ELECTRONIC LEVELS OF Cr^{2+} ION DOPED IN II-VI COMPOUNDS OF ZnS – CRYSTAL FIELD TREATMENT

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Abstract
The aim of present paper is to report the results on the modeling of the crystal field and spin-Hamiltonian parameters of Cr^{2+} doped in II-VI host matrix ZnS and simulate the energy levels scheme of such system taken into account the fine interactions entered in the Hamiltonian of the system. All considered types of such interaction are expected to give information on the new peculiarities of the absorption and emission bands, as well as of non-radiative transitions between the electronic states of impurity ions.The obtained results were disscused, compared with similar obtained results in literature and with experimental data.

1. Introduction

II-VI compounds are frequently studied materials because of their multiple applications [1], but it remains still to research the detailed nature of the electronic properties associated with the transition-metal ions doped in such host materials. Most studies [2-12] reveals that these properties can be better explained if were taken into account beside the electrostatic interactions, the Jahn-Teller effect, spin-orbit, spin-spin interactions and Tress correction between the nd electrons of the transition-metal ions doped in semiconductors and between the ions and the ligands. The tetrahedral site symmetry of the impurity Cr^{2+} ion doped in ZnS host matrix decrees, due to the static Jahn-Teller effect [2-6], from tetrahedral (T$_d$) to tetragonal (D$_{2d}$) symmetry, and gives the degeneracy of the energy levels [7, 8]. The spin-orbit, spin-spin interactions and Tress correction also influence the optical and magnetic properties of the Cr^{2+}:ZnS system.

This work reports the theoretical analysis regarding the modeling of the crystal field and spin-Hamiltonian parameters of Cr^{2+} ion doped in ZnS matrix and simulate the energy

levels scheme taking into account the fine interactions and the Jahn-Teller effect. We used for this the superposition model of crystal field, developed to separate the geometrical and physical information in crystal field parameters. The method of the complete diagonalization of the Hamiltonian is used. The obtained results were disscused, compared with similar obtained results in literature and with experimental data.

2. The modeling of the crystal field and spin-Hamiltonian parameters of Cr^{2+} doped in host matrix ZnS

Electrostatic interaction between electrons in the d^4 configuration gives rise to 16 LS terms: one spin-quintet ^5D, five spin-triplets $^3PDF_{1,2}GH$, and eight spin-singlets $^1S_{1,2}D_{1,2}F_{1,2}GI$. According to the Hund's rule, the ^5D term is the ground state. Relative energies of these terms can be expressed in terms of the Racah parameters B and C [13]. Taking into account the spin-orbit, spin-spin and Tress correction change the values of these parameters. The host matrix ZnS has a blend type structure [17] and belong to space group No.186 from International Tables for crystallography [18]. (Figure 1)
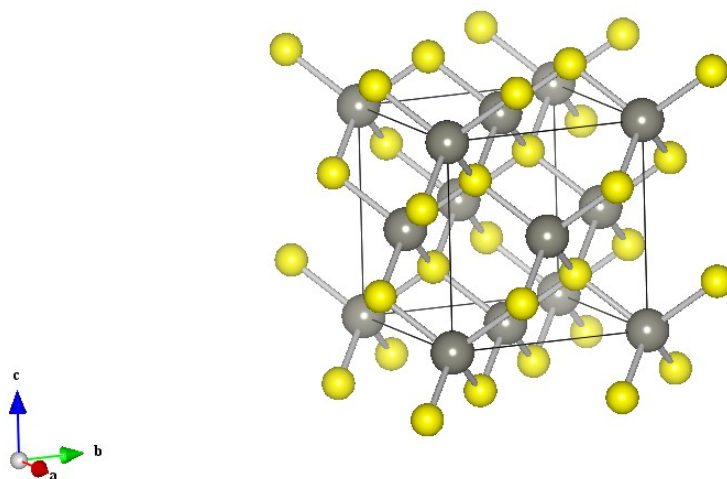

Fig. 1. The structure of ZnS crystal

By doping Cr^{2+} enters the lattice of ZnS in a substitution position on the cation Zn^{2+} site and is influenced by the tetrahedral crystal field (T_d symmetry) of the ZnS host. In a tetrahedral crystal field the ground state ^5D, which is the only spin-quintet level, is split into the ^5E doublet and the $^5T_2$ triplet levels, from which the $^5T_2$ is at lower energy [14-16]. The static Jahn-Teller effect leads to a change in symmetry from tetrahedral T_d to tetragonal D_{2d} [4,5].

The Hamiltonian for Cr^{2+} in a crystal can be written as

$$H = H_{fi} + H_{CF} + H_{JT} \qquad (1)$$

where $H_{fi} = H_{ee} + H_{so} + H_{ss} + H_{Trees}$ is Hamiltonian of free Cr^{2+} ion , H_{ee} is the electrostatic Coulomb term, H_{so}- the spin-orbit coupling, H_{ss}- the spin-spin interaction and H_{Tress} - the Tress correction. H_{CF} and H_{JT} in equation (1) are the tetragonal crystal field and the Jahn-Teller interactions, respectively.

