Dedicated to Professor Ioan-Iovitz Popescu's 80th Anniversary

CRYSTAL FIELD ANALYSIS AND LOW LYING ENERGY LEVELS FOR Cr^{3+} DOPED IN $LiNbO_3$

N.M. AVRAM[1, 2], M.G. BRIK[3], C.N. AVRAM[1], M.G. CIRESAN[1] and L. ANDREICI[1]

[1] West University of Timisoara, Department of Physics, Bd. V. Parvan 4, Timisoara 300223, Romania
[2] Academy of Romanian Scientists, Splaiul Independentei 54, Bucharest 050094,Romania
[3] University of Tartu, Institute of Physics, Riia 142, Tartu 51014, Estonia

Abstract. Due to its numerous optical applications, Cr^{3+}-doped lithium niobate $LiNbO_3$ is an extensively studied material. Despite a large number of the experimental and theoretical studies of this system, still there exists an ambiguity regarding the nature of the Cr^{3+} impurity centers. In the present work we report on the detailed crystal field parameters and energy levels calculations of the Cr_{Li}^{3+} positions. The exchange charge model of crystal field was used to calculate the crystal field parameters with taking into account the effects of the covalent bond formation between the Cr^{3+} and O^{2-} ions. The calculated CFP values were used for diagonalization of the Cr^{3+} crystal field Hamiltonian in a complete basis set spanned by all wave functions of LS terms of the $3d^3$ electron configuration. The calculated energy levels are in good agreement with the experimental data available in the literature.

Key words: crystal field, energy levels, Cr^{3+}, $LiNbO_3$.

1. INTRODUCTION

$LiNbO_3$ is an important material, whose ferroelectric, piezoelectric, electro-optical, non-linear optical and photorefractive properties are widely used in many applications in integrated optics (for modulators, wave length filters and low-loss optical waveguides [1–6]). $LiNbO_3$ crystal can be easily doped with impurity ions, such as transition metals and rare earth ions like Cr^{3+}, Mn^{2+}, Fe^{3+} or Nd^{3+} [7–10], which allows for potential applications in the laser technology. Such impurities are responsible for modifications of the optical properties of crystals required for particular laser applications [11–13 and references therein]. Below ferroelectric Curie point ($T_C \sim 1480K$) the $LiNbO_3$ crystal structure belongs to the R3c (C_{3v}^6) space group with two $LiNbO_3$ molecules in its rhombohedral elementary unit cell. All sites along the z (or optical c) axis of the crystal, including the site of Li, Nb and the octahedral structural vacancy (SV), have the C_3 (which is very close to C_{3v}) local symmetry [14].

The Li^+ ions and the Nb^{5+} ions are distributed alternatively along the C_3 axis of the crystal. In the [111] direction, the cations are distributed in the octahedra in the following sequence: Nb, vacancy, Li, Nb, vacancy, Li, etc. [14]. In the ferroelectric phase, the Li and Nb ions and SV are surrounded by six oxygens in a distorted octahedra and lie along the C_3 axis but displaced away from the centre of the octahedron. The upper and lower oxygen triangles of the octahedron are rotated with respect to each other by an angle φ. As a result, the C_{3v} symmetry of the octahedron is lowered to C_3 symmetry. The sizes of the octahedrons surrounding the Li and Nb ions are almost the same; the only difference is the extent of the distortion, expressed by angle φ. For the Li octahedrons $\varphi = 3°49'$, while the Nb octahedron has a smaller value of $\varphi = 0°41'$ [14]. This means that the Li octahedron is more distorted, thus favoring the electric dipole transitions. Since the impurity ions can influence strongly the properties of $LiNbO_3$ crystals, detailed knowledge of the location of the impurity and the defect structure of the impurity center is very important. Particularly, Cr^{3+}-doped $LiNbO_3$ crystals have been widely investigated because their lasing properties are closely related to the local structure and electronic behavior of the Cr^{3+} impurity. The nature of the Cr^{3+} luminiscent centers in $Cr^{3+}:LiNbO_3$ has been the subject of intense and some times controversial debate for a number of years. Comparing the ionic radius of Li^+ and Nb^{5+} being 0.68 Å and 0.69 Å, respectively, and that of Cr^{3+} (0.63 Å), it appears that Cr^{3+} ion is as likely to enter the Li^+ sites as the Nb^{5+} sites.

Present interpretation (see *e.g.* [15–16 and references therein]), based also on EPR data, assumes that the "main" (dominant in concentration) Cr^{3+} centers in $LiNbO_3$ crystals correspond to Cr^{3+} ions substituting regular Li^+ sites (Cr_{Li}^{3+}) in the host lattice. Most of the studies of Cr^{3+} ions in congruent $LiNbO_3$ co-doped with Mg (concentration higher than 4.5 mol %) report that a fraction of the Cr^{3+} ions tends to additionally occupy Nb^{5+} sites (Cr_{Nb}^{3+}) [16]. In both cases the local environment around the Li and Nb cations is a trigonally distorted octahedron of six O^{2-} ions: $[CrO_6]^{9-}$. The charge compensation, in both cases, can be achieved by co-doping with Mg^{2+} (when Nb^{5+} position is occupied), or by creation of the oxygen vacancies, or by dimeric $Cr^{3+}-Cr^{3+}$ charge compensation mechanism. In each case (Li^+ and Nb^{5+}), exact determination of the ions positions around impurity could be obtained as a combination of the high-resolution spectroscopy and ab initio calculations (which is beyond the scope of the present study).

