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Ab initio calculations of electronic band structure of ideal and defective CdMnS

Matanat A. Mehrabova[1]✉, Natig T. Panahov[2], Niyazi H. Hasanov[3]

[1]Institute of Radiation Problems of Azerbaijan National Academy of Sciences, B. Vahabzade str., 9, Baku, AZ-1143, Azerbaijan

[2]Azerbaijan University of Architecture and Construction, A. Sultanova str. 5, Baku, AZ-1073, Azerbaijan

[3]Baku State University, Z. Khalilov str., 23, Baku, AZ-1148, Azerbaijan

✉ m.mehraboav@science.az

Abstract. The purpose of this work was to calculate the electronic band structure of ideal and defective $Cd_{1-x}Mn_xS$. Ab initio, calculations are performed in the Atomistix Toolkit program within the Density Functional Theory and Local Spin Density Approximation on Double Zeta Double Polarized basis. We have used Hubbard U potential U_{Mn} = 3.59 eV for 3d states for Mn atoms. Supercells of 8 and 64 atoms were constructed. After the construction of $Cd_{1-x}Mn_xS$ (x = 6.25%; 25%) supercells, atom relaxation and optimization of the crystal structure were carried out. Electronic band structure, and density of states were calculated, and total energy have been defined in antiferromagnetic and ferromagnetic phases. Our calculations show that the band gap increases with the increases in Mn ion concentration. It has been established that defects such as interstitial Cd(S) atom, Cd(S) vacancy or Frankel pair in the crystal structure lead to increasing band gap, shifting of Fermi level towards the valence or conduction band.

Keywords: ab initio calculations, DFT, semimagnetic semiconductors, electronic band structure, defect

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1. Introduction

CdS (band gap 2.43 eV) is an attractive semiconductor in the photoconductive, photovoltaic, and optoelectronic materials [1-5]. They have large applications as photoconductors in the visible and near ultra-violet spectral regions, in semiconductor lasers, nonlinear optical devices [6], photovoltaic solar cells, thin film transistors, display devices [7] and also for tagging biological molecules [8]. Doping of transition metals such as Mn, Fe, Ni, Co, etc. in nonmagnetic CdS is very important to make this material multifunctional, that influences the electronic structure, produces unique magnetic and magneto-optical properties with unparalleled opportunities in the field of spintronics [9]. $Cd_{1-x}Mn_xS$ thin films have also drawn large attention because of their magnetic and magneto-optical properties [10,11]. Room temperature CdS- based semimagnetic semiconductors (SMSC), such as Mn-doped

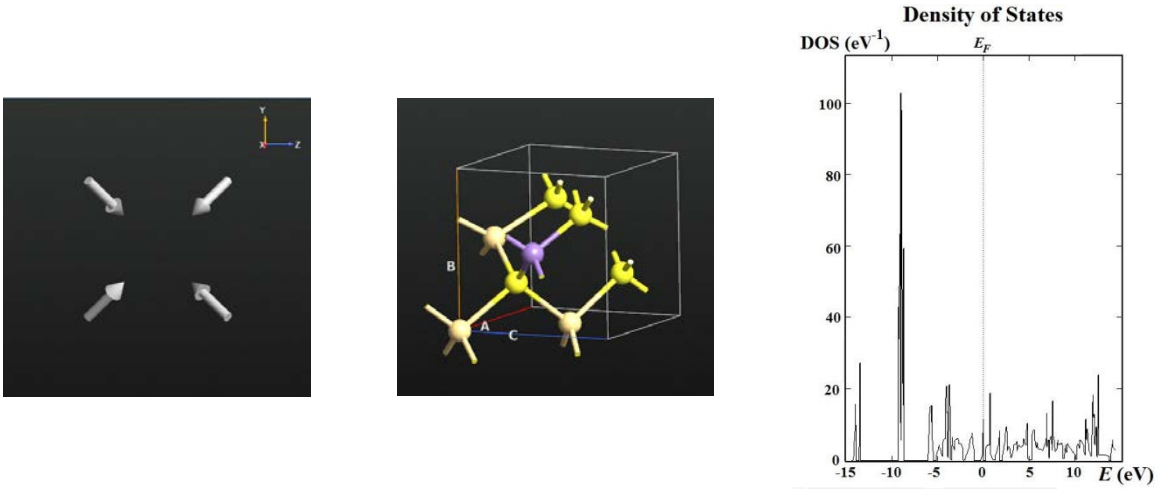
CdS are a very good photoluminance compound due to *d* states at the top of the valence band and intra-*d* shell transitions [12].

