

## High Curie temperature in Zn(Co,Ni)Se: DFT study

Vusala Nabi Jafarova<sup>1,2,3</sup>, Nermin Neriman Hashimova<sup>1</sup>, Ionut Cristian Scurtu<sup>4</sup>

<sup>1</sup>Azerbaijan State Oil and Industry University, 20 Azalig ave., AZ-1010, Baku, Azerbaijan

<sup>2</sup>Khazar University, 41 Mehseti Str., AZ1096, Baku, Azerbaijan

<sup>3</sup>Ministry of Science and Education Republic of Azerbaijan, Institute of Physics, 131 H. Javid Ave., AZ-1143, Baku, Azerbaijan

<sup>4</sup>Romanian Naval Academy, 1 Fulgerului Str., 900218, Constanta, Romania  
Ionut Cristian Scurtu: scurtucristian@yahoo.com, vcafarova@beu.edu.az

**Abstract.** In this work, we aimed to examine the first-principles study of correlation between chemical environment and ferromagnetism, and Curie temperature of  $\text{Co}_x\text{Zn}_{1-x}\text{Se}$  and  $\text{Ni}_x\text{Zn}_{1-x}\text{Se}$  diluted magnetic semiconductors for different concentrations of impurity atoms. The calculations are implemented by the norm-conserving FHI pseudopotential method within the local spin density approximation (LSDA) and Hubbard U method. The analysis of the total density of states curves shows the half-metallic ferromagnetic character with half-metallic band gap. The first-principles calculated total magnetic moments of  $\text{Co}_x\text{Zn}_{1-x}\text{Se}$  and  $\text{Ni}_x\text{Zn}_{1-x}\text{Se}$  systems are found to be equal to 3 and 4  $\mu_B$ , respectively.

**Keywords.** ZnSe:Co,Ni, ferromagnetic, antiferromagnetic, half-metal.

### 1. Introduction

The investigation of the DMSs have allowed the production of new types of materials with possible technological applications in Engineering, Medicine, Environment, Environmental Chemistry, Telecommunications, and others. Zinc selenide a semiconductor, can operate as a half-metallic compound and is a helpful material for optoelectronic and spintronic applications. Zinc selenide is a nonmagnetic material with a direct band gap of 2.70 eV and has great potential for a diversity of optical and electro-optical devices, such as short wavelength lasers, blue-green laser diodes, pure green light-emitting diodes, microwave and terahertz devices, solar cells and tunable mid-IR laser sources [1-3]. TM doped ZnSe have attracted great research interest as new productive device applicants. In Refs. [3-9] the authors reported that ZnSe:TM were appropriate for applications in spintronics and middle-IR lasing. Sato et al. [10] have predicted a high Curie temperatures for Cr- and V-doped ZnSe zinc-blende structure, Benstaali et al. [3] in ZnSe:Co, Mohamood et al. [11] in ZnSe:Ti, and Arifet et al. [12] in CdSe:Co were reported half-metallic FM due to polarization of the spin in their theoretical study and suggested these are potential candidates for spintronic application, which are in agreement with current work. In our previous work [13] we reported that the presense of one Zn vacancy defect leads half-metallic ferromagnetism in ZnSe:Mn compound.

This work is dedicated to study of the magnetism in ZnSe:Co and ZnSe:Ni by varying the impurity concentrations for the values  $x=12.5\%$  and  $6.25\%$ . In the current work the Curie temperatures are also estimated and obtained that Ni-doped ZnSe compounds are high room temperature materials.

### 2. Calculation method

The current calculations based on the density functionoanal theory (DFT) [14], which is a computational quantum mechanical modeling method for many body problems of nucleus and electron interactions. This problem can be solved into a system of one-electron Kohn-Sham equations [15]. To solve these equations in order to calculate the physical properties of investigated systems, we have used the linear combination of atomic orbitals (LCAO) method [16]. The calculations for investigated systems were

carried out using LSDA (local spin density approximation) within Hubbard U semiempirical correction (4.5 eV on  $d$ -states of Zn and 3.8 eV on  $p$ -states of Se) for the exchange-correlation potential with the ATK code.