Optical properties of Cr^{3+} centers in $LiNbO_3$ are complicated due to the formation of multiple Cr^{3+} sites in the crystal lattice, and in a few cases overlapping, optical transitions caused by intrinsic lattice defects [15, 18]. At normal hydrostatic pressure the main Cr^{3+} centers in $LiNbO_3$, in both stoichiometric and congruent samples, correspond to low field sites. This conclusion is consistent with all published experimental data [15–18]. For these centers, the electronic $^2E(t^3)$ level lie above, but close to, respective $^4T_2$ (t^2e) zero phonon line. This assessment is further confirmed by life time measurements,

which reveal a relaxation time of 8 μs, which is typical for the spin allowed $^4T_2$ - $^4A_2$ emission transition.

The main aim of the present work is to perform detailed modeling of the crystal field parameters and simulation the low lying energy levels of the Cr_{Li}^{3+} centers in Cr^{3+}:$LiNbO_3$ samples, in order to give a reliable explanation for experimental data from Refs. [15] and [17]. The exchange charge model (ECM) [19] of crystal field was used to calculate the crystal field parameters (CFP) with taking into account the effects of the covalent bond formation between the Cr^{3+} and O^{2-} ions. The CFP values were used for diagonalization of the Cr^{3+} Hamiltonian in a complete basis set spanned by all wave functions of LS terms of the $3d^3$ electron configurations. The calculated energy levels were compared with experimental data available in the literature.

2. ENERGY LEVEL SCHEME FOR Cr_{Li}^{3+} Doped In $LiNbO_3$

Energy levels of an impurity ion with unfilled d-shell in a crystal field of an arbitrary symmetry can be represented by the eigenvalues of the following crystal field Hamiltonian [19]:

$$H = \sum_{p=2,4} \sum_{k=-p}^{p} B_p^k O_p^k ,$$ (1)

where O_p^k are the linear combinations of irreducible tensor operators acting on the angular parts of the $3d$-ion wave functions, and B_p^k are the CFP containing all information about geometrical arrangement of the ligands around the central ion. Following [19], these parameters can be written as a sum of two terms:

$$B_p^k = B_{p,q}^k + B_{p,S}^k .$$ (2)

The former contribution originates from the electrostatic interaction between the valence electrons of an impurity ion and ions of crystal lattice (treated as the point charges, without taking into account their electron structure). The latter is proportional to the overlap of the wave functions of the impurity ion and ligands; it includes effects of the covalent bond formation and exchange interaction. Inclusion of these effects significantly improves an agreement between the calculated and experimentally observed energy levels. The analytical expressions for calculating both contributions to the CFP in the case of $3d$-ion is as follows [19]:

$$B_{p,q}^k = -K_p^k e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k(\theta(i),\varphi(i))}{R(i)^{p+1}} ,$$ (3)

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i \left(G_s S_s(i)^2 + G_\sigma S_\sigma(i)^2 + \gamma_p G_\pi S_\pi(i)^2 \right) \frac{V_p^k(\theta(i),\varphi(i))}{R(i)} .$$ (4)

The sums are carried out over lattice ions denoted by i with charges q_i (expressed in units of the electron charge e); $R(i)$, $\theta(i)$, $\varphi(i)$ are the spherical coordinates of the i-th ion of crystal lattice in the system of reference centered at the impurity ion. The averaged values $\langle r^p \rangle$ of p-th power of the impurity ion electron radial coordinate can be calculated using the wave functions of the $3d$-ions given in [20]. The values of the numerical factors K_p^k, γ_p and expressions for the polynomials V_p^k are all given in [19]. S_s, S_σ, S_π stand for the overlap integrals between the d-functions of the central ion and p- and s-functions of the ligands (they correspond to the following integrals (in the $\langle lm|l'm' \rangle$ notation): $S_s = \langle d0|s0 \rangle$, $S_\sigma = \langle d0|p0 \rangle$, $S_\pi = \langle d1|p1 \rangle$). G_s, G_σ, G_π are dimensionless adjustable parameters of the model determined from the positions of the first three absorption bands. For practical purposes, it is sufficient to assume them to be equal to each other: $G_s = G_\sigma = G_\pi = G$ (in this case only the first absorption band is required to determine the value of G); this simplified model is used in the present paper. The strong advantage of the ECM is that if the G parameter is determined to fit the first absorption band, the other energy levels, located higher in energy, will also fit experimental spectra fairly well. The ECM has been successfully applied for the calculations of the energy levels of both rare earth [19, 21–23] and transition metal ions in different hosts as well [24–31].