This work is devoted to ab initio calculations of $Cd_{1-x}Mn_xS$ SMSC by using Density functional theory (DFT). DFT have been successfully used for theoretical investigations of magnetic materials [13-17]. The Mn-CdS sheet with 16 atom supercell is analyzed by Kumar S., Kumar A., Ahluwalia P.K. [18]. The electronic band structure of wurtzite CdS calculated by Rantala et al. using two different self-consistent ab initio Local Density Approximation (LDA) methods [19]. Nabi [20] investigated electronic and magnetic properties of Mn-doped CdS in the wurtzite phase, using ab-initio calculations based on LDA, Generalized Gradient Approximation (GGA) and LDA + *U* exchange and correlation functional. It is found that Mn:CdS does not allow the hopping of electrons and d-d super exchange interactions are observed in Mn:CdS [20]. Ahmed N., Nabi A., Nisar J., Tariq M., Javid M.A., and Nasim M.H. [12] investigated the electronic band structure of $Cd_{1-x}Mn_xS$ (x = 6.25 %) using spin-polarized DFT within the framework of GGA, its extension via on-site Hubbard *U* interactions (GGA + *U*), and a model for exchange and correlation of potential Tran modified Becke-Johnson (TB-mBJ).

Band structure of defective CdMnS has been investigated less [20] in comparison with other SMSC. The purpose of this work was to calculate the electronic band structure of ideal and defective $Cd_{1-x}Mn_xS$ SMSC in both.

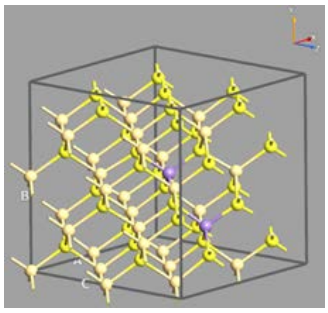
2. Methods and results

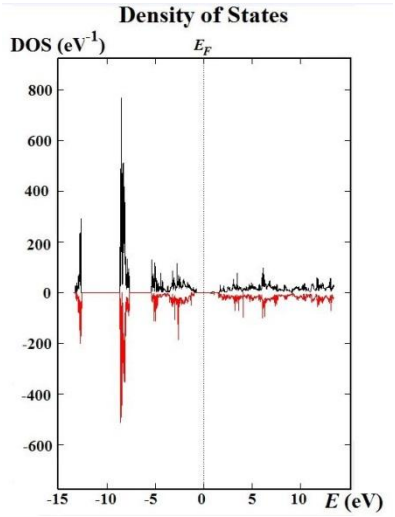
Ab initio calculations are performed in the Atomistix Toolkit (ATK) program within the DFT and Local Spin Density Approximation (LSDA) on the Double Zeta Double Polarized (DZDP) basis. We have used Hubbard *U* potential U_{Mn} = 3.59 eV for 3d states for Mn atoms [5-10]. Ideal supercells of 8 (Fig. 1) and 64 (Fig. 2) atoms were constructed. After the construction of $Cd_{1-x}Mn_xS$ (x = 0; 6.25 %; 25 %) supercells, atom relaxation and optimization of the crystal structure were carried out to eliminate forces and minimize stresses. Electron band structure (EBS) and density of states (DOS) were calculated, and the total energy has been defined in AFM and FM phases.



a b c

Fig. 1. $Cd_{1-x}Mn_xS$, x=0.25 supercell: a – forces; b – bulk configuration; c – density of states





a b

Fig. 2. $Cd_{1-x}Mn_xS$, x = 0.0625 supercell: a – bulk configuration; b – density of states

The electron band structure of $Cd_{1-x}Mn_xS$ (x = 0.0625) SMSC is determined from the projected density of states (PDOS) (Fig. 3). The obtained PDOS plots are presented in Fig. 3. The analysis of these graphs shows that in the valence band, the electron band structure of $Cd_{1-x}Mn_xS$ consists of three parts: (1) the upper part of the valence band is mainly formed by *p*-orbitals of S and Cd atoms, *s*-orbitals of Cd and Mn atoms with some contribution of *d*-orbitals of Mn atoms; (2) the middle part is formed by *d*-orbitals of Cd atoms, which are 8–9 eV lower than the valence band maximum (3) the lower part is formed by *s*-orbitals of S and Mn atoms, and *p*-orbitals of Mn atoms which are located 13 eV lower than the valence band maxim. The bottom of the conductivity band is formed by *s*-and *p*-orbitals of Mn atoms and *p*-orbitals of Cd atoms, *d*-orbitals of S atoms (Fig. 3).

