

Comparative Study between Energy Levels of Cr³⁺ and Co²⁺ Ions Doped in MgF₂ Crystal

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The aim of this paper is to present a comparison of the energy level schemes of Cr³⁺ (3d³ electrons) and Co²⁺ (3d⁷ electrons), each of ions doped, separately, in MgF₂ crystal. We report on the detailed and consistent crystal field analysis of Cr³⁺ spectra in MgF₂ crystal and compare with results, previously obtained, for Co²⁺, doped in same host matrix. The results are based on application of the exchange charge model of crystal field to the calculation of crystal field parameters and energy levels of both ions doped in MgF₂. The calculations have been performed on previously optimized geometry of MgF₂ crystal. The obtained results are compared with experimental data and discussed.

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1. Introduction

Crystals of MgF₂ were used as a standard host material and its optical absorption and emission for the 3d transition-metal doped in this crystal are well known [1]. MgF₂ has a rutile-type structure, with space group *P42/mnm*, two formula units in a unit cell and lattice constants $a = 4.6213 \text{ \AA}$, $c = 3.0159 \text{ \AA}$ [2].

The unit cell of MgF₂ is tetragonal and the Mg²⁺ ion is surrounded by six fluorine occupying the tops of distorted octahedral of *D_{2h}* site symmetry [3]. In MgF₂ crystals, the ligand distance is primarily restricted by the lattice constant and the nearest neighbor Mg-F distances are of the order of 1.98 Å. The optical properties of 3d ions in MgF₂ crystals have confirmed that Cr³⁺ and Co²⁺ ions are substitution in Mg²⁺ sites [3, 4]. In previous paper we have analyzed the Co²⁺:MgF₂ system, so in present paper we focus on Cr³⁺:MgF₂. After doping Cr³⁺ in MgF₂ crystal this ion will substitute the Mg²⁺ with octahedral coordination formed by F⁻ ions. Because the ionic radii for Cr³⁺ and Mg²⁺ are close (0.61 Å for Cr³⁺ and 0.65 Å for Mg²⁺ ion) [5] the local symmetry of Cr³⁺ ion does not change, it keeps *D_{2h}*.

Despite the optical properties of 3d ions in MgF₂ crystal have been widely investigated [1] it should be pointed out that reports on the consistent crystal field analysis of Co²⁺ and Cr³⁺ doped MgF₂ crystal with on of crystal field parameters (CFP), from optimized structural data,

and energy levels scheme, are scarce. In our previous paper [6] we have calculated the CFP and low lying energy levels for Co²⁺ doped in MgF₂ crystal, in the frame of exchange charge model (ECM) of crystal field. In present paper we present the results of such calculations for Cr³⁺ doped MgF₂.

Trivalent chromium has been known for more than 45 years as an optical active ion. Crystals doped with Cr³⁺ ions have numerous technical, optical and spectral applications ([1, 7] and references therein).

We shall discuss here the results of application of the ECM of crystal field [8] for the calculation of the CFPs and energy levels of Cr³⁺ doped MgF₂. The Cr³⁺ (3d³) and Co²⁺ (3d⁷) ions have complementary electronic configurations and being doped, separately, in the same host materials, we have compared the obtained results. For both ions, the satisfactory agreement of calculated results and experimental data [3, 4] are obtained. Some common characteristics of crystal field and energy levels for two systems are presented and discussed.

2. Method of calculations

The experimental support for our calculations are the results given in [4]. In order to analyse the crystal field of Cr³⁺ doped in MgF₂ crystal we follow papers [8, 9]. In the framework of the ECM of crystal field the energy levels of an impurity ion are considered as the eigenvalues of the following Hamiltonian:

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$$H = \sum_{p=2,4} \sum_{k=-p}^p (B_{p,q}^k + B_{p,s}^k) O_p^k. \quad (1)$$

Here O_p^k are the linear combinations of irreducible tensor operators, and crystal field B_p^k parameters (CFP) containing all information about geometrical structure of an impurity center. Explicit equations for CFP are given in [8]. The ECM has been successfully applied for the calculations of the energy levels of both rare earth [10–14] and transition metal ions in different hosts as well [15–21].

According the basic paper [8], the $B_{p,q}^k$ parameters are functions of ionic positions obtained from structural data [2] and averaged values $\langle r^p \rangle$ of p -th power of the impurity ion electron radial coordinate. The last term in Eq. (1) includes all effects of the covalent bond formation and exchange interaction and depends on the same ionic position, as first term, and on the overlap integrals between Cr^{3+} and F^- ions. These overlap integrals were calculated numerically and their dependence on distance between both ions is described by the following exponential functions [22]:

$$S_s = \langle d0 | s0 \rangle = 2.7775 \exp(-1.0277R),$$

$$S_\sigma = \langle d0 | p0 \rangle = 1.1674 \exp(-0.7105R),$$

$$S_\sigma = \langle d0 | p0 \rangle = 2.093 \exp(-1.0235R),$$

$$3.00 < R < 4.00 \quad (\text{a.u.}) \quad (2)$$

The values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ (in atomic units, a.u.) are [23]: 1.43402 and 4.26283, respectively.