In current studies, TM (Co, Ni)-doped ZnSe were investigated under the same conditions (same supercells, same lattice parameters, same  $k$ -point sampling, etc.). The geometric models for DMS ZnSe:Co, ZnSe:Ni are built by replacing host Zn atoms with TM. Hubbard U corrections are used for correct band gap prognosis for bulk ZnSe [17, 18]. The electron-ion interactions was treated by the norm-conserving Fritz-Haber-Institute (FHI) ion pseudopotentials within Double Zeta Polarized (DZP) basis set. This method was chosen to reproduce, as closely as possible, the experimentally measured band gap and lattice parameters. For ZnSe:TM (TM=Co; Ni), a simulation cell containing either 32 and 64 atoms (the expansion of the primitive wurtzite unit cell) was used. The simulations are carried out for different supercells generated with the initial lattice parameters  $a=b=3.98 \text{ \AA}$  and  $c=6.53 \text{ \AA}$  [19]. One and two impurity atoms added at Zn cation sites in 32- and 64-atom supercells to study the ferromagnetism of Co- and Ni-doped ZnSe from Mulliken population analysis. A  $k$ -sampling Monkhorst-Pack grids  $5 \times 5 \times 5$  used and all atomic positions have been geometry optimized. The valence electron configurations which included 12 electrons for Zn [Ar]  $+3d^{10} 4s^2$ , 6 electrons for Se [Ar]  $+4s^2 4p^4$ , 9 electrons Co [Ar]  $+3d^7 4s^2$ , and 10 electrons for Ni [Ar]  $+3d^8 4s^2$  were taken into consideration. The kinetic cut-off energy of 100 Ry (50 Ha) was employed through-out the calculations which was tested to be fully converged with for to total energy. Magnetic properties were investigated after a full geometry optimization of all systems (for all lattice parameters and atomic positions) with force and stress tolerances of  $0.01 eV/\text{\AA}$  and  $0.01 eV/\text{\AA}^3$ , respectively.

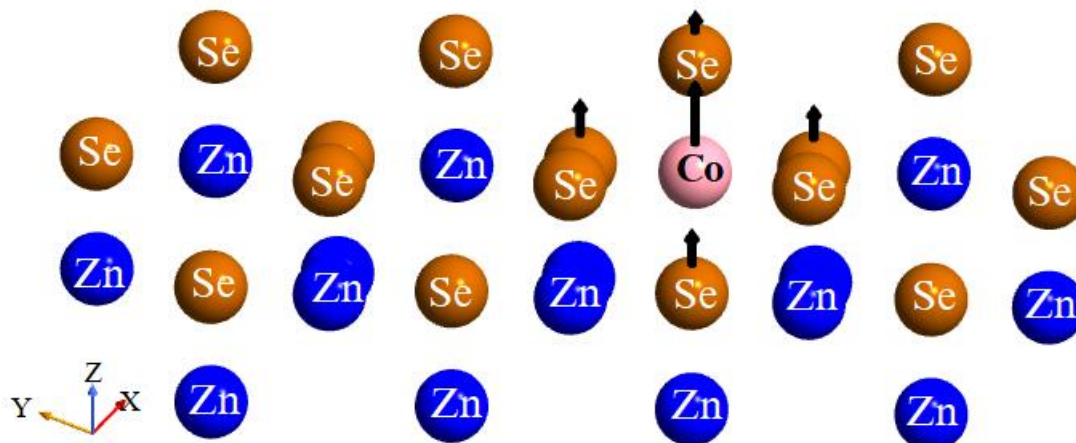
The undoped ZnSe formed in wurtzite structure by two atoms with space group  $P6_3mc$  [20]. Note that the investigated doped supercells do not have appropriate hexagonal symmetry.

In current work, we reported magnetic properties of Co:ZnSe and Ni:ZnSe in the wurtzite phase for various impurity atom concentrations for the values  $x=0.125, 0.0625$ . Lastly, the defect formation energy and Curie temperature are also calculated.

