THEORETICAL INVESTIGATION OF OPTICAL AND EPR SPECTRA OF Ni^{2+} IONS DOPED IN RbCdF$_3$ CRYSTAL

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Abstract
The aim of this paper is the theoretical investigations of the Ni^{2+} doped in CsCdF$_3$ in an deformed octahedral environments. The optical energy levels scheme has been calculated in the frame of exchange charge model of crystal field, using the geometry of the title crystal. In this model the crystal field parameters was calculated and then the Hamiltonian of the system was diagonalized. The spin-Hamiltonian parameters of Ni^{2+} ion in low symmetry of the title host matrix were calculated using perturbation theory, with double spin-orbit interaction approximation in the cluster model. In these calculations we used the Racah parameter values best fited the experimental data during simulation of the optical spectra. The obtained results are in satisfactory agreement with the experimental data, which confirm the validity of used models in both optical and EPR spectra.

1. Introduction

RbCdF$_3$ has a cubic perovskite structure at room temperature and undergoes a structural phase transition at 124K. This transition is of second order and consists of alternate tiltings of the fluorine octahedral around a <100> axis together with an elongation along the rotation axis [1] [2]. It is a suitable as host materials for a variety of inorganic active ions, transition metals and lanthanides, in view of its development of tunable solid state laser [3] [4]. There are a lot of studies in literature [5] [6 - and reference therein] regarding various aspects related to the Ni^{2+} doped crystals. Nevertheless, it should be point out that reports on the consistent crystal field analysis of Ni^{2+}- doped RbCdF$_3$ crystal with calculations of crystal field parameters (CFPs) from structural data are source.

In this paper we present the results of application of the exchange charge model (ECM) of crystal field [7] to the calculation of the crystal field parameters (CFPs) and energy levels of Ni^{2+} ion in cubic RbCdF$_3$. Also, we give the result of calculation of g parameter of the crystal, in cubic phase, using the perturbation theory [8].

2. Crystal structure of RbCdF3

RbCdF$_3$ crystallizes in a perovskite structure [9], with space group Pm3m, lattice constant is 4.395Å; there is one unit formula in unit cell [10]. After doping Ni^{2+} ions substitute for Cd^{2+} ions, at octahedral site with Ni – F distance 2.1975Å [10]. No charge compensation is needed, since electrical charges of Ni^{2+} and Cd^{2+} ions are equal.
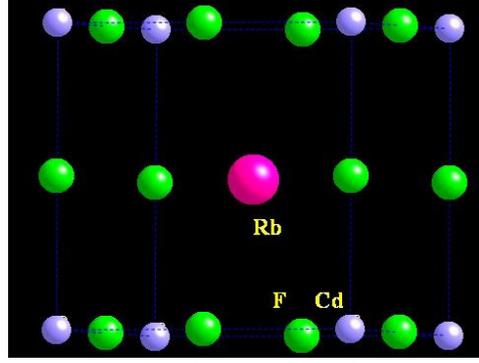

Fig.1 Crystal structure of CsCdF$_3$

3. Method of calculation

In the framework of the exchange charge model of crystal field [7] the energy levels of an impurity ion are considered as the eigenvalues of the following Hamiltonian

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

Here O_p^k are the linear combinations of irreducible tensor operators, and crystal field B_p^k parameters (CFP) are defined as a sum of two contributions $B_p^k = B_{p,q}^k + B_{p,S}^k$

The first term is connected with the Coulomb interaction between impurity ion

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

electrons and crystal lattice ions:

Abd the second term is due to exchange interaction between impurity ion and nearest ligands electrons:

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i (G_s S_s(i)^2 + G_\sigma S_\sigma(i)^2 + \gamma_p G_\pi S_\pi(i)^2) \frac{V_p^k(\theta(i), \varphi(i))}{R(i)}$$

Overlap integrals

The main advantages of exchange charge model are:

- CFP can be <u>calculated</u> from available crystal structure data, but not obtained *a posteriori* as a result of a fitting procedure.

- Small number of phenomenological parameters: only one (if $G_S=G_\sigma=G_\pi$).

- Reliability of the obtained results: deviation between the calculated and observed energy levels is about several hundred cm^{-1} for $3d$ ions and several tens cm^{-1} for $4f$ ions.

- Possibility to analyze covalent effects for different impurity centers by comparing bilinear form constructed from the overlap integrals calculated using wave functions of the impurity ions and ligands.

4. Results of calculation

Numerous applications of the ECM to the analysis of rare-earth and transition metal doped crystals [7, 11-16, and references therein] show this model to be a powerful and reliable tool for analysis and interpretation of crystal field effects and optical absorption. The CFPs were calculated using the ionic positions obtained from structural data [9-10]. To ensure convergence of CFPs (especially those ones of the second rank), a large cluster consisting of 41760 ions for F, 22841 for Cd and 23965 for F was taken into account. The overlap integrals between Ni^{2+} and F^- ions were calculated numerically using the wave functions from Refs. [17, 18]. For the calculation of g factor we used the method of perturbation theory [19]. The results of calculations are given in Tab. 1.

Table 1. Observed and calculated (this work) energy levels

	Calculated (this work)	Experimental [6]
$^3A_2(F)$	0	0
$^3T_2(F)$	6600	6600
$^3T_1(F)$	11250	11253
$^1E(D)$	14075	14925
$^1T_2(D)$	20158	20000
$^3T_1(P)$	22998	22727
g factor	2.341	2.347 [17]

5. Conclusions

Consistent calculations of the CFPs values and energy levels for Ni^{2+} ions in the crystal $RbCdF_3$ were performed in the present paper using the ECM of crystal field. For the first time for the considered crystal the CFPs values were calculated from crystal structure data, with taking into account low symmetry component of crystal field. Calculated energy levels (including splitting of the orbital triplets) and g factor match well available in the

literature absorption spectra. Calculated complete energy level schemes can be used for analysis of the Ni^{2+} excited state absorption in the considered spinel, and the sets of CFPs can be used as initial (starting) sets for analysis of Ni^{2+} energy levels in other isostructural crystals.

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