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Theoretical calculations of energy levels scheme of Cr^{3+} - doped $LiAl_5O_8$ spinel

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Crystal field (CF) analysis of the energy levels scheme of Cr^{3+} ion doped in $LiAl_5O_8$ spinel is performed. Using the crystal structure data and exchange charge model of CF, the CF parameters were calculated and Cr^{3+} CF Hamiltonian was diagonalized in the basis set spanned by 120 wave functions of all 8 LS terms of Cr^{3+} ion. The obtained energy levels and estimated Racah parameters *B* and *C* were compared with experimental spectroscopic data for the $LiAl_5O_8$:Cr^{3+} crystal; good agreement has been demonstrated.

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1. Introduction

Lithium aluminate ($LiAl_5O_8$) with an inverse spinel structure has interesting optical properties. This material, when doped with transitional metal ions, such as Ni^{2+}[1], Fe^{3+} [2,3], Co^{2+}[4], Mn^{2+} [5], is known as rather efficient phosphor material. Triply ionized state (Cr^{3+}) is the most stable state of chromium ions; after crystal field splitting, all 8 LS terms of the $3d^3$ electron configuration give rise to a number of energy levels, which make Cr^{3+} a suitable dopant material in various opto-electronic devices [6-8] and, in particular, in solid-state laser crystals [9]. Cr^{3+}-doped inverse spinel $LiAl_5O_8$ crystal exhibits unusual magnetic properties, which open possible important applications in microwave techniques, holography and cathode battery [5-and reference therein]. The ordered phase of $LiAl_5O_8$ doped with transition metal and rare earth ions, was a subject of many research works devoted to its optical properties [11–19].

Nevertheless, it should be pointed out that reports on the consistent crystal field (CF) analysis of Cr^{3+} doped $LiAl_5O_8$ crystals with calculations of crystal field parameters (CFPs) from structural data and energy levels scheme are scarce.

In this paper we present the results of application of the exchange charge model (ECM) of CF [20] to the calculation of the crystal field parameters (CFPs) and energy levels scheme of the Cr^{3+} ion doped in $LiGa_5O_8$ spinel.

The paper is organized as follows: in the next section a short review of crystallographic data for considered crystal is given. Then we proceed with a brief description of the calculating technique and discussion of the obtained results. Finally, the paper is concluded with a short summary.

2. Crystal structure of $LiAl_5O_8$ crystal

At room temperature $LiAl_5O_8$ crystallizes in an inverse spinel structure, with space group $P4_332$, lattice constant 7.908 Å and four formula units in one unit cell [11] (Fig. 1).

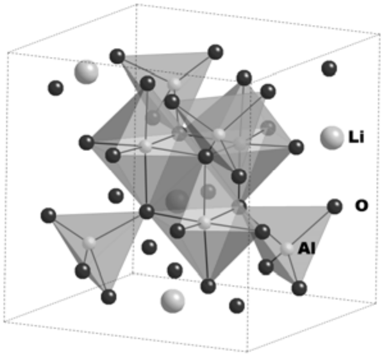

Fig. 1. Crystal structure of $LiAl_5O_8$. Two kinds of coordination polyhedra around Al^{3+} ions (tetrahedrons and octahedrons) are shown.

After doping Cr^{3+} ions substitute for Al^{3+} ions (it should be noted here that there are two inequivalent aluminum positions: octahedral and tetrahedral) [11]. Cr^{3+} ions show preference to substitute for Al^{3+} ions at the octahedral sites with C_2 site symmetry. The lattice distortion caused by this substitution is minimal because of the closeness of ionic radii of Al^{3+} and Cr^{3+}. No charge compensation is needed, since electrical charges of both ions are equal.

3. Modeling of crystal field effects and calculation of energy levels scheme for Cr^{3+} in $LiAl_5O_8$

The energy levels scheme of 3*d* electrons of the Cr^{3+} ions in a CF field will be calculated using the following crystal field Hamiltonian [20]:

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

where O_p^k are the linear combinations of spherical operators (which act on the angular parts of a 3*d* ion wave functions), and B_p^k are Crystal Field Parameters (CFPs) containing all information about geometrical structure of an impurity center. Salient feature of the Exchange Charge Model (ECM) is that these parameters can be written as a sum of two terms [20]:

$$B_p^k = B_{p,q}^k + B_{p,S}^k . \tag{2}$$

The first contribution arises from the electrostatic interaction between a 3*d* ion and ions of crystal lattice (treated as the point charges, without taking into account their electronic structure), and the second one is proportional to the overlap of the wave functions of a central ion and ligands. This term accounts for all effects of the covalent bond formation and exchange interaction, and inclusion of these effects significantly improves agreement between the calculated and experimentally observed energy levels. Expressions for calculating both contributions to the CFPs in the case of 3*d*-ion are as follows [20]:

