). This partially explains why we cannot obtain good fitting on the assumption that Cr^{3+} is at the Li^+ site (as would be required to reconcile the present predictions with the earlier predictions [10]), whereas the assumption of Cr^{3+} at the Nb^{5+} site yields satisfactory agreement with the optical data as well as with the predicted ZFS.

On the other hand, some researchers have recently suggested that there are two centres for Cr^{3+} in $LiNbO_3$, which is also in accordance with the fact that the possibility for Cr^{3+} at Li sites is reduced after Mg doping [13]. However, there are still some contradictions between EPR and optical results, as well as between the results of various workers analysing the main EPR spectra. We suggest that the lattice relaxation model [49] may be useful in gaining a better understanding of the Cr^{3+} defect structure in $LiNbO_3$. Lattice relaxation must occur around the impurity, and the surrounding atom arrangement is not exactly the same as around a 'normal' Li or an Nb antisite. Study of the lattice relaxation may help to differentiate better between the various possible models of the site occupancy of Cr^{3+} ions in $LiNbO_3$.

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Appendix

The wavefunctions $|^{2S+1}L,\ M_S,\ M_L\rangle$ of the ground state $^4A_2$ are listed in table A1. The spin–orbit coupling and the CF terms induce a mixing of the free-ion states. Full computer outputs in either the $|^{2S+1}L,\ M_S,\ M_L\rangle$ basis or the $|^{2S+1}L,\ J,\ M_J\rangle$ basis are available from the authors upon request.

Table A1. The wavefunctions of the ground state $^4A_2$.

$^4A_2(+\frac{3}{2})$					
(−0.002 284 + i0.000 051)(4P	−1.5	0⟩	(−0.063 253 + i0.002 362)(4P	1.5	0⟩
(−0.017 271 + i0.000 709)(4F	−1.5	−3⟩	(−0.497 973 + i0.027 944)(4F	1.5	−3⟩
(0.005 139 − i0.000 289)(4F	0.5	−2⟩	(−0.025 953 + i0.000 580)(4F	−1.5	0⟩
(−0.718 206 + i0.026 822)(4F	1.5	0⟩	(0.009 982 − i0.000 373)(4F	0.5	1⟩
(0.018 018 − i0.000 065)(4F	−1.5	3⟩	(0.478 540 − i0.008 902)(4F	1.5	3⟩
(0.005 261 − i0.000 295)(2D1	0.5	−2⟩	(0.004 066 − i0.000 152)(2D1	0.5	1⟩
(−0.005 759 + i0.000 323)(2D2	0.5	−2⟩	(−0.004 016 + i0.000 150)(2D2	0.5	1⟩
(−0.003 204 + i0.000 120)(2F	0.5	1⟩	(0.005 821 − i0.000 217)(2G	0.5	1⟩
(−0.006 433 + i0.000 120)(2G	0.5	4⟩			
$^4A_2(-\frac{3}{2})$					
(0.063 252 − i0.002 373)(4P	−1.5	0⟩	(−0.002 281 + i0.000 120)(4P	1.5	0⟩
(0.477 867 − i0.026 894)(4F	−1.5	−3⟩	(−0.017 973 + i0.001 282)(4F	1.5	−3⟩
(−0.009 982 + i0.000 374)(4F	−0.5	−1⟩	(0.718 201 − i0.026 939)(4F	−1.5	0⟩
(−0.025 924 + i0.001 362)(4F	1.5	0⟩	(0.005 146 − i0.000 096)(4F	−0.5	2⟩
(−0.498 668 + i0.009 358)(4F	−1.5	3⟩	(0.017 276 − i0.000 584)(4F	1.5	3⟩
(−0.004 066 + i0.000 153)(2D1	−0.5	−1⟩	(0.005 269 − i0.000 099)(2D1	−0.5	2⟩
(0.004 016 − i0.000 151)(2D2	−0.5	−1⟩	(−0.005 767 + i0.000 108)(2D2	−0.5	2⟩
(−0.003 204 + i0.000 120)(2F	−0.5	−1⟩	(−0.006 424 + i0.000 362)(2G	−0.5	−4⟩
(−0.005 821 + i0.000 218)(2G	−0.5	−1⟩			
$^4A_2(+\frac{1}{2})$					
(−0.063 218 + i0.001 184)(4P	0.5	0⟩	(−0.491 913 + i0.018 434)(4F	0.5	−3⟩
(0.005 817 − i0.000 218)(4F	−0.5	−2⟩	(0.010 052 − i0.000 188)(4F	1.5	−1⟩
(−0.719 235 + i0.013 471)(4F	0.5	0⟩	(0.011 576 − i0.000 217)(4F	−0.5	1⟩
(−0.004 927 + i0.000 000)(4F	1.5	2⟩	(0.485 547 − i0.000 000)(4F	0.5	3⟩
(0.002 978 − i0.000 112)(2D1	−0.5	−2⟩	(−0.004 197 + i0.000 079)(2D1	0.5	0⟩
(0.002 440 − i0.000 046)(2D1	−0.5	1⟩	(−0.003 254 + i0.000 122)(2D2	−0.5	−2⟩
(0.004 867 − i0.000 091)(2D2	0.5	0⟩	(−0.002 431 + i0.000 046)(2D2	−0.5	1⟩
(−0.002 012 + i0.000 000)(2F	0.5	3⟩	(0.002 493 − i0.000 093)(2G	0.5	−3⟩
(0.005 286 − i0.000 099)(2G	0.5	0⟩	(0.003 287 − i0.000 062)(2G	−0.5	1⟩
(−0.002 471 + i0.000 000)(2G	0.5	3⟩	(−0.003 825 + i0.000 000)(2G	−0.5	4⟩
$^4A_2(-\frac{1}{2})$					
(0.063 184 − i0.002 368)(4P	−0.5	0⟩	(0.484 781 − i0.027 266)(4F	−0.5	−3⟩
(−0.004 919 + i0.000 277)(4F	−1.5	−2⟩	(−0.011 570 + i0.000 434)(4F	0.5	−1⟩
(0.718 856 − i0.026 938)(4F	−0.5	0⟩	(−0.010 046 + i0.000 376)(4F	−1.5	1⟩
(0.005 820 − i0.000 109)(4F	0.5	2⟩	(−0.492 172 + i0.009 218)(4F	−0.5	3⟩
(−0.002 439 + i0.000 091)(2D1	0.5	−1⟩	(0.004 195 − i0.000 157)(2D1	−0.5	0⟩
(0.002 980 − i0.000 056)(2D1	0.5	2⟩	(0.002 429 − i0.000 091)(2D2	0.5	−1⟩
(−0.004 865 + i0.000 182)(2D2	−0.5	0⟩	(−0.003 256 + i0.000 061)(2D2	0.5	2⟩
(0.002 009 − i0.000 113)(2F	−0.5	−3⟩	(−0.003 819 + i0.000 215)(2G	0.5	−4⟩
(−0.002 467 + i0.000 139)(2G	−0.5	−3⟩	(−0.003 286 + i0.000 123)(2G	0.5	−1⟩
(−0.005 283 + i0.000 198)(2G	−0.5	0⟩	(0.002 494 − i0.000 047)(2G	−0.5	3⟩

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