Comparative Study between Energy Levels of Cr$^{3+}$ and Co$^{2+}$ Ions Doped in MgF$_2$ Crystal

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The aim of this paper is to present a comparison of the energy level schemes of Cr$^{3+}$ ($3d^3$ electrons) and Co$^{2+}$ ($3d^7$ electrons), each of ions doped, separately, in MgF$_2$ crystal. We report on the detailed and consistent crystal field analysis of Cr$^{3+}$ spectra in MgF$_2$ crystal and compare with results, previously obtained, for Co$^{2+}$, 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 MgF$_2$. The calculations have been performed on previously optimized geometry of MgF$_2$ crystal. The obtained results are compared with experimental data and discussed.

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1. Introduction

Crystals of MgF$_2$ 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]. MgF$_2$ has a rutile-type structure, with space group $P4_2/mnm$, two formula units in a unit cell and lattice constants $a = 4.6213 \, \text{Å}$, $c = 3.0159 \, \text{Å}$ [2].

The unit cell of MgF$_2$ is tetragonal and the Mg$^{2+}$ ion is surrounded by six fluorine occupying the tops of distorted octahedral of $D_{2h}$ site symmetry [3]. In MgF$_2$ 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 MgF$_2$ crystals have confirmed that Cr$^{3+}$ and Co$^{2+}$ ions are substitution in Mg$^{2+}$ sites [3, 4]. In previous paper we have analyzed the Co$^{2+}$:MgF$_2$ system, so in present paper we focus on Cr$^{3+}$:MgF$_2$. After doping Cr$^{3+}$ in MgF$_2$ crystal this ion will substitute the Mg$^{2+}$ with octahedral coordination formed by F$^-$ ions. Because the ionic radii for Cr$^{3+}$ and Mg$^{2+}$ are close (0.61 Å for Cr$^{3+}$ and 0.65 Å for Mg$^{2+}$ ion) [5] the local symmetry of Cr$^{3+}$ ion does not change, it keeps $D_{2h}$.

Despite the optical properties of 3d ions in MgF$_2$ crystal have been widely investigated [1] it should be pointed out that reports on the consistent crystal field analysis of Co$^{2+}$ and Cr$^{3+}$ doped MgF$_2$ 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 Co$^{2+}$ doped in MgF$_2$ crystal, in the frame of exchange charge model (ECM) of crystal field. In present paper we present the results of such calculations for Cr$^{3+}$ doped MgF$_2$.

Trivalent chromium has been known for more than 45 years as an optical active ion. Crystals doped with Cr$^{3+}$ 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 Cr$^{3+}$ doped MgF$_2$. The Cr$^{3+}$ ($3d^3$) and Co$^{2+}$ ($3d^7$) 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 Cr$^{3+}$ doped in MgF$_2$ 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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\[ H = \sum_{p=2,4} \sum_{k=-p}^{p} (B_{p,q}^k + B_{p,s}^k)O_p^k. \]  

Here \( O_p^k \) are the linear combinations of irreducible tensor operators, and crystal field \( B_{p,q}^k \) 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 to 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 \( \text{Cr}^{3+} \) and \( \text{F}^- \) ions. These overlap integrals were calculated numerically and their dependence on distance between both ions is described by the following exponential functions [22]:

\[ S_x = (d0| s0) = 2.7775 \exp(-1.0277R), \]
\[ S_y = (d0| p0) = 1.1674 \exp(-0.7105R), \]
\[ S_z = (d0| p0) = 2.9033 \exp(-1.0235R), \]

3.00 < \( R \) < 4.00 (a.u.)

(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 \( \text{Mg}^{2+} \) and \( \text{F}^- \) 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 3\( d^2 \) 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 Cr\textsuperscript{3+}:MgF\textsubscript{2}, calculated in this paper and that corresponding for Co\textsuperscript{2+}:MgF\textsubscript{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 \( B_2^{-2}, B_0^0, B_4^{-2}, B_0^0 \) and \( B_4^4 \) values are different from zero, according with the \( D_{2h} \) site symmetry of Co\textsuperscript{2+} and Cr\textsuperscript{3+} doped in MgF\textsubscript{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 Co\textsuperscript{2+}:MgF\textsubscript{2} and for Cr\textsuperscript{3+}:MgF\textsubscript{2}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Co\textsuperscript{2+}:MgF\textsubscript{2} [6]</th>
<th>Cr\textsuperscript{3+}:MgF\textsubscript{2} (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B\textsubscript{2}^{-2}</td>
<td>PCC</td>
<td>ECC</td>
</tr>
<tr>
<td>B\textsubscript{2}^{-1}</td>
<td>921</td>
<td>6103</td>
</tr>
<tr>
<td>B\textsubscript{0}^{0}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{2}^{-2}</td>
<td>-116</td>
<td>-1998</td>
</tr>
<tr>
<td>B\textsubscript{1}^{0}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{0}^{0}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{0}^{4}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{1}^{-2}</td>
<td>-2269</td>
<td>-6963</td>
</tr>
<tr>
<td>B\textsubscript{1}^{-1}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{1}^{4}</td>
<td>-108</td>
<td>95</td>
</tr>
<tr>
<td>B\textsubscript{1}^{0}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{0}^{4}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{0}^{2}</td>
<td>-1339</td>
<td>-6450</td>
</tr>
</tbody>
</table>

The obtained values of CFPs for Cr\textsuperscript{3+}:MgF\textsubscript{2}, were used to diagonalize the crystal field Hamiltonian (1) in the space spanned by all 50 wave functions of \( LS \) terms of Cr\textsuperscript{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\textsuperscript{3+} doped in MgF\textsubscript{2}. Calculated energy levels are shown in Table II.

### Table II

Observed and calculated (this work) energy levels (in \( \text{cm}^{-1} \)) of Cr\textsuperscript{3+} ion in MgF\textsubscript{2}.

<table>
<thead>
<tr>
<th>Energy levels (( O_h ) group rotations)</th>
<th>This work</th>
<th>Experimental values [4]</th>
<th>Calculated ( O_h ) symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3A_{2g} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( ^3T_{2g} )</td>
<td>15013</td>
<td>14947</td>
<td>14948</td>
</tr>
<tr>
<td>( ^2E_g )</td>
<td>15184</td>
<td>15263</td>
<td>15267</td>
</tr>
<tr>
<td>( ^2T_{1g} )</td>
<td>15883</td>
<td>15696</td>
<td>15625</td>
</tr>
<tr>
<td>( ^4T_{1g}(P) )</td>
<td>20406</td>
<td>20406</td>
<td>20284</td>
</tr>
</tbody>
</table>

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 Co$^{2+}$:MgF$_2$ [6]. In last case the ground state is $4T_{1g}$ triplet, instead $1A_{2g}$ in case of Cr$^{3+}$:MgF$_2$.

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

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

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 3$d$ 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 $\beta$ are: 0.50 for Cr$^{3+}$:MgF$_2$ and 0.63 for Co$^{2+}$: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 Co$^{2+}$: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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References