The band gap for the $Cd_{1-x}Mn_xS$ SMSC with x = 0.25 supercells is equal to E_g = 1.6 eV and total energy is equal to E_t = –6698.61546 eV. For the x = 0.0625 supercell band gap is equal to E_g = 1.25 eV and total energy is equal to E_t = 59267.92943 eV. The calculated band gap much closer to theoretical 1.25 eV, 1.27 eV [12,20] and experimental value [26]. The values of band gap with GGA calculations and effect of Hubbard "U" term on band gap using GGA+U calculations were used in [12,20].

Calculations show that the band gap increase with an increase in Mn ion concentration (Table 1). These theoretical results have a good agreement with experimental results [27]. The optical transmission of the $Cd_{1-x}Mn_xS$ thin films show that the band gap increases with the increases in manganese ion concentration.

Table 1. Band gap and total energy for $Cd_{1-x}Mn_xS$

x	E_g, eV	E_t, eV
0	0.83	-1910,95
0.0625	1.25	-59267,93
0.25	1.6	-6698,62

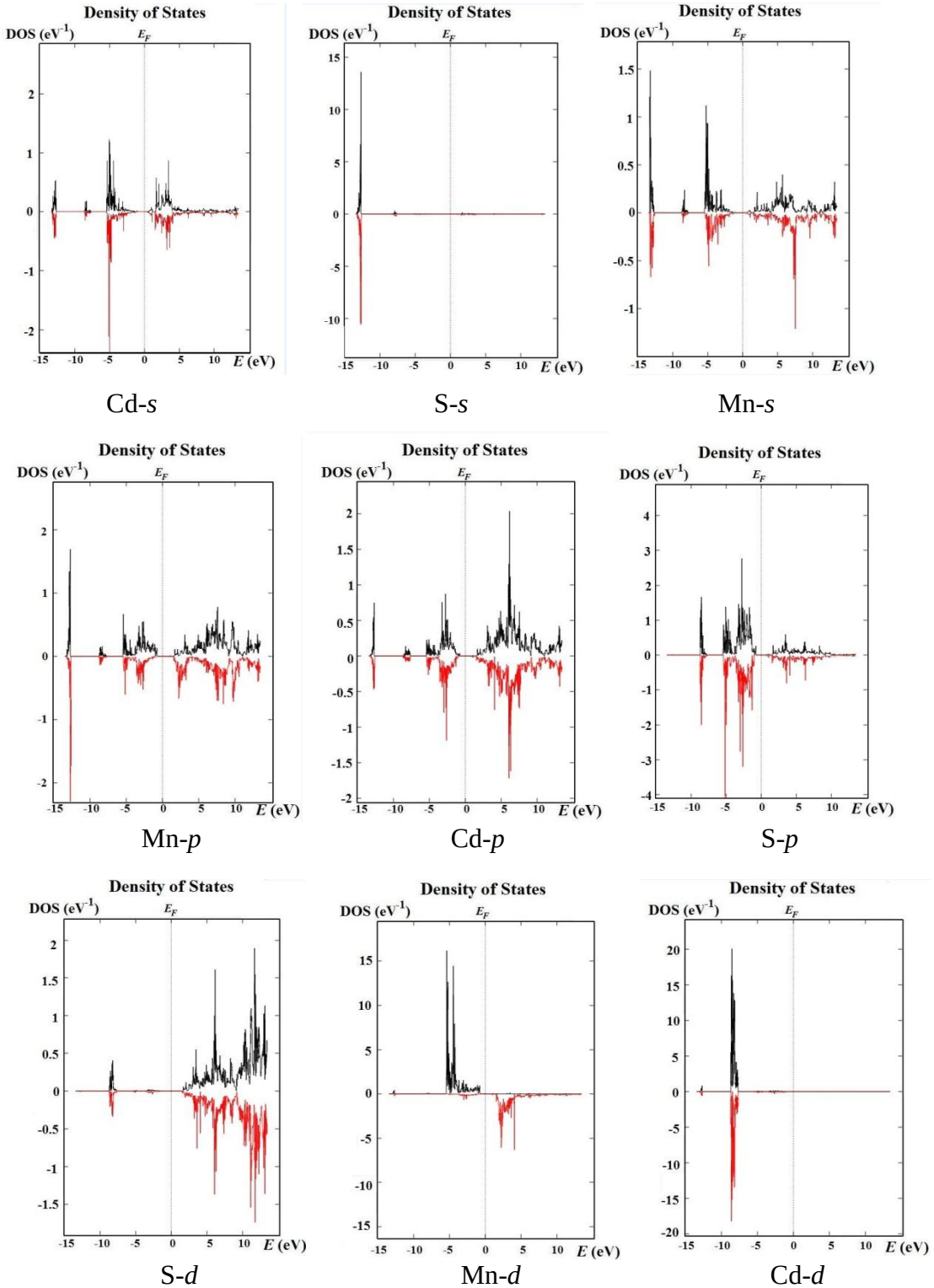


Fig. 3. PDOS of $Cd_{1-x}Mn_xS$ (x = 0.0625) SMSC

EBS and DOS of the defective $Cd_{30}Mn_2Se_{32}$ supercell are calculated. We consider vacancy-type defects. Atom relaxation and optimization of the crystal structure were carried out, and forces and stresses were minimized (Fig. 4).

a b

Fig. 4. Forces: a – before optimization; b – after optimization

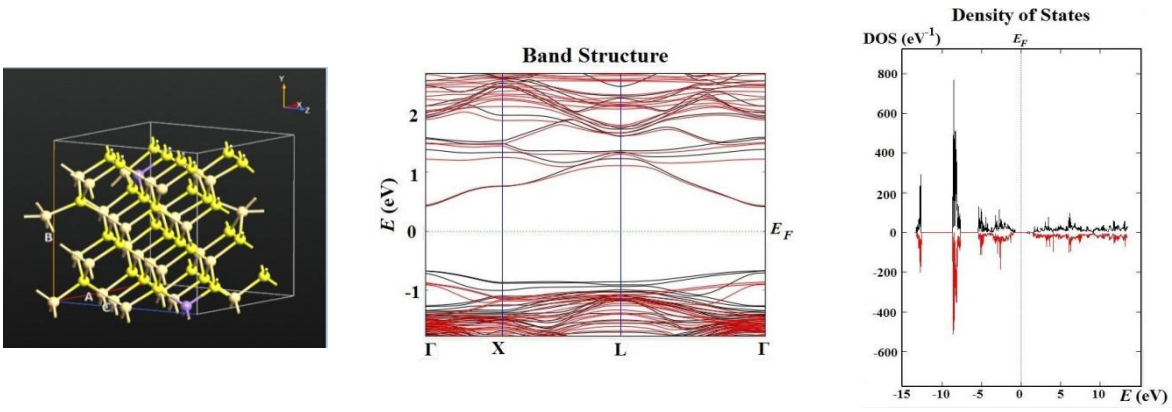


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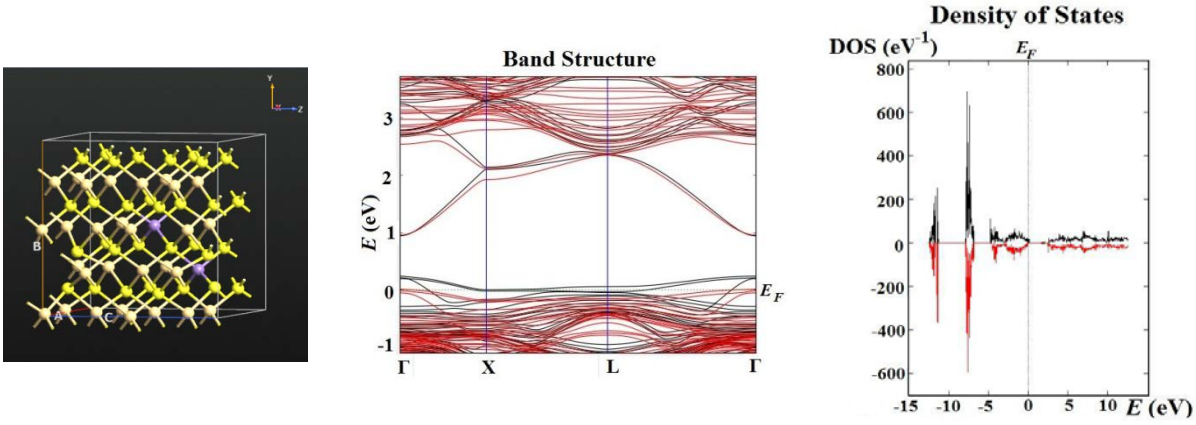
Fig. 5. S vacancy in $Cd_{1-x}Mn_xS$, x = 0.625; *a* – bulk configuration; *b* – EBS; *c* – DOS



a b c

Fig. 6. Cd vacancy in $Cd_{1-x}Mn_xS$, x = 0.625; *a* – bulk configuration; *b* – EBS; *c* – DOS