### 3. Results and discussion

#### 3.1. Magnetic properties of Zn(Co,Ni)Se

The magnetic moments for Co and Ni, and its neighboring host atoms have been calculated in detail using DFT-LSDA+U method. Undoped ZnSe is non-magnetic material, but on doping TM elements, the main contribution to magnetization comes from impurity atoms, due to  $p$ - $d$  hybridization between Se- $4p$  and TM  $3d$ -states. The spin-polarization structures of  $Zn_{15}Co_1Se_{16}$  supercell is shown in Fig. 1. In all spin-polarization structures, the magnetic moments of atoms are shown with arrows, these are significant values than other atoms.



**Figure 1.** Spin-polarization view for  $Zn_{15}Co_1Se_{16}$ . The black arrows show the magnetic moments.

The first-principles calculated total magnetic moments of Co-doped ZnSe supercells are found to be equal to  $3 \mu_B$  which in a good agreement with the results of Refs. [3, 21, 22]. The values of total magnetic moments for  $Zn_xCo_{1-x}Se$  alloys obtained  $3 \mu_B$  for wurtzite phase in Ref. [3] and  $3.87 \mu_B$  for zinc blende structure in Ref. [21] using WIEN2k code within LSDA and GGA method, respectively.

The integer number of magnetic moments per supercell is mainly due to impurity atoms (significant contribution from  $d$ -states) and a small contribution from host Zn and Se atoms. The computed value of magnetic moment per Co is found to be  $2.325 \mu_B$  (main contribution from Co  $d$ -states:  $\sim 2 \mu_B$ ) for  $Zn_{1-x}Co_xSe$  system which in an agreement with value of  $2.2 \mu_B$  theoretically obtained in Ref. [22]. Insignificant negative contribution to the magnetization from 15 Zn atoms ( $-0.13 \mu_B$ ) and positive contribution from 16 Se atoms ( $0.81 \mu_B$ ). The significant positive contribution from 4 Se atoms ( $\sim 0.7 \mu_B$ ) which chemically bonded cobalt impurity atom.

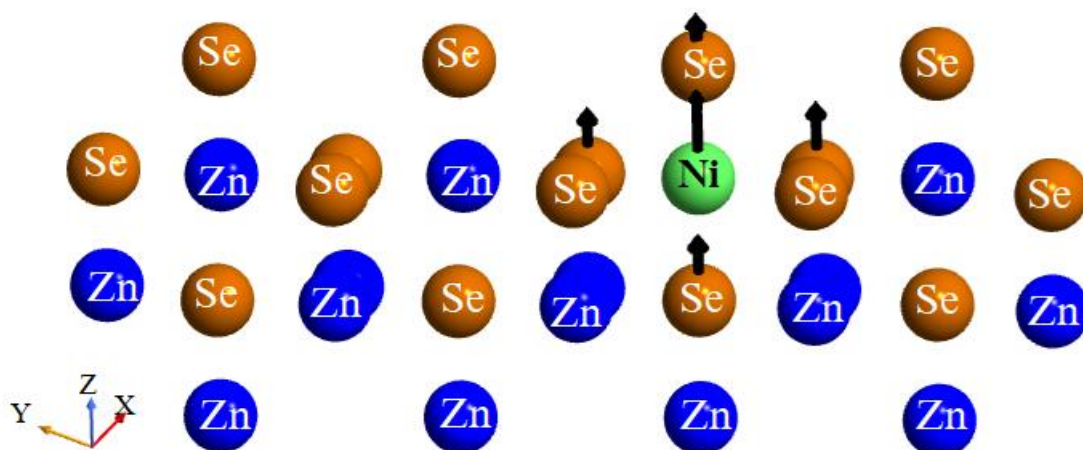
The first-principles results for Co-Co bond lengths and the total energy differences between antiferromagnetic (AFM) and ferromagnetic (FM) alignments  $\Delta E = E_{AFM} - E_{FM}$  for different ZnSe:Co systems are shown in Table 1.

