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Original paper

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AB INITIO CALCULATIONS OF ELECTRONIC BAND STRUCTURE OF CdMnS SEMIMAGNETIC SEMICONDUCTORS

MATANAT A. MEHRABOVA[1], NATIG T. PANAHOV[2], NIYAZI H. HASANOV[3]

[1]*Institute of Radiation Problems of Azerbaijan National Academy of Sciences (Baku, Azerbaijan)*

[2]*Azerbaijan University of Architecture and Construction (Baku, Azerbaijan)*

[3]*Baku State University (Baku, Azerbaijan)*

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Abstract. This work is devoted to theoretical investigations of $Cd_{1-x}Mn_xS$ semimagnetic semiconductors (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 antiferromagnetic (AFM) and ferromagnetic (FM) phases. Ab initio, calculations are performed in the Atomistix Toolkit (ATK) program within the Density Functional Theory (DFT) and Local Spin Density Approximation (LSDA) on Double Zeta Double Polarized (DZDP) basis. We have used Hubbard U potential U_{Mn} = 3.59 eV for 3*d* 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 and atom relaxation and optimization of the crystal structure were carried out. Electronic band structure and density of states were calculated, the total energy has been defined in antiferromagnetic (AFM) and ferromagnetic (FM) phases. Our calculations show that the band gap increases with the increase in Mn ion concentration. It has been established that Cd or S vacancy in the crystal structure leads to the change of band gap, Fermi level shifts towards the valence or conduction band.

Keywords: Ab initio calculations, DFT, semimagnetic semiconductors, electronic band structure, vacancy.

Conflict of interests. The authors declare no conflict of interests.

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Introduction

CdS is an attractive semiconductor in the photoconductive, photovoltaic, and optoelectronic materials. The dope of transition metals in nonmagnetic CdS is very important to make this material multifunctional. Room temperature CdS based SMSC, such as Mn doped CdS is a very good photo-luminance compound due to *d* states at the top of the valence band and intra-*d* shell transitions [1].

This work devoted to theoretical investigations of $Cd_{1-x}Mn_xS$ SMSC. The Mn-CdS sheet with 16 atom supercell is analyzed by Kumar S., Kumar A., Ahluwalia P.K. [2]. The electronic band structure of wurtzite CdS calculated by Rantala et al. using two different self-consistent ab initio LDA methods [3]. Nabi [4] investigated electronic and magnetic properties of Mn doped CdS in wurtzite phase, using ab-initio calculations based on Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) and LDA + U exchange and correlation functionals.

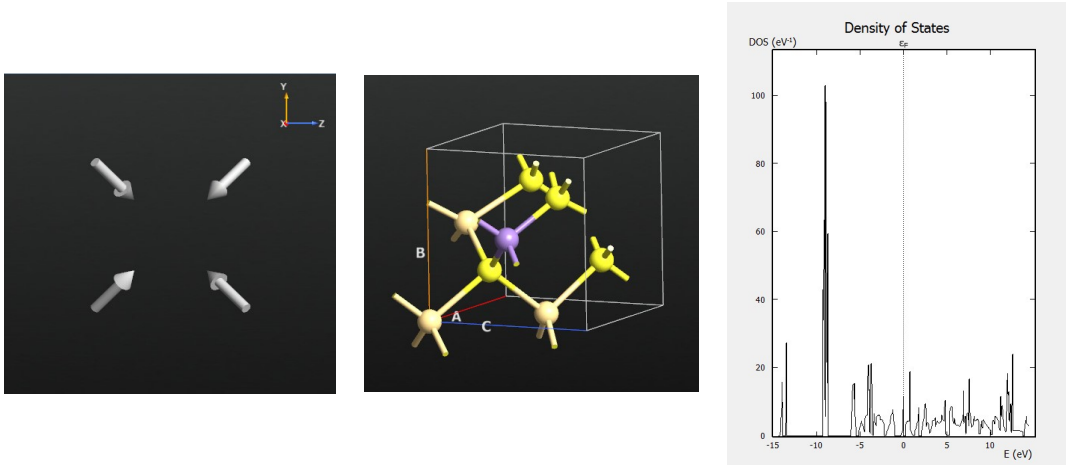
Ahmed N., Nabi A., Nisar J., Tariq M., Javid M.A., and Nasim M.H. [1] investigated the electronic band structure of $Cd_{1-x}Mn_xS$ (x = 6.25 %) using spin-polarized DFT within the framework

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).

The purpose of this work was to calculate the electronic band structure (EBS) of ideal and defective $Cd_{1-x}Mn_xS$ SMSC in both AFM and FM phases.