In the case of S vacancy (V_S), the band gap is E_q = 1.3 eV, and the total energy equals E_t = –58907.65 eV (Fig. 5); for Cd vacancy (V_{Cd}) the band gap is E_g = 1.55 eV, the total energy is E_t = –57712.51 eV (Fig. 6). Figures 5 and 6 show that Cd or S vacancy in a crystal leads to an increase in the band gap, as a change in the total energy occurs, the Fermi level shifts towards the valence or conduction band.

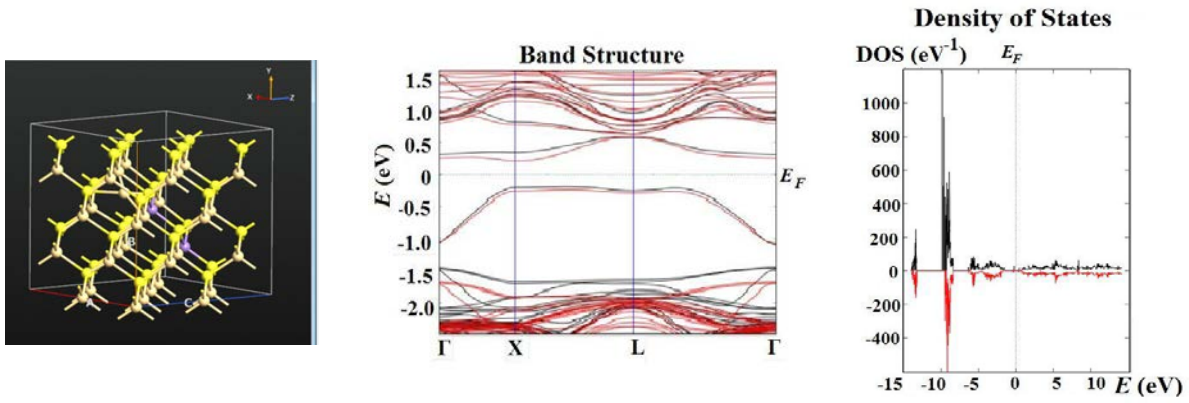


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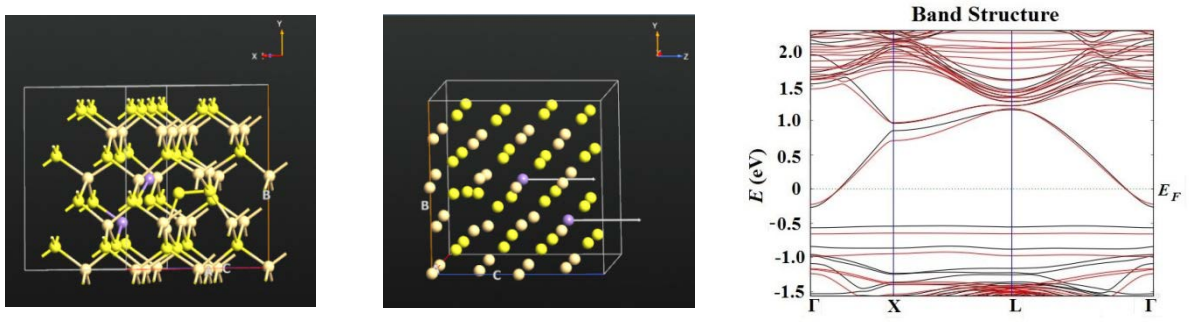
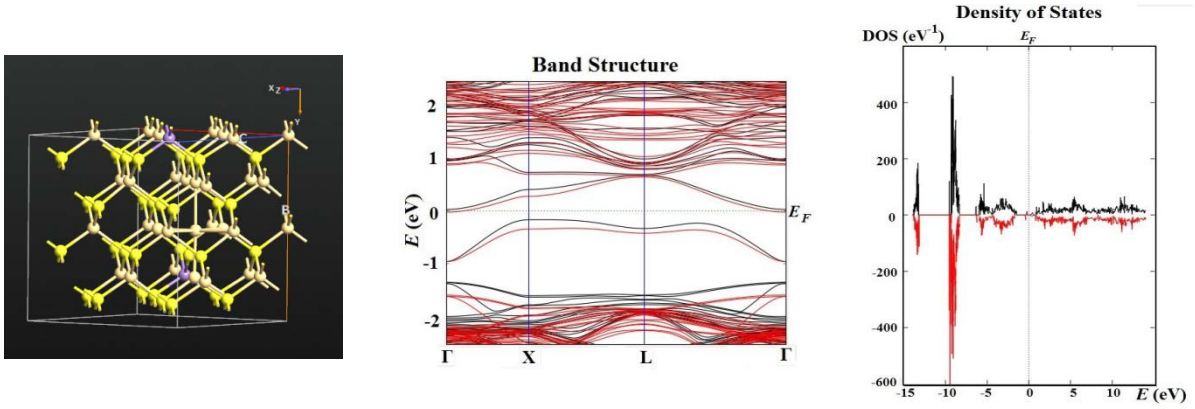
Fig. 7. Interstitial Cd atom in $Cd_{1-x}Mn_xS$, x = 0.625; a – bulk configuration; b – EBS; c – DOS