**Table 1.** The Co-Co bond lengths and the total energy differences between AFM and FM alignments for different ZnSe:Co systems using LSDA+U.

System	$d_{Co-Co}$ [Å]	$E_{AFM}$ [eV]	$E_{FM}$ [eV]	$\Delta E$ [eV]
$Zn_{14}Co_2Se_{16}$	7.96	-30326.08060	-30326.05138	-0.02922
$Zn_{30}Co_2Se_{32}$	9.50	-61957.01379	-61957.01286	-0.00093

From Table 1, the total energy differences between AFM and FM alignments show AFM stability ZnSe:Co systems which is in agreement with Ref. [22].

The spin-polarization structures for  $Zn_{15}Ni_1Se_{16}$  supercell is shown in Fig. 2. In the case of Ni-doping ZnSe the obtained values of total and partial magnetic moments for supercell and per impurity atom are found to be equal 4 and  $1.223 \mu_B$ , respectively. The main contribution to the magnetization from  $d$ -states of Ni atom ( $\sim 1.2 \mu_B$ ), the small negative contribution from 15 Zn atoms. The significant positive contribution from 4 Se atoms ( $0.85 \mu_B$ ) which chemically bonded nickel dopant atom.



**Figure 2.** The spin-polarization of  $Zn_{15}Ni_1Se_{16}$ . Magnetic moments of atoms are shown by black arrows.

The first-principles obtained results for Ni-Ni bond lengths and the total energy differences between antiferromagnetic (AFM) and ferromagnetic (FM) alignments  $\Delta E = E_{AFM} - E_{FM}$  for different ZnSe:Ni systems are shown in Table 2.

**Table 2.** The Ni-Ni bond lengths and the total energy differences between AFM and FM alignments for different ZnSe:Ni systems using LSDA+U.

System	$d_{Ni-Ni}$ [Å]	$E_{AFM}$ [eV]	$E_{FM}$ [eV]	$\Delta E$ [eV]
Zn <sub>14</sub> Ni <sub>2</sub> Se <sub>16</sub>	7.96	-30727.85236	-30727.97240	0.12004
Zn <sub>30</sub> Ni <sub>2</sub> Se <sub>32</sub>	9.50	-62358.71828	-62358.74156	0.02328

As seen from Table 2 the FM state more stable than AFM state for ZnSe:Ni alloys. First-principles spin-polarized electronic structures and DOS calculations show that the Ni-doped ZnSe systems are high-spin and half-metallic materials, but Co-doped ZnSe systems are not half-metallic. The large half-metallic gap of Ni-doped ZnSe makes this compound potential materials for practical applications in Engineering and Environmental Chemistry, Medicine and Telecommunications.

### 3.2. Formation energy and Curie temperature of Zn(Co,Ni)Se

It is known that the stability of TM doped systems can be defined by the defect formation energy of structure. Formation energy calculations are performed for the fully relaxed different defected (substitution defect, i.e., replacing a single Zn cation with Co<sup>2+</sup> and Ni<sup>2+</sup> ions) systems. The formation energy calculations were studied for systems containing 32 atoms.

The formation energy of TM<sup>2+</sup> doped ZnSe systems is assigned as the energy needed to introduce such impurity in bulk ZnSe and can be calculated by the following expression [23]

$$E_{form.} = \frac{1}{N} [E_{tot.}(Zn_{1-x}TM_xSe) - E_{tot.}(ZnSe) + n \cdot \mu_{Zn} - n \cdot \mu_{TM}], \quad (1)$$

where N is the total number of atoms in supercell,  $E_{tot.}(Zn_{1-x}TM_xSe)$  and  $E_{tot.}(ZnSe)$  are the total energies of doped and pure ZnSe systems having the same dimension to supercell, correspondingly. Terms  $n$ ,  $\mu_{Zn}$ , and  $\mu_{TM}$  are the number of doping atoms, the chemical potentials of Zn and TM (Co or Ni) atoms, respectively.