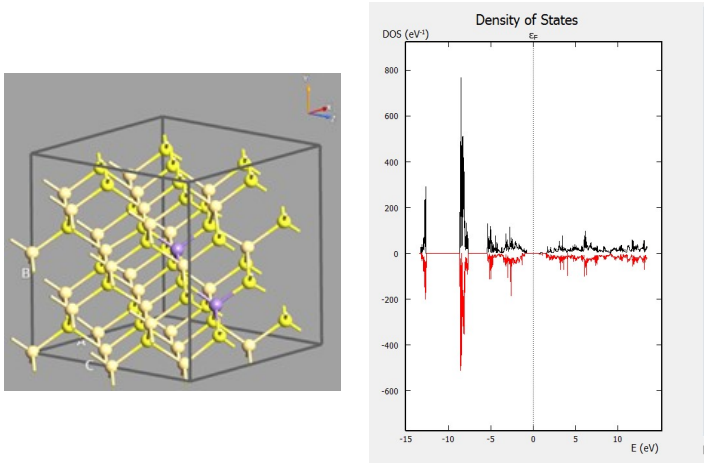
Methods and results

Ab initio calculations are performed in the Atomistix Toolkit (ATK) program within the DFT and LSDA on the DZDP basis. We have used Hubbard U potential U_{Mn} = 3.59 eV for 3*d* states for Mn atoms [5, 6]. An 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 and density of states were calculated, 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, 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, *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).

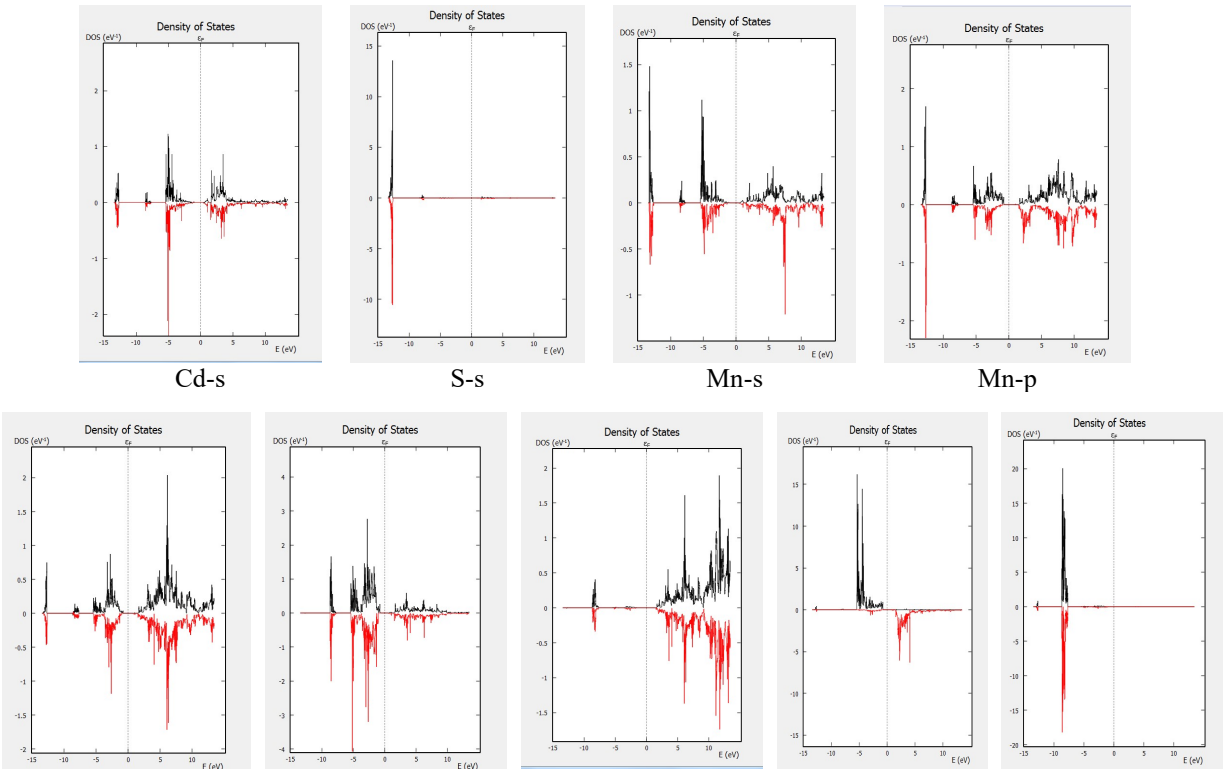
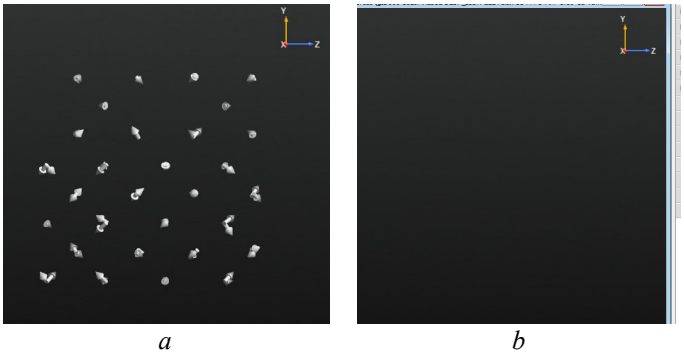


Fig. 3. PDOS of $Cd_{1-x}Mn_xS$ ($x = 0.0625$) SMSC

The band gap for the $Cd_{1-x}Mn_xS$ 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.

