

# Electronic and magnetic properties of ZnS crystal doped by Mn and Cu substitution atoms

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Electronic and magnetic properties of ZnS crystal doped by Mn and Cu atoms have been evaluated by means of Green's function method. The calculated partial and total spin-resolved densities of electron states point to the crucial changes in the crystal electronic structure induced by Mn and Cu substitution atoms. The changes are related to an appearance in band gap the narrow hybridized  $p$ - and  $d$ -symmetry zones which were absent in ZnS crystal.

По методу функции Грина рассчитаны электронные и магнитные свойства кристалла ZnS, легированного атомами Mn и Cu. Полученные парциальные и полные спин-поляризованные плотности электронных состояний указывают на коренную перестройку электронной структуры кристалла, обусловленную атомами замещения Mn и Cu. Изменения связаны с появлением в запрещенной зоне узких гибридных зон  $p$ - и  $d$ -симметрии, отсутствующих в кристалле ZnS.

## 1. Introduction

Diluted magnetic semiconductors attract great attention of researches, since they can be used in spintronics, integrated optoelectronic devices, and nano-structured quantum devices [1]. ZnS, a typical II–VI compound semiconductor, is a promising host material for producing commercial lumino-phors. It has been used as base material for cathode-ray tube luminescent materials, as efficient lumino-phor in flat panel displays, in thin-film electroluminescent devices, and infrared windows [2]. II–VI compounds show novel magneto-optical and magneto-transport properties if the cation is partly substituted by Mn with its half-filled  $3d$ -shell. The effects of defects on properties of II–VI crystals are described in detail in works [3,4]. The importance of accounting the substitution Mn and Cu atoms in ZnS has been grounded in work [5]. Therefore, the aims of this paper are the following: 1) to calculate partial and total electronic densities of states (DOS) in crystal  $Zn_{1-x}Mn_xS$ ;

2) to calculate partial and total DOS in crystal  $Zn_{1-x-y}Mn_xCu_yS$ ; 3) to evaluate the magnetic moments on all the atoms in a cell.

## 2. Calculations

Electronic structure calculations are performed by means of the AkaiKKR program [6]. The exchange-correlation potential, based on the local spin-density approximation with the parameterization by Moruzzi, Janack, and Williams [7], has been used here. The  $k$  integration over Brillouin zone is performed using the Monkhorst-Pack method [8], with grid  $8 \times 8 \times 8$ . ZnS has the zinc blende crystal structure, and the lattice constants is  $a = 5.4093 \text{ \AA}$ . Iterations were continued until the convergence in the calculation of total energy of the crystal with an accuracy of  $10^{-8}$  Ry. Such precision was achieved in about 100 iteration steps. The relativistic effects were included within the scalar relativistic approximation. The density of electronic states is evaluated from Equation,

Table 1. Electronic and magnetic properties of the crystal  $Zn_{1-x-y}Mn_xCu_yS$ . Here  $\varepsilon_F$  is the Fermi energy (eV), up means spin up, dn denotes spin down;  $n(\varepsilon_F)$  is the density of states, 1/eV/cell/spin. The magnetic moment is given in  $\mu_B$  (Bohr magneton). The spin moment is denoted  $\mu_s$ .

	$Zn_{0.98}Mn_{0.02}S$	$Zn_{0.97}Mn_{0.02}Cu_{0.01}S$
$\varepsilon_F$ , up	8.710	7.753
$\varepsilon_F$ , dn	8.691	7.761
$n(\varepsilon_F)$ , up	1.090	1.046
$n(\varepsilon_F)$ , dn	26.240	1.089
$\mu_s$ on Zn	0.0010	0.0011
$\mu_s$ on Mn	3.8220	3.9485
$\mu_s$ on Cu	–	0.0062
$\mu_s$ on S	0.0056	0.0061
$\mu_s$ on Vo	0.0005	0.0005
$\mu_s$ on Vt	0.0030	0.0165

$$n(E) = -1/\pi \text{Im} \int d\mathbf{r} G(\mathbf{r}, \mathbf{r}, E), \quad (1)$$

where  $G$  is the retarded Green's function [9]. Octahedral vacancy (Vo) is localized at the interstitial coordinates (1/2; 1/2; 1/2) and the tetrahedral one (Vt) is situated at the point (3/4; 3/4; 3/4).

