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Crystal Field Analysis of Cr^{3+} Energy Levels in $LiGa_5O_8$ Spinel

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Detailed and consistent crystal field analysis of the $LiGa_5O_8$:Cr^{3+} absorption spectrum is performed in the present paper by using the exchange charge model of crystal field. We calculate the crystal field parameters from the crystal structure date and diagonalize the crystal field Hamiltonian to obtain the energy level structure of Cr^{3+} ions in $LiGa_5O_8$. The obtained energy levels and estimated Racah parameters B and C were compared with the experimental spectroscopic data; good agreement was demonstrated.

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1. Introduction

Cr^{3+}-doped inverse lithium gallium spinel ($LiGa_5O_8$) crystal is a material with interesting magnetic and luminescence properties [1–6].

This crystal has important applications in microwave technique, holography, cathode battery, and optical devices [5]. There are a lot of studies in the literature ([7] and references therein) regarding various aspects related to the Cr^{3+}-doped crystals. Nevertheless, it should be pointed out that the reports on the consistent crystal field analysis of Cr^{3+}-doped $LiGa_5O_8$ crystals with calculations of crystal field parameters (CFPs) from structural data are scarce.

In this paper we present the results of application of the exchange charge model (ECM) of crystal field [8] to the calculation of the CFPs and energy levels for Cr^{3+} ion in $LiGa_5O_8$ spinel.

The paper is organized as follows: in the next section a short review of the crystallographic data for the 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.

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2. Crystal structure of $LiGa_5O_8$

$LiGa_5O_8$ crystallizes in an inverse spinel structure [9], with space group $P4332$, lattice constant is 8.203 Å; there are 4 formula units in one unit cell [10]. After doping Cr^{3+} ions substitute for Ga^{3+} ions (it should be noted here that there are two inequivalent gallium positions: octahedral, and tetrahedral, with Ga–O distance 1.776 Å [10]). Cr^{3+} ions show preference to substitute for Ga^{3+} ions at the octahedral sites with site symmetry C_2. The lattice distortion caused by this substitution is minimal because of the closeness of ionic radii: 0.62 and 0.63 Å for $Ga^{3+}$and Cr^{3+}, respectively. No charge compensation is needed, since electrical charges of both ions are equal.

3. Exchange charge model of crystal field

The energy levels of $3d$ electrons of the Cr^{3+} ions in a crystal field will be calculated using the following crystal field Hamiltonian [8]:

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

where O_p^k are the linear combinations of spherical operators (which act on the angular parts of a $3d$ ion wave functions), and B_p^k are CFPs containing all information about geometrical structure of an impurity center. Salient feature of the ECM is that these parameters can be written as a sum of two terms [8]:

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

The first contribution arises from the electrostatic interaction between a $3d$ ion and ions of crystal lattice (treated as the point charges, without taking into account their electron 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 $3d$-ion are as follows [8]:

$$B_{p,q}^k = -K_p^k e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k(\theta_i, \varphi_i)}{R_i^{p+1}}, \tag{3}$$

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

The sums are carried out over lattice ions denoted by i with charges q_i; R_i, θ_i, φ_i are the spherical coordinates of the i-th ion of crystal lattice in the system of reference centered at the central ion. The averaged values $\langle r^p \rangle$ of p-th power of the central ion electron radial coordinate can be found in the literature or calculated numerically. The values of the numerical factors K_p^k, γ_p and expressions for the polynomials V_p^k are given in [8]. $S(s), S(\sigma), S(\pi)$ correspond to the overlap integrals between d-functions of the central ion and p- and s-functions of the ligands: $S(s) = \langle d0|s0\rangle, S(\sigma) = \langle d0|p0\rangle, S(\pi) = \langle d1|p1\rangle$. G_s, G_σ, G_π are dimensionless adjustable parameters of the model, whose values can be determined from the positions of the first three absorption bands. We assume that they can be approximated to a single value, i.e. $G_s = G_\sigma = G_\pi = G$, that can be estimated from only one (the lowest in energy) absorption band. This is usually a reasonable approximation. 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.

Numerous applications of the ECM to the analysis of rare-earth and transition metal doped crystals ([8, 11–16] and references therein) show this model to be a powerful and reliable tool for analysis and interpretation of the crystal field effects and optical absorption spectra.

4. Results of calculations and discussion

The CFPs were calculated using the ionic positions obtained from the structural data [10]. To ensure convergence of CFPs (especially those ones of the second rank), a large cluster consisting of 56631 ions was taken into account. The overlap integrals between Cr^{3+} and O^{2-} ion were calculated numerically using the wave functions from Refs. [17, 18].

The calculated CFPs values are shown in Table I (the point charge and exchange charge contributions are denoted by PCC and ECC, respectively, and shown separately).

TABLE I

Crystal field parameters (in cm^{-1}) for Cr^{3+} in $LiGa_5O_8$.

Parameter	PCC	ECC	Total value
B_2^{-2}	1254.6	0.0	1254.6
B_2^{-1}	–8322.0	0.0	–8322.0
B_2^{0}	– 495.9	0.0	–495.9
B_2^{1}	2509.5	0.0	2509.5
B_2^{2}	1488.5	0.0	1488.5
B_4^{-4}	0.0	0.0	0.0
B_4^{-3}	602.3	0.0	602.3
B_4^{-2}	−72.7	0.0	–72.7
B_4^{-1}	–86.0	0.0	–86.0
B_4^{0}	938.4	3526.1	4464.5
B_4^{1}	36.3	0.0	0.0
B_4^{2}	134.3	0.0	0.0
B_4^{3}	254.4	0.0	0.0
B_4^{4}	4557.4	17630.5	22187.9

As seen from Table I, only the B_4^0 and B_4^4 ECC values are different from zero. The value of the ECM fitting parameter G was determined from the position of the first absorption band in the corresponding absorption spectra [3, 4] and is equal to 3.899.

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, $^2PD_1D_2FGH$). Spin–orbit interaction was not considered, since the absorption bands in the experimental spectra are broad and no fine structure is observed. The Racah parameters $B = 668$ cm^{-1}, $C = 3150$ cm^{-1} are used during diagonalization of the Hamiltonian of the system. The calculated energy levels are shown in Table II.

TABLE II

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

Energy levels (O_h group notations)	This work		Observed [3]	Calculated [19]
	Calculated	Averaged		
$^4A_{2g}$	0	0	0	0
$^2E_{2g}$	14017 14251	14134	14071	14339
$^2T_{1g}$	14733 14808 15071	14871	15046	14976
$^4T_{2g}$	16346 17211 17247	16935	16936	17088
$^2T_{2g}$	21236 22077 22440	21918	21225	21213
$^4T_{1g}$	23164 23539 24794	23833	23829	23698
$^2A_{1g}$	29018	29018	–	29152

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. [19] obtained by fitting experimental data. The higher energy levels (though they also were obtained) are not shown here for the sake of brevity.

5. Conclusions

Consistent calculations of the CFPs values and energy levels for Cr^{3+} ions in spinel crystal $LiGa_5O_8$ were performed in the present paper using the ECM of crystal field. For the first time for the considered crystal the CFPs values were calculated from the crystal structure data, with taking into account the low symmetry component of crystal field. The calculated energy levels (including splitting of the orbital triplets) match well available in the literature absorption spectra. The 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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