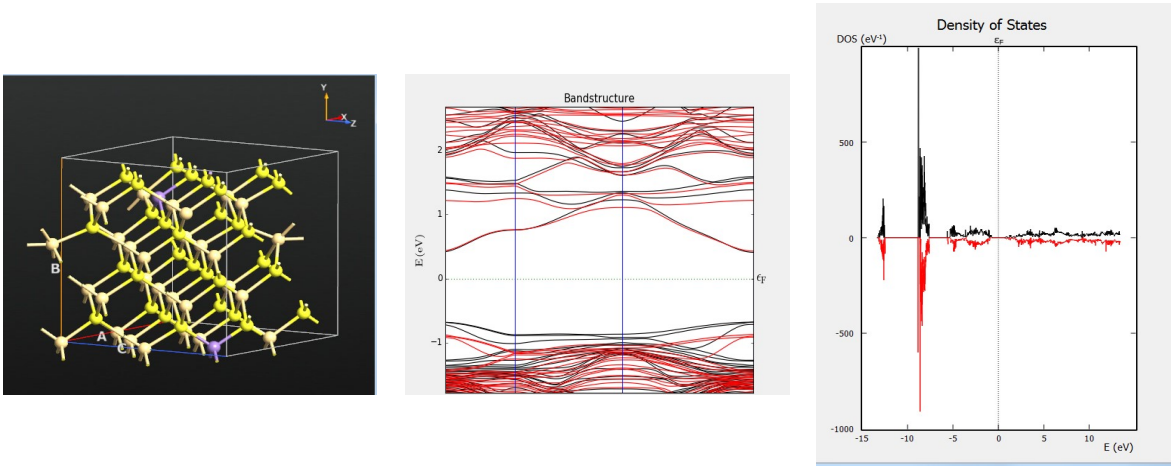
EBS and DOS of the defective $Cd_{30}Mn_2Se_{32}$ supercell are calculated. We consider vacancy type as a defect. Atom relaxation and optimization of the crystal structure were carried out, forces and stresses were minimized (Fig. 4).



a *b*

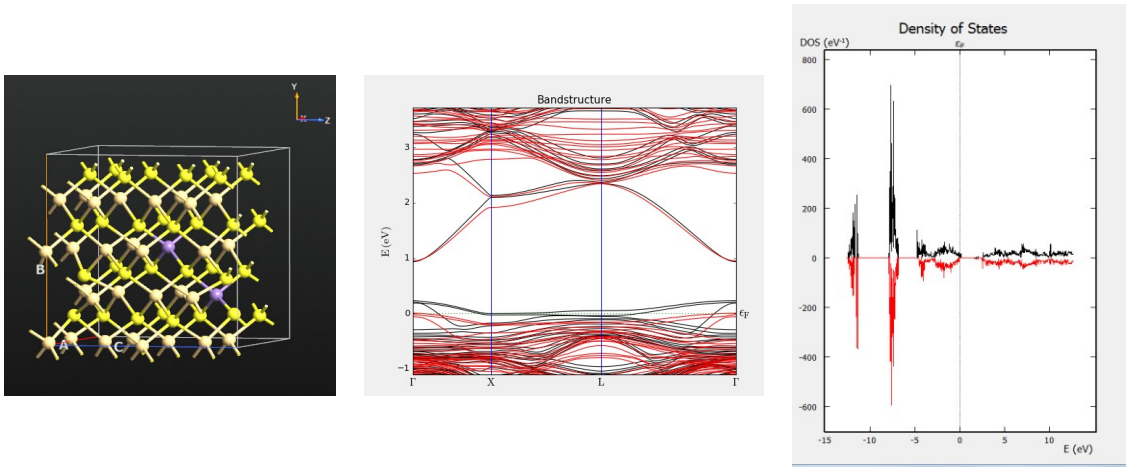
Fig. 4. Forces: *a* – before optimization; *b* – after optimization

In the case of S vacancy (V_S), the band gap is $E_g = 1.3$ eV, the total energy equals $E_t = -58907.646$ eV (Fig. 5); for Cd vacancy (V_{Cd}) the band gap is $E_g = 1.55$ eV, the total energy is $E_t = -57712.50684$ eV (Fig. 6). It can therefore be concluded that the 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.



a *b* *c*

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

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 in a crystal lead to an increase in the band gap, decrease in the total energy, shifting of the Fermi level towards the valence or conduction ban.

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Authors' contribution

Mehrabova M.A. and Panahov N.T. carried out calculations in the program.

Hasanov N.H. defined the objectives of the research, took part in the preparation of the text of the article, and interpretated the results of the experiments.

Information about the authors

Mehrabova M.A., D.Sc., Associated Professor, Leading Researcher at the Institute of Radiation Problems of Azerbaijan National Academy of Sciences.

Panahov N.T., PhD., Associated Professor, Leading Researcher at the Azerbaijan University of Architecture and Construction.

Hasanov N.H., Lecturer at the Department of Physics of Baku State University.

Address for correspondence

AZ1143, Azerbaijan,
Baku, B.Vahabzade St., 9,
Institute of Radiation Problems of ANAS;
tel. +994-50-731-81-77;
e-mail: m.mehrabova@science.az
Mehrabova Matanat Ahmed