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

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i \left(G_s S(s)_i{}^2 + G_\sigma S(\sigma)_i{}^2 + \gamma_p G_\pi S(\pi)_i{}^2 \right) \frac{V_p^k\left(\theta_i,\varphi_i\right)}{R_i} \tag{4}$$

In these equations the crystal lattice ions enumerated by index i with charges q_i and spherical coordinates R_i, θ_i, φ_i (with the reference system centered at the impurity ion itself). The averaged values $\left\langle r^p \right\rangle$, with r being the radial coordinate of the *d* electrons of the impurity ion, can be obtained either from the literature or calculated numerically, using the radial parts of the corresponding ion's wave functions. The values of the numerical factors K_p^k, γ_p , the expressions for the polynomials V_p^k and the definitions of the operators O_p^k can all be found in Ref. [20]. $S(s), S(\sigma), S(\pi)$ in Eq. (4) correspond to the overlap integrals between the *d*-functions of the central ion and *p*-, *s*-functions of ligands: $S(s) = \left\langle d0 | s0 \right\rangle, S(\sigma) = \left\langle d0 | p0 \right\rangle, S(\pi) = \left\langle d1 | p1 \right\rangle$ (here the $\left\langle lm \right|$ notation is employed, where *l* and *m* are the orbital and magnetic quantum numbers, respectively). The G_s, G_σ, G_π entries are the dimensionless adjustable parameters of the model, whose values are determined from the positions of the first three absorption bands in the experimental spectrum by a direct matching calculated energy levels to those deduced from the experimental spectra. They can be approximated to a single value, i.e. $G_s = G_\sigma = G_\pi = G$, which then can be estimated from one absorption band only.

Numerous applications of the ECM to the analysis of rare-earth [21-23] and transition metal [24-29] doped crystals show this model to be a powerful and reliable tool for modelation, analysis and interpretation of crystal field effects and optical absorption spectra.

The CFPs were calculated using the ionic positions obtained from structural data [11]. To ensure convergence of CFPs (especially those ones of the second rank), a large cluster consisting of 65449 ions was taken into account. The overlap integrals between Cr^{3+} and O^{2-} ion were calculated numerically [30] and given in Table 1.

Table 1. Overlap integrals between Cr^{3+} and O^{2-} ions in $LiAl_5O_8$ (3.0< r < 4.0 atomic units) and averaged values of $\left\langle r^2 \right\rangle$ and $\left\langle r^4 \right\rangle$ (in a.u.) calculated with wave functions from Ref. [31].

$S_s = \left\langle d0 \vert s0 \right\rangle$	$-0.90111\exp(-0.59683r)$
$S_\sigma = \left\langle d0 \vert p0 \right\rangle$	$0.83835\exp(-0.64118r)$
$S_\pi = \left\langle d1 \vert p1 \right\rangle$	$1.54570\exp(-0.91718r)$
$\left\langle r^2 \right\rangle$	1.43402
$\left\langle r^4 \right\rangle$	4.262822

The calculated CFPs values are shown in Table 2 (the point charge and exchange charge contributions are denoted by PCC and ECC, respectively, and are shown separately, to stress out importance of the covalent effects in this host).

Table 2. Crystal field parameters (in cm^{-1}) for Cr^{3+} in $LiAl_5O_8$

Parameter	PCC	ECC	Total value
B_2^{-2}	385.9	191.3	577.2
B_2^{-1}	-742.1	-101.9	-844.0
B_2^0	-63.7	330.9	267.2
B_2^1	-3079.0	2943.7	-135.3
B_2^2	89.3	997.1	1086.4
B_4^{-4}	-218.9	-712.9	-931.8
B_4^{-3}	-13598.4	-33304.3	-46902.7
B_4^{-2}	3127.8	7600.5	10728.3
B_4^{-1}	1917.2	4848.1	6765.3
B_4^0	-747.3	-1859.0	-2606.3
B_4^1	-2003.1	-4611.3	-6614.4
B_4^2	205.8	644.3	850.1
B_4^3	-15788.4	-38748	-54536.4
B_4^4	-2831.3	-7066.3	-9897.6
	G=2.26	B=648 cm^{-1}	C=3120 cm^{-1}

The ECM parameter G was determined using the experimental data on the splitting of the ground ^4F term, in particular, position of the first absorption band [17]. The chosen values of the Racah parameters *B* and *C*, which provide the best agreement with experimental data, are also given in Table 2. The main contribution of the ECC to CFPs serves as a firm justification of application of ECM for Cr^{3+}: $LiAl_5O_8$.