When calculating CFP, a special attention should be paid to the convergence of the lattice sums in Eq. (3). As a first approximation, it is possible to consider the nearest ligands only, but since the second rank point charges parameters $B_{2,q}^k$ decrease not so fast as the fourth rank parameters $B_{4,q}^k$ (as $1/R^3$ and $1/R^5$, respectively), the contribution of the ligands from the second and further coordination spheres can be quite significant. To increase accuracy in calculating the point charge contribution to the CFP, a large cluster consisting of 1 Cr^{3+} ion, 3343 Li^{2+} ions, 3344 Nb^{5+} ions and 9216 O^{2-} ions were considered. This cluster enables to take into account the contribution of ions located at the distances at least up to 55 Å from the central ion. For the exchange charge parameters (Eq. (4)) only the nearest ligands were taken into account, since the overlap between an impurity ion and ligands from other than the first coordination sphere can be safely neglected. The overlap integrals between the Cr^{3+} and O^{2-} ions needed for calculating the exchange charge contribution $B_{p,S}^k$ to the CFP were computed numerically using the radial wave functions of the above mentioned ions given in [20]. The dependences of the overlap integrals on the inter ionic distance r (r is measured in atomic units) approximated by the exponential functions are [30] $S_s = \langle d0|s0 \rangle = -0.90111\exp(-0.59683r)$, $S_\sigma = \langle d0|p0 \rangle = 0.83835\exp(-0.64118r)$, $S_\pi = \langle d1|p1 \rangle = 1.54570\exp(-0.91718r)$, $\langle r^2 \rangle = 1.43402$ and $\langle r^4 \rangle = 4.262822$ (both in au). The CFP values were obtained by using Eqs. (2) – (4), above exponential

functions for the overlap integrals and crystal structure data from [14] (which enable to get the Cartesian coordinates of the ligands in the system of reference defined with respect to the crystallographic axes) are shown in Table 1. Analysis of the CFP values confirms predominantly trigonal symmetry of the Cr_{Li}^{3+} position, since the main contribution to the crystal field Hamiltonian comes from the B_2^0, B_4^0, B_4^3, B_4^{-3} CFP. Non-zero values of some other CFP are merely computational artifacts, which arise from contribution of ions from further coordination spheres and were neglected.

Table 1

CFP (in cm^{-1}) for octahedral coordinated Cr^{3+} ion in $LiNbO_3$. The point charges contribution (PCC) and exchange charges contribution (ECC) are shown separately. In last line is given the Racah parameters B and C, and the G parameter of ECM used during diagonalization the Hamiltonian (1)

Parameters	PCC (cm^{-1})	ECC (cm^{-1})	Total values (cm^{-1})
B_2^0	-1026	-2501	-3527
B_4^{-3}	-2485	3734	1249
B_4^0	-307	-1026	-1333
B_4^3	-11188	-63220	-74408
$B = 566$ cm^{-1}	$C = 3408$ cm^{-1}	$G = 5.834$	

The crystal field Hamiltonian (1) was diagonalized in the space spanned by all 120 wave functions of the $3d^3$ electron configuration. The adjustable parameter G was defined by fitting the calculated position of the first spin-allowed $^4A_{2g} - {}^4T_{2g}$ absorption band. Finally, the obtained energy levels are listed in Table 2. Only the lowest energy levels are shown in the table, since they can be directly compared with the experimental data.

Table 2

Crystal field splittings of the lowest terms (in cm^{-1}) for Cr_{Li}^{3+} in $LiNbO_3$

O_h irred. repres.	Experimental values (cm^{-1}) [15]	Calculated (this work) (cm^{-1})	Baricenter (cm^{-1})
$^4A_{2g}$ (^4F)	0	0	0
$^4T_{2g}$ (^4F)	13540	13382 13384 13853	13540
^2E_g (^2G)	13790	13789 13792	13791
$^2T_{1g}$ (^2G)	14050	14628 15147 15147	14974
$^4T_{1g}$ (^4F)	19140	18111 18113 21286	19170

Comparing the calculated results in ECM of crystal field with the experimental data shows good agreement between two sets of energy levels, which confirms the validity of the used model and thus explains the order of the lowest energy levels for Cr_{Li}^{3+} in $LiNbO_3$. Indeed, the low crystal field case (when the first excited state is the spin-quartet $^4T_{2g}$) describes adequately the experimental spectroscopic results.

3. CONCLUSIONS

In the present work we report on the detailed crystal field parameters modeling and the simulation of the low lying energy levels for Cr_{Li}^{3+} in $LiNbO_3$. The exchange charge model (ECM) was used to calculate the crystal field parameters (CFP) with taking into account the effects of the covalent bond formation between the Cr^{3+} and O^{2-} ions. The influence of the C_3 low-symmetry component of crystal field on the splitting of the Cr^{3+} energy levels was also considered. The calculated CFP values were used for diagonalization of the Cr^{3+} Hamiltonian in a complete basis set spanned by all wave functions of the LS terms of a $3d^3$ electron configuration. The calculated energy levels agree with the experimental data available in the literature. Thus, the ECM model represents an adequate frame for explanation the experimental data for Cr_{Li}^{3+} :$LiNbO_3$ system with low crystal field model.

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