

Exchange Charge Model for $\text{Fe}^{3+}:\text{LiAl}_5\text{O}_8$

M. VAIDA* AND C.N. AVRAM

Department of Physics, West University of Timisoara, 300223, Timisoara, Romania

The aim of this paper is the theoretical investigation of Fe^{3+} doped in the ordered phase of LiAl_5O_8 . We used the shell model and pair potential approximation to optimize the geometric structure of LiAl_5O_8 . This approach enables the modeling of the crystal field parameters of LiAl_5O_8 and then calculates the energy levels scheme of Fe^{3+} ions doped in tetrahedral sites in the title crystal. Consistent crystal field analysis and the energy level splittings for LiAl_5O_8 doped with Fe^{3+} ions was performed in the frame of the exchange charge model of crystal field. The comparison of the theoretically obtained results for energy levels with the experimental data, yields satisfactory agreement and confirms the validity of the exchange charge model.

PACS numbers: 71.70.Ch, 78.20.Bh, 34.20.Cf, 71.70.-d

1. Introduction

The ordered phase of LiAl_5O_8 doped with transition metal ions, has received much attention and significant efforts have been devoted to the study of its optical properties [1–7].

Crystallographic studies have shown that LiAl_5O_8 forms a modified inverse-spinel-like structure whose unit cell contains four formula units.

In the spinel structure, the cations may occupy both tetrahedral and octahedral sites. These are located at the interstices of a close packed oxygen lattice which contains 64 sites having tetrahedral coordination and 32 sites having octahedral coordination [1].

The distribution of the cations among these sites varies according to the temperature.

In the case of LiAl_5O_8 , two stable crystalline phases are possible, depending on the formation temperature of the system. Below 1295°C , LiAl_5O_8 is found to be in the ordered phase being characterized by the space group $P4_332$ [1, 2].

A cationic site in the structure (Al^{3+}) is available for Fe^{3+} substitution. Fe^{3+} , when present in the LiAl_5O_8 matrix, exhibits interesting fluorescent and magnetic hyperfine properties.

By doping the Fe^{3+} in LiAl_5O_8 , the ordered phase consists of a cluster of the type $[\text{FeO}_4]^{5-}$, in which the trivalent iron is located in the tetrahedral coordination sites of lithium aluminate [2, 3].

The doping of lithium aluminate crystal with Fe^{3+} tetrahedral or octahedral coordinated is possible and allows observable energy transitions in higher and lower energy regions in addition to the broad bands generated in absorption and emission processes.

Ferric iron has a $3d^5$ electronic configuration and the optical transitions of Fe^{3+} in crystal field of host matrix

occurs between energy levels with different spin multiplicities, therefore are forbidden and are always associated with weak bands in spectra [4, 5].

In the present work, we shall theoretically investigate the crystal field parameters (CFP) of LiAl_5O_8 doped with Fe^{3+} in tetrahedral sites, in the frame of the exchange charge model (ECM) of crystal field. To get the best results in agreement with experience, we should first optimize the crystal structure, and then calculate the CFP by using the new geometric structure of the crystal.

2. Calculations of the crystal structures

To get better results in calculating the CFP, we should optimize the geometric structure of the crystal. For crystal structure calculations, we will use shell model and pair potential approximation and also the GULP 3.0 computer program [8].

The sequence of calculations for geometric optimization of doped crystal is as follows: the calculation of local crystal structure with impurity center and then the calculation of crystal field parameters and energy levels. The lattice energy can be written as

$$U_{\text{lat}} = \frac{1}{2} \sum_i \sum_{k(\neq i)} V_{ik} + \frac{1}{2} \sum_i k_i \delta_i^2, \quad (1)$$

where $k_i \delta_i^2$ — the energy of the core-shell interaction of the i -th ion and V_{ik} — the interaction energy between the i -th and the k -th ions, which can be expressed as

$$V_{ik} = \frac{X_i X_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \frac{Y_i X_k}{|\mathbf{r}_i - \mathbf{r}_k - \boldsymbol{\delta}_i|} + \frac{X_i Y_k}{|\mathbf{r}_i - \mathbf{r}_k - \boldsymbol{\delta}_k|} + \frac{Y_i Y_k}{|\mathbf{r}_i - \mathbf{r}_k + \boldsymbol{\delta}_i - \boldsymbol{\delta}_k|} + f_{ik}(|\mathbf{r}_i - \mathbf{r}_k|) + g_{ik}(|\mathbf{r}_i - \mathbf{r}_k + \boldsymbol{\delta}_i - \boldsymbol{\delta}_k|), \quad (2)$$

where the function

$$f_{ik}(r) = -A_{ik} \exp(-B_{ik}r)/r \quad (3)$$

describes the short-range screening of the electrostatic interaction between ion cores, the function

* corresponding author; e-mail: vaida.mirela@yahoo.com

$$g_{ik}(r) = C_{ik} \exp(-D_{ik}r) - \lambda_{ik}/r^6 \quad (4)$$

describes the short-range repulsion between the ion shells (written in the form of the Born–Mayer potential) and the Van der Waals interaction; X_i and Y_i are the core and shell charges of the i -th ion, r_i is the vector defining the position of the ion core. δ is the vector defining the position of the ion shell relative to the ion core [9].