### 3. Results and discussion

Table shows the obtained electronic and magnetic properties of  $Zn_{1-x-y}Mn_xCu_yS$ , where  $x = 0.02$  is the concentration of Mn atoms and  $y = 0.01$  of Cu atoms, respectively. From Table it can be revealed that the crystal with Cu impurity is characterized with lower values of Fermi energy, compared to the corresponding values from the first column.

Fig. 1 shows partial and total density of electronic states in ZnS crystal with substitution impurity of Mn. The first two curves demonstrate that due to the Mn impurity in band gap arising unoccupied narrow band  $p$ - and  $d$ -symmetry with spin down. Two further curves show the narrow filled bands of  $p$ - and  $d$ -symmetry, with spin up caused by the presence of impurity Mn. It should be noted that filled with electrons and empty states are narrow and strongly hybridized. The two highest curves represent the full (total) DOS for spin down and spin up. Obviously, these dependencies were changed in the band gap region caused by the influence

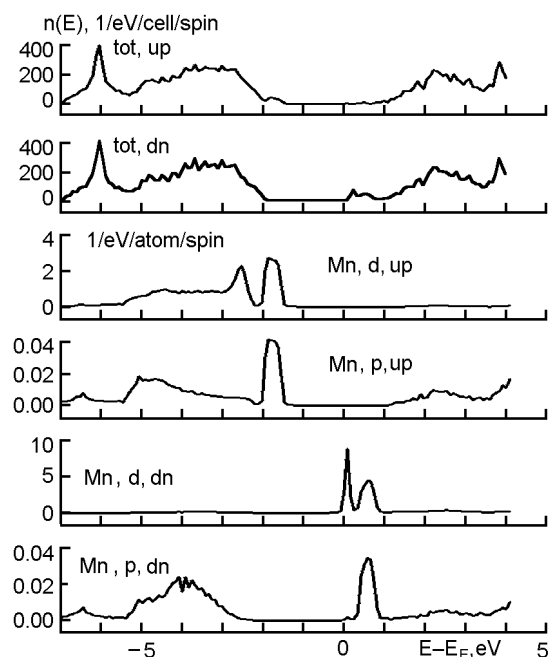


Fig. 1. Partial and total electronic DOS in crystal ZnS doped with Mn (2 %) substituting Zn.

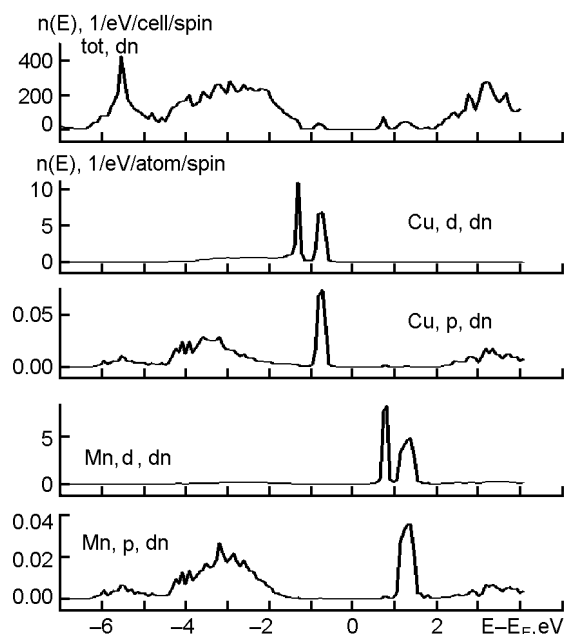


Fig. 2. Partial and total electronic DOS in crystal ZnS doped by Mn (2 %), Cu (1 %), substituting Zn, with spin down.

of Mn impurity. However, the structure of the modified DOS now can be easily explained by means of the partial DOS  $p$ - and  $d$ -symmetry.

Fig. 2 depicts the density of states in the crystal ZnS with Mn and Cu substitution impurities. All curves in Fig. 2 correspond to the orientation of spin down. Comparing