The Curie temperatures of Co- and Ni-doped ZnSe systems are estimated by using the Heisenberg model [24]

$$T_C = \frac{2}{3} \frac{\Delta E}{k_B x}, \quad (2)$$

where  $k_B$  is the Boltzmann constant.

In this work, the defect formation energies and the Curie temperatures are estimated for different Zn<sub>1-x</sub>Co<sub>x</sub>Se and Zn<sub>1-x</sub>Ni<sub>x</sub>Se systems using the reported results of energy difference between the AFM and FM alignments, and listed in Table 3.

**Table 3.** The first-principles calculated values of formation energies, and the Curie temperatures for  $Zn_{1-x}Co_xSe$  and  $Zn_{1-x}Ni_xSe$  systems, per two Zn atoms replaced by  $Co^{2+}$  or  $Ni^{2+}$  ion ( $x$ -impurity concentration).

System	$x$ , %	$E_{form.}[eV]$	$T_C$ [K]
$Zn_{14}Co_2Se_{16}$	12.5	40.92	-904
$Zn_{14}Ni_2Se_{16}$	12.5	28.35	3714

The obtained formation energy values of Co- and Ni-doped ZnSe are positive, indicating that it is hard to incorporate Co (or Ni) atom to ZnSe. The systematically investigation of stability of the FM phase in ZnSe-based DMSs show that Ni-doped systems are HMFM materials with higher Curie temperature. From our calculations the Curie temperatures are found to decrease with the decreasing of impurity atom concentrations for  $Zn_{1-x}Ni_xSe$  systems. First-principles calculated value of the Curie temperatures show that the ZnSe:Ni are suitable materials for DMSs.

#### 4. Conclusion

Using an accurate DFT-LSDA+U approach, have been explored the spin-polarized electronic and magnetic properties of  $Zn_{1-x}Co_xSe$  and  $Zn_{1-x}Ni_xSe$  for  $x=12.5\%$ ,  $6.25\%$ . While the introduction of  $Ni^{2+}$  ion and the presence of Zn vacancy in ZnSe structure lead the half-metallic ferromagnetic coupling. But for the Co-doped ZnSe systems are not observed half-metallic state. The obtained values of total magnetic moments have been found to be  $3.0$  and  $4.0 \mu_B$  for  $Zn_{1-x}Co_xSe$  and  $Zn_{1-x}Ni_xSe$ , and the mainly contribution to the magnetization comes mostly from  $d$ -states of impurity atoms. Results of the energy differences between the antiferromagnetic and the ferromagnetic states for both systems nearly represent a stable ferromagnetic phase. The presence of Zn vacancy in ZnSe:Co systems affect the magnetization, which  $\sim 2.0 \mu_B$  increases the total magnetic moment of the supercell ( $\sim 5.0 \mu_B$ ).