The parameters from Eqs. (1)–(4) are given in Tables I and II, and in Table III are given the experimental and the optimized cell parameters.

TABLE I

The short range interaction potential parameters (atomic units) [10].

Pair	A	B	C	D	λ
$O^{2-}-O^{2-}$	25.4	0.694	32.3	0.00	0.00
Li^+-O^{2-}	426	0.300	0.00	0.00	0.00
$Al^{3+}-O^{2-}$	0.241×10^4	0.263	0.00	0.00	0.00
$Fe^{3+}-O^{2-}$	0.322×10^4	0.264	0.00	0.00	0.00

$k_O = 20.5$ $k_{Fe} = 180$ $k_{Al} = 404$

TABLE II

The position of ions in the cell of $LiAl_5O_8$ and their charges [10].

Atom	x	y	z	X_i	Y_i
Li	0.625	0.625	0.625	1.000	–
Al ₁	0.125	0.3686	–0.1186	0.043	2.957
Al ₂	–0.0251	–0.0251	–0.0251	0.043	2.957
O ₁	0.3859	0.3859	0.3859	0.513	2.513
O ₂	0.1146	0.1329	0.3847	0.513	2.513
Fe	–	–	–	1.971	1.029

TABLE III

Cell parameters.

Cell parameters		
	Experimental parameters	Optimized parameters
$a = b = c$ [nm]	0.7908	0.8010
$\alpha = \beta = \gamma$ [degrees]	90	90

To take the distortion into account, we fixed the elementary cell sidebar according to measured values. The ions inside the cell could relax to minimal energy.

For the calculations of the structure of impurity centers, we used the Mott–Littleton method. In the calculations, the internal region around impurity ion consists of about 1544 ions (1.2 nm) and 2086 ions (1.6 nm) in the adjoining region to the internal region could relax restrictedly. The final geometry relaxed doped crystal is used for crystal field parameter calculations.

3. Crystal field parameters and energy levels calculation

For CFPs and energy levels calculation, we will use ECM, founded by Malkin [11] for rare earths doped in crystals. This model was also used for transitional metals ions doped in different host materials [12–17]. Accord-

TABLE IV

The overlap integrals between Fe^{3+} and O^{2-} ions.

$$\begin{aligned} S_s &= \langle d0|s0 \rangle = -1.27900 \exp(-0.84348R) \\ S_\sigma &= \langle d0|p0 \rangle = 1.07520 \exp(-0.77613R) \\ S_\pi &= \langle d1|p1 \rangle = 1.31250 \exp(-0.95354R) \end{aligned}$$

TABLE V

CFPs (in cm^{-1}) for tetrahedral coordinated Fe^{3+} ion in $LiAl_5O_8$.

Parameter	PCC	ECC	Total value
B_2^{-2}	–6851	7	–6844
B_2^{-1}	–11686	214	–11472
B_2^0	–63	–40	–103
B_2^1	16863	12367	29230
B_2^2	2601	5611	8213
B_4^{-4}	–1359	–485	–1844
B_4^{-3}	–7329	798	–6531
B_4^{-2}	–1483	114	–1368
B_4^{-1}	2355	–118	2237
B_4^0	–77	–114	–191
B_4^1	194	50	244
B_4^2	579	999	1578
B_4^3	–3955	2858	–1097
B_4^4	641	1583	2224

ing to ECM, the energy levels of the impurity ions, are the eigenvalues of the crystal field Hamiltonian, which depends on the geometry of the doped crystal. This dependence is contained in CFPs. In ECM, the CFPs are given by [11]:

$$B_p^k = B_{p,q}^k + B_{p,s}^k \quad (5)$$

$B_{p,q}^k$ represents the point charge contribution from ligands (to calculate it, we need to know the arrangement of the ligands around the central ion) and $B_{p,s}^k$ represents the exchange charge contribution. The overlap integrals between Fe^{3+} and O^{2-} ions functions (as shown in Table IV), were calculated numerically [18] using the wave functions from Refs. [19, 20].

To ensure the convergence of CFPs, large clusters of 12865 ions (916 ions of Li^+ , 4605 ions of Al^{3+} and 7344 ions of O^{2-}) were considered.

The calculated CFPs values are given in Table V (point charge, PCC, and exchange charge contributions, ECC, shown separately). CFPs were used to diagonalize the crystal field Hamiltonian. The spin–orbit interaction was neglected. Calculated energy levels are shown in Table VI.

TABLE VI
Observed and calculated energy levels (in cm^{-1})
of Fe^{3+} in $LiAl_5O_8$.