The obtained values of CFPs were used to diagonalize the crystal field Hamiltonian (1) in the space spanned by all 120 wave functions of LS terms of Cr^{3+} ion (^4P, ^4F, $^2PD_{(1,2)}FGH$). Spin-orbit interaction was not considered, since the absorption bands in the experimental spectra are broad and no fine structure is observed. The calculated energy levels are shown in Table 3.

Table 3. Observed and calculated (this work) low-lying energy levels (in cm^{-1}) of Cr^{3+} ion in $LiGa_5O_8$.

Energy levels (O_h group notations)	This work			
	Calculated	Averaged	Observed [17]	Calculated [18]
$^4A_{2g}$	0	0	0	0
$^2E_{2g}$	14117 14153	14135	14126	14420
$^2T_{1g}$	14437 14763 14847	14682	15018	15268
$^4T_{2g}$	17180 17410 17826	17472	17470	17689
$^2T_{2g}$	21330 21574 21680	21528	21247	21343
$^4T_{1g}$	23300 24338 24617	24085	24080	25385
$^2A_{1g}$	29363	29363	_	29512

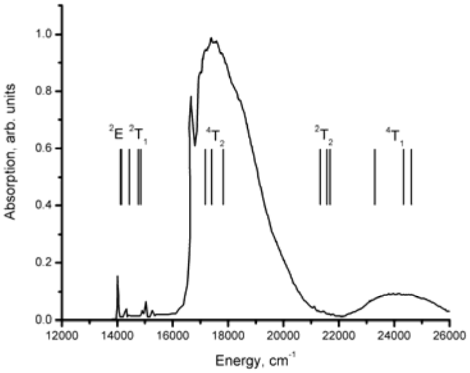

Fig. 2. Comparison of the experimental excitation spectrum (solid line), [17] and calculated energy levels (vertical lines) of Cr^{3+} in $LiAl_5O_8$.

As seen from this Table, the calculated values are in good agreement with experimental data. They are closer to the experimental values than those from Ref. [18] obtained by fitting experimental data. The covalence effects play an essential role in the considered system. It can be revealed by using the following non-dimensional quantity

$$\beta = \frac{1}{2}\sqrt{\left(\frac{B_1}{B_0}\right)^2 + \left(\frac{C_1}{C_0}\right)^2}, \qquad (5)$$

where the subscripts “1” and “0” are related to the values of the Racah parameters in a crystal and in a free state, respectively. This quantity can serve as a qualitative measure of the nephelauxetic effect (significant decrease of the Racah parameters for 3d ions in a crystal with respect to those in a free state). For free Cr^{3+} ion these parameters are $B_0 = 918$ cm^{-1}, $C_0 = 3850$ cm^{-1} [32]. With the values of B, C parameters from Table 2 the obtained value for β is 0.62, which means that the covalence effect is “strong“ in this system and contribution to CFP given by Eq.(3) is important.

Fig. 2 visualizes good agreement between the calculated energy levels for Cr^{3+} in $LiAl_5O_8$ and experimental absorption spectrum [17]; calculated positions of the energy levels agree well with the main absorption peaks, and the widths of the absorption bands correlates with low-symmetry splitting of the orbital triplets.

4. Conclusions

In the present paper consistent calculations of the CFPs values and energy levels for Cr^{3+} ions in the spinel crystal $LiAl_5O_8$ were performed using the ECM of crystal field. For the first time for the considered crystal the CFPs values were calculated from crystal structure data, with taking into account low symmetry component of crystal field. It should be emphasized that no a priori assumption about the symmetry of the Cr^{3+} position were superimposed. The calculated energy levels (including splitting of the orbital triplets) match well available in the literature absorption spectra. Calculated complete energy level schemes can be used for analysis of the Cr^{3+} excited state absorption in the considered spinel, and the sets of CFPs can be used as initial (starting) sets for analysis of Cr^{3+} energy levels in other isostructural crystals.

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