

ENERGY LEVEL SCHEMES OF DIVALENT Co IN ZINC AND MAGNESIUM GALLATE

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Abstract

The aim of this paper is to make a crystal field analysis of the energy levels structure for the title materials. We report on the detailed and consistent crystal field analysis of Co²⁺ spectra in both materials, which was performed in the framework of the exchange charge model of crystal field. Overlap integrals between Co²⁺ and O²⁻ ions were calculated numerically and Co²⁺ electron density moments were evaluated. The energy level schemes for each material are obtained and compared with each other. Comparison of the theoretical results with the experimental data yields satisfactory agreement.

1. Introduction

Co²⁺-doped ZnGa₂O₄ and MgGa₂O₄ crystals with spinel structure have been reported as promising candidates for the solid state laser in the visible and near infrared regions [1–5]. Co²⁺ ions substitute for Zn²⁺ and Mg²⁺ ions at the tetrahedral sites. In spite of extensive spectroscopic studies undertaken in Refs. [1–5] there exists considerable controversy regarding the positions of the Co²⁺ energy levels. In the present work we report on the consistent applications of the exchange charge model [6] of crystal field (CF) to the above mentioned crystals. This is the first CF analysis for these systems which is based on the calculations of the crystal field parameters (CFP) from the crystal structure data. Consequent diagonalization of the CF Hamiltonian in the space spanned by the wave functions of all LS multiplets of Co²⁺ ion resulted in getting complete energy level schemes of Co²⁺ ions in both crystals. The obtained energy levels and estimated Racah parameters *B* and *C* were compared with results of previous studies [1–5]. The order of the Co²⁺ energy levels was clarified and a misinterpretation of its energy level scheme in the literature was eliminated.

2. Crystal structure of ZnGa₂O₄ and MgGa₂O₄

Both crystals have a cubic structure with lattice constants 8.3358 Å for ZnGa₂O₄ [7] and 8.2721 Å for MgGa₂O₄ [8]. After doping, Co²⁺ ions substitute for Zn²⁺ ions, entering tetrahedral positions. Since electrical charges of both substituted and substituting ions are equal, no charge compensating additions are needed.

3. Method of calculations

In the framework of the exchange charge model of crystal field [6] the energy levels of an impurity ion are considered as the eigenvalues of the following Hamiltonian

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

Here O_p^k are the linear combinations of irreducible tensor operators, and crystal field parameters (CFP) B_p^k are defined as a sum of two contributions:

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

Where the first term corresponds to the Coulomb interaction between impurity ion electrons and crystal lattice ions:

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

And the second one to exchange interaction between impurity ion's and nearest ligands' electrons:

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

4. Results of calculations

To ensure convergence of the crystal lattice sums needed for calculations of CFP (especially for the second rank parameters), large clusters consisting of more than 30,000 ions were considered for both crystals. The overlap integrals needed for calculating the exchange charge contribution to the CFP, were calculated using the wave functions from Refs. [9]. The calculated CFP values are shown in Table 1.

Table 1. CFP values (in cm^{-1}) for Co^{2+} in MgGa_2O_4 and ZnGa_2O_4

Parameter	$\text{MgGa}_2\text{O}_4:\text{Co}^{2+}$	$\text{ZnGa}_2\text{O}_4:\text{Co}^{2+}$
B_2^{-2}	7.6	-16.7
B_2^{-1}	15.2	-19.0
B_2^0	0.0	6.5
B_2^1	15.2	-30.6
B_2^2	0.0	9.1
B_4^{-4}	0.0	-3650.3
B_4^{-3}	0.0	1072.2
B_4^{-2}	0.0	-179.2
B_4^{-1}	0.0	-907.0
B_4^0	-939.1	-995.7
B_4^1	0.0	-2562.8
B_4^2	0.0	-303.5
B_4^3	0.0	2526.4
B_4^4	-4695.6	-3897.6

Table 2. Energy levels of Co^{2+} ion in MgGa_2O_4 and ZnGa_2O_4

Energy levels (T_d group notations)	$\text{MgGa}_2\text{O}_4:\text{Co}^{2+}$		$\text{ZnGa}_2\text{O}_4:\text{Co}^{2+}$	
	Calculated	Observed [2,3]	Calculated	Observed [2]
4A_2	0	0	0	0
4T_2	3578	~3300	4135	4103
			4138	
			4144	
			7120	
4T_1	6230	6500-7700	7122	~7800
			7124	
			14623	
2E	15107	-	14623	-
			15136	
2T_1	15614	-	15136	-
			15139	
			15785	
4T_1	16203	15385-16000	15792	~15527
			15810	

Table 2 shows the results of the present calculations of the Co^{2+} energy levels in comparison with experimental data. In this Table only those energy levels which are in the spectral region studied experimentally are shown for the sake of brevity. The calculated and observed energy levels are in reasonable agreement. The values of the Racah parameters B and C are (in cm^{-1}) 780 and 3450 for MgGa_2O_4 and 700 and 3400 for ZnGa_2O_4 .

respectively. It should be pointed out that the 2E level was located very high, even above the 4T_1 (4P). Our calculations do not support this point of view (Table 2).

5. Conclusions

Consistent calculations of crystal field parameters (CFP) for Co^{2+} ion in $MgGa_2O_4$ and $ZnGa_2O_4$ were performed using the exchange charge model of crystal field and crystal structure data. Covalent effects arising from the chemical bond formation between Co^{2+} ion and ligands were considered by calculation of the overlap integrals between the Co^{2+} $3d$ and ligands $2p$ and $2s$ wave functions. The obtained values of CFP have been used for diagonalization of the Co^{2+} ion Hamiltonian and getting its energy level schemes in both crystals. On the basis of these calculations, assignment of the ground state absorption spectra was performed and compared with experimental data. Correction to the published in the literature energy level scheme of Co^{2+} ion was suggested. In spite of only *one* fitting parameter of the exchange charge model, good agreement between the calculated and experimental results was demonstrated.

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