$B = 650\text{ cm}^{-1}$, $C = 3668\text{ cm}^{-1}$, $G = 3.12$			
Energy levels (O_h notations)	This work		Observed [1]
	Calculated	Averaged	
${}^6A_{1g}$	0	0	0
${}^4T_1({}^4G)$	17571	18953	18084
	18412		
	20876		
${}^4T_2({}^4G)$	21105	21969	22472
	22285		
	22517		
${}^2T_2({}^4G)$	22645	23430	–
	22835		
	24811		
${}^4A_1 + {}^4E({}^4G)$	24890	25673	25724
	24991		
	27139		
${}^4T_2({}^4D)$	27188	28979	28328
	29319		
	30429		
${}^4E({}^4D)$	30579	30679	30193
	30780		

Crystal field parameters depend on the crystal geometry, on the local symmetry of the impurity ion and on the overlap integrals. By optimizing the crystal geometry, all these values will be modified, and also the calculated energy of the energy levels will be in more satisfactory agreement with the experimental results.

4. Conclusions

In the present paper, we used the shell model and pair potential approximation to optimize the geometric structure of the ordered phase of $LiAl_5O_8$.

Crystal structure data were used to calculate the CFP values of $LiAl_5O_8$ doped with Fe^{3+} in tetrahedral sites, which were used then to calculate the lowest terms of all considered ions.

Consistent crystal field analysis was performed in the frame of the ECM of crystal field.

We diagonalized the Fe^{3+} Hamiltonian of the crystal field in the space spanned by all 100 wave functions

of 16 LS terms of $3d^5$ electronic configuration, and the scheme of the energy levels of system was obtained.

A comparative study between the theoretically obtained results for energy levels and the experimental data yields the satisfactory agreement and confirms the need for optimized geometry for better ECM calculations.

References

- [1] R. Famery, F. Queyroux, J.C. Gilles, P. Herpin, *J. Solid State Chem.* **30**, 257 (1979).
- [2] N.T. Melamed, F. de S. Barros, P.J. Viccaro, J.O. Artman, *Phys. Rev. B* **5**, 3377 (1972).
- [3] J. Maria Neto, T. Abritta, F. De S. Barros, N.T. Melamed, *J. Lumin.* **22**, 109 (1981).
- [4] T. Abritta, N. Cella, H. Vargas, *Chem. Phys. Lett.* **161**, 12 (1989).
- [5] S.S. Pedro, O. Nakamura, R.B. Barthem, L.P. Sosman, *J. Fluoresc.* **19**, 211 (2009).
- [6] T. Abritta, F. De Souza Barros, N.T. Melamed, *J. Lumin.* **33**, 141 (1985).
- [7] T. Abritta, F. De Souza Barros, *J. Lumin.* **40-41**, 187 (1988).
- [8] J.D. Gale, *J. Chem. Soc., Faraday Trans.* **93**, 629 (1997).
- [9] A.E. Nikiforov, S.Yu. Shashkin, *Spectroscopy of Crystals*, Nauka, Leningrad 1989, p. 44.
- [10] T.S. Bush, J.D. Gale, C.R.A. Catlow, P.D. Battle, *J. Mater. Chem.* **4**, 831 (1994).
- [11] B.Z. Malkin, in: *Spectroscopy of Solids Containing Rare-Earth Ions*, Eds. A.A. Kaplyanskii, B.M. Macfarlane, North-Holland, Amsterdam 1987, p. 30.
- [12] C. Jousseumene, D. Vivien, A. Kuhn-Harari, B.Z. Malkin, *Opt. Mater.* **24**, 143 (2003).
- [13] S.I. Klokishner, B.S. Tsukerblat, O.S. Reu, A.V. Palii, S.M. Ostrovsky, *Opt. Mater.* **27**, 1445 (2005).
- [14] M.G. Brik, C.N. Avram, N.M. Avram, *J. Phys. Chem. Solids* **69**, 1796 (2008).
- [15] M.G. Brik, N.M. Avram, C.N. Avram, *Physica B* **371**, 43 (2006).
- [16] M.G. Brik, N.M. Avram, *J. Phys. Chem. Solids* **67**, 1599 (2006).
- [17] M.G. Brik, N.M. Avram, C.N. Avram, *Spectrochim. Acta A* **63**, 759 (2006).
- [18] M.G. Brik, N.M. Avram, C.N. Avram, *Crystal Field Analysis: Optical Properties of 3d-Ions in Crystals*, Eds. N.M. Avram, M.G. Brik, Springer-TUP, in press.
- [19] E. Clementi, C. Rosetti, *At. Data Nucl. Data* **14**, 77 (1974).
- [20] M.V. Eremin, in: *Spectroscopy of Laser Crystals*, Eds. A.A. Kaplyanskii, Nauka, Leningrad 1989, p. 30 (in Russian).