a b c

Fig. 8. Interstitial S atom in $Cd_{1-x}Mn_xS$, x = 0.625; a – bulk configuration; b – magnetic moments; c– EBS

Supercell of $Cd_{1-x}Mn_xS$ of 64 atoms with interstitial Cd (I_{Cd}) atom and interstitial S (I_S) atom were constructed. After the construction of $Cd_{1-x}Mn_xS$ (x=6.25 %) supercell with interstitial Cd or S atom, atom relaxation and optimization of crystal structure were carried out. Electron band structure, density of states were calculated, and total energy have been defined (Fig. 7,8). In the case of interstitial Cd atom, the band gap is equal to Eg=1.35 eV, total energy is equal to E_t=-60817.73 eV (Fig. 7). For the interstitial S atom, the band gap is equal to E_g=1.75 eV, and total energy is equal to E_t=-59624.67 eV (Fig. 8). Figures 7 and 8 show that interstitial Cd or S atoms in crystal structure lead to an increase in the band gap.



a b c

Fig. 9. Frenkel pair in $Cd_{1-x}Mn_xS$, x = 0.625; a – bulk configuration; b – EBS; c – DOS

Supercell of $Cd_{1-x}Mn_xS$ of 64 atoms with Frankel pair was constructed. After the construction of $Cd_{1-x}Mn_xS$ (x=6.25 %) supercell with Frankel pair, atom relaxation and optimization of crystal structure were carried out. Electron band structure, density of states were calculated, and total energy have been defined. In the case of Frankel pair, the band gap is equal to E_g=2 eV, total energy is equal to E_t=-60817.77 eV (Fig. 9).

It can be concluded that vacancy, interstitial atom, or Frenkel pair type defects in crystal lead to an increase in the band gap, Fermi level shifts towards the valence or conduction band (Table 2).

Table 2. Band gap and total energy for Interstitial Cd (S) atom and Cd (S) vacancy in $Cd_{1-x}Mn_xS$, x=0.25

x=0.0625	Ideal	V_{Cd}	V_S	I_{Cd}	I_S	FP
E_g, eV	1.25	1.55	1.3	1.35	1.75	2
E_t, eV	-59267.93	-57712.51	-58907.65	-60817.73	-59624.67	60817.77

3. Conclusion

Ab initio calculations have been performed to analyze the electronic band structure of an ideal and defective $Cd_{1-x}Mn_xS$ SMSC (x = 0.25; 0.0625). It has been defined that with an increase in Mn ion concentration in the $Cd_{1-x}Mn_xS$, there is an increase in the band gap and an increase in the total energy. The calculations show that the defects as a vacancy, interstitial atom, or Frenkel pair in a crystal lead to an increase in the band gap, shifting the Fermi level towards the valence or conduction band.

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THE AUTHORS

Mehrabova M.A.
e-mail: mehrabova@mail.ru
ORCID: 0000-0003-4417-0522

Panahov N.T.
e-mail: panahovn@yahoo.com
ORCID: 0000-0002-9178-0641

Hasanov N.H.
e-mail: n.h.hasanov@rambler.ru
ORCID: 0000-0002-5122-4712