To ensure reasonable convergence of lattice sums needed for calculations of the crystal field parameters (CFPs), large clusters (11.90 Å) of Mg^{2+} and F^- ions were considered. After calculating CFPs, based on the optimized structure of the host matrix, the crystal field Hamiltonians were diagonalized in the space spanned by wave functions of all 50 LS terms of $3d^3$ electron configuration. The obtained energy levels were compared with results of experimental data and discussed. During the diagonalization of the Hamiltonian the estimated Racah parameters B , C and G parameter of the exchange charge model have done.

3. Results of calculations and discussion

The calculated CFPs values of $\text{Cr}^{3+}:\text{MgF}_2$, calculated in this paper and that corresponding for $\text{Co}^{2+}:\text{MgF}_2$, previously obtained [6], are shown in Table (the point charge and exchange charge contributions are denoted by PCC and ECC, respectively, and shown separately).

It can be seen from Table that only crystal field parameters B_2^{-2} , B_2^0 , B_4^{-2} , B_4^0 and B_4^4 values are different from zero, according with the D_{2h} site symmetry of Co^{2+} and Cr^{3+} doped in MgF_2 . In both cases the ECC contributions are significant, that means the main contributions of covalent effects to crystal field parameters, and ECM used for CFPs.

TABLE I
Crystal field parameters for $\text{Co}^{2+}:\text{MgF}_2$ and for $\text{Cr}^{3+}:\text{MgF}_2$.

Parameter	$\text{Co}^{2+}:\text{MgF}_2$ [6]			$\text{Cr}^{3+}:\text{MgF}_2$ (this work)		
	PCC	ECC	Total value	PCC	ECC	Total value
B_2^{-2}	921	6103	7024	1056	2138	3194
B_2^{-1}	0	0	0	0	0	0
B_2^0	-116	-998	-1114	-133	1463	1330
B_2^1	0	0	0	0	0	0
B_2^2	0	0	0	0	0	0
B_4^{-4}	0	0	0	0	0	0
B_4^{-3}	0	0	0	0	0	0
B_4^{-2}	-2269	-6963	-9232	-2646	-17761	-20407
B_4^{-1}	0	0	0	0	0	0
B_4^0	-108	95	-13	-126	-500	-626
B_4^1	0	0	0	0	0	0
B_4^2	0	0	0	0	0	0
B_4^3	0	0	0	0	0	0
B_4^4	-1339	-6450	-7789	-1561	-11956	-13517

The obtained values of CFPs for $\text{Cr}^{3+}:\text{MgF}_2$, were used to diagonalize the crystal field Hamiltonian (1) in the space spanned by all 50 wave functions of LS terms of Cr^{3+} ion. 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 $B = 516 \text{ cm}^{-1}$, $C = 3797 \text{ cm}^{-1}$ and parameter of ECM, $G = 3.298$ are used during diagonalization of the Hamiltonian of the system. The value of the ECM fitting parameter G was determined from the position of the first absorption band in the corresponding absorption spectra of Cr^{3+} doped in MgF_2 . 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 MgF_2 .

Energy levels (O_h group rotations)	This work		Experimental values [4]	Calculated O_h symmetry
	Calculated ECM	Averaged ECM		
$^4A_{2g}$	0	0	0	0
$^4T_{2g}$	14554 15013 15273	14947	14948	14948
2E_g	15184 15342	15263	15267	15242
$^2T_{1g}$	15415 15789 15883	15696	–	15625
$^4T_{1g}(P)$	19304 20496 21418	20406	20284	20284

As one can see from Table II calculated values with ECM (column 2) give orbital splitting of energy levels, due to crystal field with D_{2h} symmetry. The barycenter energies (column 3) and calculated energy

with Tanabe-Sugano matrices (column 5 — O_h symmetry) are in satisfactory agreement with experimental data (column 4). The same conclusions have established in case of $\text{Co}^{2+}:\text{MgF}_2$ [6]. In last case the ground state is $^4T_{1g}$ triplet, instead $^4A_{2g}$ in case of $\text{Cr}^{3+}:\text{MgF}_2$.

The covalence effects play an essential role in both considered systems. It can be revealed by using the following non-dimensional quantity:

$$\beta = \sqrt{\left(\frac{B_1}{B_0}\right)^2 + \left(\frac{C_1}{C_0}\right)^2} / 2, \quad (3)$$

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 ions these parameters are [24] $B_0 = 918 \text{ cm}^{-1}$, $C_0 = 3850 \text{ cm}^{-1}$ for Cr^{3+} , and $B_0 = 1038 \text{ cm}^{-1}$, $C_0 = 4366 \text{ cm}^{-1}$ for Co^{2+} . With the above values of B , C parameters for Cr^{3+} and that from [6] for Co^{2+} , the obtained values for β are: 0.50 for $\text{Cr}^{3+}:\text{MgF}_2$ and 0.63 for $\text{Co}^{2+}:\text{MgF}_2$. This means that the covalence effect is “strong” in these systems and ECC contribution to CFPs are important.

4. Conclusions

The crystal field parameters and energy for lowest levels of Cr^{3+} doped in MgF_2 crystal have been calculated and the obtained results are compared with that for $\text{Co}^{2+}:\text{MgF}_2$. The calculations have been performed in the frame of ECM of crystal field, taken into account site symmetry of the impurity ion, the contributions from ions charges of lattices and covalent effects from doped lattice. For more accuracy of the crystal field parameters calculation the geometry optimization of the doped host matrices has been made. For both systems the covalent effects are strong and obtained results for energy level schemes are in satisfactory agreement with experimental data.

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