As a result of Jahn-Teller interaction, the local symmetry of the chromium ion is reduced to D_{2d}, whereby the $^5T_2$ and ^5E states are split as

$$
\begin{aligned}
^5T_2 &\rightarrow {}^5\hat{B}_2 + {}^5\hat{E} \\
^5E &\rightarrow {}^5\hat{A}_1 + {}^5\hat{B}_1
\end{aligned}
\qquad (2)
$$

where $^5\hat{A}_1$, $^5\hat{B}_1$, $^5\hat{B}_2$ and $^5\hat{E}$ are the irreducible representations of the tetragonal group D_{2d}. Further, the degeneracy of these states is lifted by the spin-orbit, spin-spin and Tress interactions:

$$
\begin{aligned}
^5\hat{A}_1 &\rightarrow \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5 \\
^5\hat{B}_1 &\rightarrow \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_5 \\
^5\hat{B}_2 &\rightarrow \Gamma_1 + \Gamma_2 + \Gamma_4 + \Gamma_5 \\
^5\hat{E} &\rightarrow \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5
\end{aligned}
\qquad (3)
$$

The superposition model of the crystal field is based on several postulates [9]:

(i)   The crystal field acting on the open-shell electrons of a paramagnetic ion is the resultant of a sum of contribution coming from individual ions in the crystal.

(ii)   Only contributions from the neighbouring ions (ligands) are taken into account.

(iii)   Each single-ion contribution in the sum is axially symmetric about the line joining its centre to that of the paramagnetic ion.

The EPR spectrum of Cr^{2+} doped in ZnS had been measured by Vallin [7] and discussed in [8]. The ground-state splitting of $3d^4$ configuration of Cr^{2+} in the tetragonal ligand-field of ZnS host matrix can be described only by a spin Hamiltonian including all three EPR parameters related to the spin operators: a, D and F. The parameter a represents a cubic component of the crystalline electric field, D and F represent an axial component of that. Those parameters should be simultaneously considered to determine the distortion of the crystalline lattice.

The Hamiltonian matrix of d^4 ions has a dimension of 210x210 if including all the spin states, reducible to a smaller dimension if neglecting the spin singlet. The matrix 210x210 splits into four one-fold degenerated matrices, of 33x33, 23x23, 27x27, 27x27 and one two-

fold degenerated matrix of 50x50. Finally, each matrix element of the Hamiltonian (1) can be expressed as a linear combination of the Racah parameters B, C, the spin-orbit ζ parameter, M^0 and M^2 Marvin integrals [19], the α Tress correction and $B_2{}^0$, $B_4{}^0$ and $B_4{}^3$ crystal field parameters.

For the modeling crystal field parameters, the superposition model [20] of the crystal field has been used. The Crystal field parameters are [9]

$$B_2^0 = 2q\langle r^2 \rangle_0 \, 3\cos^2\theta - 1/R^3$$

$$B_4^0 = 2qe\langle r^4 \rangle_0 \, 35\cos^4\theta - 30\cos^2\theta + 3/R^5$$

$$B_4^4 = -2qe\langle r^4 \rangle_0 (35/2)^{1/2}\sin^4\theta/R^5$$

where R and θ denote the bond length and bond angle, respectively, q is the charge of ligand, e is electron charge.

3. Results of calculations and discussions.

There was determined the distortion parameters of the local lattice structure for Cr^{2+} in ZnS [8] as $\Delta R = 0,13\,\text{Å}$ and $\Delta\theta = 1,417°$.

For a cubic approximation, Grebe et al. [] have fitted the spectra of $ZnS:Cr^{2+}$ and got: Dq_0=-510 cm^{-1}, B=500 cm^{-1}, C=2850 cm^{-1}, ζ_0=230 cm^{-1}, ζ=223,6 cm^{-1}, R_0=2,341 Å and $\theta_0 = 54,7356°$.

Using the formulas obtained from the superposition model for the CF Hamiltonian [9] and adapted for the $3d^4$ configuration, we calculate the values for the B_k^q crystal field parameters:

$$B_2^0 = 18,535$$

$$B_2^2 = 0$$

$$B_4^0 = 240,611$$

$$B_4^2 = 0$$

$$B_4^4 = -876,092$$

Then, we can calculate the values of energy corresponding to the five levels obtained by splitting in tetrahedral field:

$$\Psi_1 \to E_1 = 6B_2^0 + 12B_4^0 - 12B_4^4 = 13511,645$$

$$\Psi_2 \to E_2 = -3B_2^0 - 48B_4^0 + 3B_2^2 - 12B_4^2 = -11604,93$$

$$\Psi_3 \to E_3 = -3B_2^0 - 48B_4^0 - 3B_2^2 + 12B_4^2 = -11604,93$$

$$\Psi_4 \rightarrow E_4 = 42B_4^0 + 6B_4^4 - 2\Delta_A = -7514,56$$

$$\Psi_5 \rightarrow E_5 = 42B_4^0 + 6B_4^4 + 2\Delta_A = 17212,78$$

where

$$\Delta_A = \sqrt{\left[9\left(B_2^0 - 5B_4^0 + B_4^4\right)^2 + 3\left(B_2^2 + 3B_4^2\right)^2\right]} = 6181,8366$$

For the spin-Hamiltonian parameters we obtain the results from Table 1.

Table1. Spin-Hamiltonian parameters for Cr^{2+}:ZnS

Parameter	Calculated	Observed [5]
$g_{\parallel}$	1.934	1.94
$g_{\perp}$	1.952	1.98
D	-1.92	-1.86
a	0.181	0.193(7)
F	-0.132	-0.14(7)

The obtained results are in good agreement with the experimental data.

4. Conclusions.

We have studied the crystal field and spin-Hamiltonian parameters of Cr^{2+} ion doped in ZnS , in the frame of superposition model of crystal field, using the complete diagonalization of the Hamiltonian of the system. Due to the static Jahn-Teller effect the tetrahedral T_d site symmetry decrees to tetragonal D_{2d} symmetry, and gives the degeneracy of the energy levels. The spin-orbit, spin-spin interactions and Tress correction also, further split the energy levels. All this interactions have been taken into account. The obtained results are in agreement with similar one published earlier and with experimental data.

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