#### References

- [1] F. Goumrhar, L. Bahmad, O. Mounkachi, A. Benyoussef, "Ab-initio calculations for the electronic and magnetic properties of Cr doped ZnTe," *Comp. Condensed Matter.*, vol. 32, no. 03, pp.1850025-112, 2018, doi: 10.1142/S021797921850025X.
- [2] B. Xiao, M. Zhu, B. Zhang, J. dong, L. Ji, H. Yu, X. Sun, W. Jie, Y. Xu, "Optical and electrical properties of vanadium-doped ZnTe crystals grown by the temperature gradient solution method," *Opt. Mater. Express*, vol. 8, no. 2, pp. 431-439, 2018, doi: 10.1364/OME.8.000431.
- [3] W. Benstaali, S. Bentata, A. Abbad, A. Belaidi, "Ab-initio study of magnetic, electronic and optical properties of ZnSe doped-transition metals," *Mater. Sci. Semicond. Process.*, vol. 16, no. 2, pp. 231-237, 2013, doi: 10.1016/j.mssp.2012.10.001.
- [4] C. Kim, D.V. Martyshkin, V.V. Fedorov, S.B. Mirov, "Middle-infrared random lasing of  $Cr^{2+}$  doped ZnSe, ZnS, CdSe powders, powders imbedded in polymer liquid solutions, and polymer films," *Optics Commun.*, vol. 282, no. 10, pp. 2049-2052, 2009, doi: 10.1016/j.optcom.2009.02.023.
- [5] J.E. Williams, V.V. Fedorov, D.V. Martyshkin, I.S. Moskalev, R.P. Camata, S.B. Mirov, "Mid-IR laser oscillation in  $Cr^{2+}$ :ZnSe planar waveguide," *Optics Express*, vol. 18, pp. 25999, 2010, .
- [6] N. Myoung, D.V. Martyshkin, V.V. Fedorov, S.B. Mirov, "Energy scaling of  $4.3 \mu m$  room temperature Fe: ZnSe laser," *Optics Letters*, vol. 36, no. 1, pp. 94-96, 2011, doi: 10.1364/OL.36.000094.
- [7] I.S. Moskalev, V.V. Fedorov, S.B. Mirov, "10-Watt, pure continuous-wave, polycrystalline  $Cr^{2+}$ :ZnS laser," *Optics Express*, vol. 17, no. 4, pp. 2048-2056, 2009, doi: 10.1364/OE.17.002048.
- [8] V.I. Kozlovsky, V.A. Akimov, M.P. Frolov, Y.V. Korostelin, A.I. Landman, V.P. Martovitsky, V.V. Mislavskii, Y.P. Podmar'kov, Y.K. Skasyrsky, A.A. Voronov, "Room-temperature tunable mid-

- infrared lasers on transition-metal doped II–VI compound crystals grown from vapor phase,” *Phys. Stat. Sol. B*, vol. 247, no. 6, pp. 1553-1556, 2010, doi: 10.1002/pssb.200983165.
- [9] S.Zh. Karazanov, P. Ravindran, A. Kjekshus, H. Svenson, “Electronic structure and optical properties of ZnX (X=O, S, Se, Te): A density functional study,” *Phys. Rev. B*, vol. 75, no. 15, pp. 155104-1-14, 2007, doi: 10.1103/PhysRevB.75.155104.
- [10] K. Sato, H. Katayama-Yoshida, “Ab initio Study on the Magnetism in ZnO-, ZnS-, ZnSe and ZnTe-Based Diluted Magnetic Semiconductors,” *Phys. Stat. Sol. (b)*, vol. 229, no. 2, pp. 673-680, 2002, doi: 10.1002/1521-3951(200201)229:2<673::AID-PSSB673>3.0.CO;2-7.
- [11] Q. Mahmood, M. Hassan, M.A. Faridi, B. Sabir, G. Murtaza, A. Mahmood, “The study of electronic, elastic, magnetic and optical response of  $Zn_{1-x}Ti_xY$  (Y = S, Se) through mBJ potential,” *Curr. Appl. Phys.*, vol. 16, no. 5, pp. 549-561, 2016, doi: 10.1016/j.cap.2016.03.002.
- [12] S. Arif, B. Amin, I. Ahmad, M. Maqbool, R. Ahmad, M. Haneef, N. Ikram, “Investigation of half metallicity in Fe doped CdSe and Co doped CdSe materials,” *Curr. Appl. Phys.*, vol. 12, no. 1, pp. 184-187, 2012, doi: 10.1016/j.cap.2011.05.034.
- [13] V.N. Jafarova, “Study the electronic and magnetic properties of Mn-doped wurtzite ZnSe using first-principle calculations,” *Indian J. Phys.*, vol. 97, pp. 2639-2647, 2023, doi: 10.1007/s12648-023-02598-y.
- [14] P. Hohenberg, W. Khon, “Inhomogeneous electron gas,” *Phys. Rev. B*, vol. 136, no. 3, pp. B864-B871, 1964, doi: 10.1103/physrev.136.b864.
- [15] D.M. Ceperley, B.J. Alder, “Ground state of the electron gas by a stochastic method,” *Phys. