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Calculation of Optical and Spin-Hamiltonian Parameters for Mn^{4+} Doped in $LiGa_5O_8$

M.G. Ciresan[a,*], M.L. Stanciu[a] and N.M. Avram[a,b]

[a]Department of Physics, West University of Timisoara, Bd. V. Parvan 4, Timisoara 300223, Romania

[b]Academy of Romanian Scientists, Splaiul Independentei 54, 050094 Bucharest, Romania

The aim of this paper is to investigate, from theoretical point of view, the optical spectra and EPR (g-factors) parameters for Mn^{4+}:$LiGa_5O_8$. The optical energy levels scheme has been obtained by the diagonalization of the Hamiltonian of the system, using all 50 wave functions of the LS terms of $3d^3$ electron configuration. The crystal field parameters have been obtained in the exchange charge model of crystal field, taking into account the structure of the host matrix and effects of the covalent bond formation between the Mn^{4+} with O^{2-}. The satisfactory agreement with experimental data is obtained.

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1. Introduction

The study of spinel metal oxides has recently attracted a great deal of attention due to their unique properties and potential applications [1, 2]. The intense interest in such materials is derived from their unique chemical and physical properties, which gives rise to their potential uses in the fields of nonlinear optics, luminescence, electronics, catalysis and optoelectronics [1–5]. The spinel $LiGa_5O_8$ has been used as a host for luminescent studies of many transition metal ions [6, 7]. Besides this, $LiGa_5O_8$ has been widely studied to test its viability as a tunable laser system [8].

$LiGa_5O_8$ adopts an inverse spinel structure with space group $P4_332$ (constant lattice $a = 0.8203$ nm), with four formula units in the cubic cell [9]. In our case Mn^{4+} (0.052 nm) ions replace the Ga^{3+} (0.062 nm) ions in the $LiGa_5O_8$ and form the octahedral complex $[MnO_6]^{8-}$. The site symmetry group for Mn^{4+} doped in $LiGa_5O_8$ is not trigonal, unlike that in normal spinels, it is orthorhombic and belongs to the C_2 point group [10]. Significant efforts have been devoted by different research groups, in the past and till recently, to the study of the optical properties of impurity-doped $LiGa_5O_8$. Several lithium gallium oxides has been reported such as $LiGa_5O_8$:Co, $LiGa_5O_8$:Ni, $LiGa_5O_8$:Cr, $LiGa_5O_8$:Mn, $LiGa_5O_8$:Fe [11] etc. However, for the Mn-doped $LiGa_5O_8$, the results are scarce: few results on optical spectra and lack of EPR results.

In this paper, we theoretically investigate the optical spectra and calculate the EPR (g-factors) parameters for Mn^{4+}:$LiGa_5O_8$. The experimental supports for our calculation are results from [10]. In Fig. 1 is shown the crystal structure of $LiGa_5O_8$.

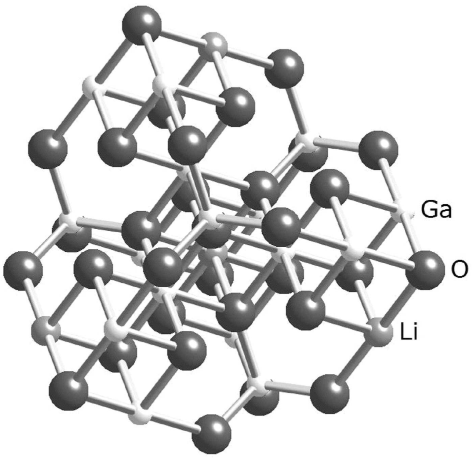

Fig. 1. Crystal structure of $LiGa_5O_8$. Two kinds of coordination polyhedra around Ga^{3+} ions (tetrahedrons and octahedrons) are shown.

2. Theoretical method

The crystal field created by the ligands of the host matrix $LiGa_5O_8$ split the energy levels of the impurity ions Mn^{4+}. In order to calculate the split energy levels in $[MnO_6]^{8-}$ complex, we used exchange charge model (ECM). The expressions for calculating both contributions to the crystal field parameters (CFP) B_p^k ($B_{p,q}^k$ and $B_{p,s}^k$) in the case of $3d$-ion is given in [12]. The first term refers to the contribution originating from the electrostatic interaction between the valence electrons of an impurity ion and ions of crystal lattice. The latter is proportional to the overlap of the wave functions of the impurity ion and ligands; it includes the effects of the covalent bond formation and the exchange interaction. The inclusion of these effects significantly improves the agreement between the calculated and experimentally observed energy levels.

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[*] corresponding author; e-mail: marcel_ciresan@yahoo.com

The ECM has been successfully applied for the calculations of the energy levels of both rare earth [13–17] and transition metal ions in different hosts as well [18–26].

When calculating CFP, a special attention should be paid to the convergence of the lattice sums. As a first approximation, it is possible to consider the nearest ligands only, but since the second rank point charges parameters $B^k_{2,q}$ decrease slower than the fourth rank parameters $B^k_{4,q}$ (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 the accuracy in calculating the point charge contribution to the CFP, large cluster consisting of 9718 Ga^{3+} ions, 1958 Li^+ ions, and 15488 O^{2-} ions was considered. This cluster enables taking into account the contribution of the ions located at the distances at least up to 4 nm from the central ion. For the exchange charge parameters 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 Mn^{4+} and O^{2-} ions needed for calculating the exchange charge contribution $B^k_{p,s}$ to the CFP were computed numerically using the radial wave functions of the above mentioned ions given in [27]. The dependences of the overlap integrals on the inter-ionic distance r (r is measured in atomic units) were approximated by the exponential functions given in Table I.

TABLE I

Overlap integrals between Mn^{4+} and O^{2-} ions in $LiGa_5O_8$ ($2.93 < r < 3.93$ atomic units) and averaged values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ (in a.u.) calculated with wave functions from [27].

$S_s = \langle d0 \vert s0 \rangle$	$-0.92125 \exp(-0.69807r)$	$\langle r^2 \rangle$	$\langle r^4 \rangle$
$S_\sigma = \langle d0 \vert p0 \rangle$	$0.85114 \exp(-0.74151r)$	1.098760956	2.401997006
$S_\pi = \langle d1 \vert p1 \rangle$	$1.46440 \exp(-1.10230r)$		

The CFP values obtained by using ECM model, exponential functions from Table I for the overlap integrals and crystal structure data from [28] (which provides the Cartesian coordinates of the ligands in the system of reference defined with respect to the crystallographic axes) are shown in Table II.

As seen from Table II, only the B^0_4 and B^4_4 ECC values are different from zero.

Regarding the spin-Hamiltonian parameters, in absence of the experimental data (in paper [29] this was not measured because of the overlapping with the EPR of Mn^{2+} ions) we calculate them by using the density functional theory (DFT) method and program ORCA [30]. Therefore, we obtained for g the following values: $g_x = 1.9251$, $g_y = 2.0010$, $g_z = 2.0023$. The parameter g has three distinct values because the local symmetry around impurity ions is orthorhombic and belongs to the C_2 point group.

The crystal field Hamiltonian 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 III.

TABLE II

CFP (in cm^{-1}) for orthorhombic coordinated Mn^{4+} ion in $LiGa_5O_8$. Point charges contribution (PCC) and exchange charges contribution (ECC) are shown separately.

Parameter	PCC	ECC	Total value
B_2^{-2}	941	0	941
B_2^{-1}	−6305	0	−6305
B_2^0	−375	0	−375
B_2^1	1882	0	1882
B_2^2	1138	0	1138
B_4^{-4}	0	0	0
B_4^{-3}	337	0	337
B_4^{-2}	−41	0	−41
B_4^{-1}	−48	0	−48
B_4^0	525	4738	5263
B_4^1	20	0	20
B_4^2	75	0	75
B_4^3	142	0	142
B_4^4	2551	23689	26240

TABLE III

Crystal field splittings of the lowest terms (in cm^{-1}) for Mn^{4+} in $LiGa_5O_8$ ($G = 9.585$, $B = 653$ cm^{-1}, $C = 3289$ cm^{-1}).

O_h irred. repres.	O_h symmetry	Experimental values [10]	Calculated this work	
$^4A_{2g}(^4F)$	0	0	0	Average
$^2E_g(^2G)$	14730	14724	14574 14719	14646
$^2T_{1g}(^2G)$	15273	15273	15178 15252 15389	15273
$^4T_{2g}(^2F)$	20000	20000	19540 20173 22287	20000
$^2T_{2g}(^2G)$	22475	–	22837 23082 26512	24144
$^4T_{1g}(^4F)$	26881	26881	26512 26596 27720	26942
$^2A_{1g}(^2G)$	32390	–	32461	32461

3. Discussion

The determination of Mn^{4+} centers from the optical data is fairly clear and consistent with previous works on the isoelectronic Cr^{3+} in the same material [29]. The shift of the electronic transitions Mn^{4+} and Cr^{3+} ions in $LiGa_5O_8$ shows the same trends with different materials [29]. After doping Mn^{4+} ions substitute Ga^{3+} ions, in this case a charge compensation is necessary. The covalence parameter $\beta = B/B_0$, with B being the Racah parameter for Mn^{4+} in crystal and B_0 being the Racah parameter for free ions of Mn^{4+} respectively, is 0.61, smaller than for Cr^{3+} ($\beta \approx 0.73$), i.e. a more covalence character.

4. Conclusion

In the present work we report on the detailed crystal field calculations of the energy levels for Mn^{4+} in $LiGa_5O_8$. The ECM was used to calculate the CFP with taking into account the effects of the covalent bond formation between the Mn^{4+} and O^{2-} ions. The influence of the low-symmetry component of crystal field on the splitting of the Mn^{4+} energy levels was also considered. The calculated CFP values were used for diagonalization of the Mn^{4+} 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 are in the agreement with the experimental data available in the literature. In addition, we calculate the g tensor using DFT method and obtained for them three distinct values because the local symmetry around impurity ions is orthorhombic and belongs to the C_2 point group.

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