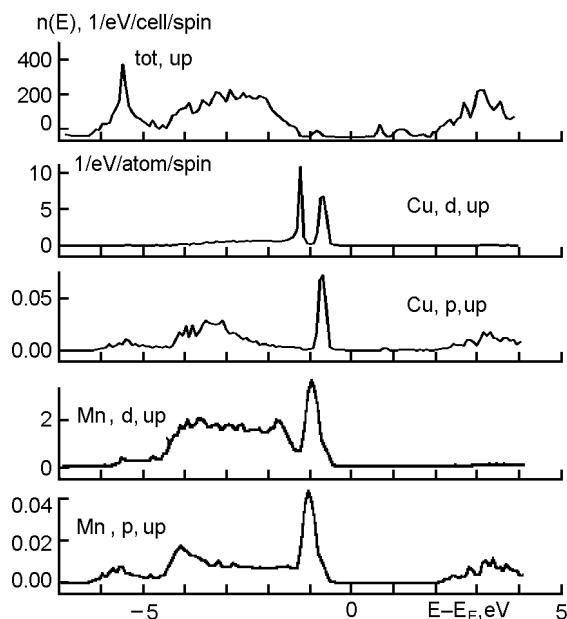


Fig. 3. Partial and total electronic DOS in crystal ZnS doped with Mn (2 %), Cu (1 %) substituting Zn, with spin up.

the first two curves (bottom) in Fig. 1 and 2, we can see that they are virtually identical in form and describe the unoccupied electron states. However, the corresponding curves shown in Fig. 2 are shifted toward higher energy values. Two further curves indicate the presence in the band gap  $p$ - and  $d$ -states of Cu, filled with electrons. The highest curve in Fig. 2 shows the total density of electronic states with spin down. Four curves located below in Fig. 2 indicate implicitly to the structure of the full density of states.

Fig. 3 represent the density of states in ZnS crystal with Mn and Cu substitution impurities, with spin up. We see that in a band gap the Mn-induced narrow filled bands of  $p$ - and  $d$ -symmetry occur, and due to Cu atoms the narrow filled  $p$ - and  $d$ -bands arise. It should be noted that the partial density of states of  $p$ - and  $d$ -symmetry of Mn atoms with spin down (Fig. 2) and spin up (Fig. 3) significantly different in shape and energy values. This asymmetry directly indicates the presence of substantial spin magnetic moment on Mn atom. It is also confirmed by data in Table 1. And vice versa, the partial density of states  $p$ - and  $d$ -symmetry of Cu atoms with spin down (Fig. 2) and spin up (Fig. 3) are almost identical in shape and energy values. This fact points directly to a small spin polarization of electron density of Cu atoms and

therefore to small contribution of copper atoms to the value of magnetic moment. Confirmation of this conclusion is also evident from Table.

#### 4. Conclusions

Electronic density of states in ZnS crystal with Mn and Cu substitution impurities has been evaluated. Comparing partial density of the states of Mn atoms, shown in Fig. 1–3, we have seen that the additional doping by Cu atoms does not change the form of partial density of the states in the narrow bands, caused by Mn impurity. Fig. 2 shown unoccupied  $p$ - and  $d$ -bands of Mn atoms, and filled with electrons in  $p$ - and  $d$ -states of Cu atoms. Comparing partial density of the states of copper atoms with spin down (Fig. 2), and spin up (Fig. 3), we have revealed that filled narrow bands of  $p$ - and  $d$ -symmetry are characterized by practically the same dependencies, as confirmed by the data in Table showing a small magnetic moment on Cu atoms. On the contrary, the densities of the states on Mn atoms, corresponding opposite spin, are radically different, and so the contribution to the magnetic moment on Mn atoms (Table 1) is the greatest. Similarly, contributions to the magnetic moment of the atoms of Zn and S are small. The corresponding partial density of the states on Zn and S atoms are almost identical for both orientations of the spins. The DOS curves (Fig. 3), induced by Mn and Cu atoms, with spin up, demonstrated the narrow filled bands of  $p$ - and  $d$ -symmetry.

We found out that the value of spin magnetic moment of Mn atom is well matched with the obtained in [1] ( $3.82 \mu_B$ ).

From Fig. 1–3 it can be concluded that description of the kinetic phenomena in such crystals can not be performed within the effective mass approximation. Dipole transitions are possible between  $p$ - and  $d$ -states of Mn and Cu atoms. Therefore, the results of this work can be applied to explain the nature of the photoelectron spectra [5].

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## **Електронні та магнітні властивості кристала ZnS, легованого атомами заміщення Mn і Cu**

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Електронні та магнітні властивості кристала ZnS, легованого атомами Mn та Cu, розраховані за методом функції Гріна. Отримані парціальні та повні спин-поляризовані щільності електронних станів вказують на докорінну перебудову електронної структури кристала, спричинену атомами заміщення Mn та Cu. Зміни зв'язані з появою у забороненій зоні вузьких гібридизованих зон  $p$ - і  $d$ -симетрії, відсутніх у кристалі ZnS.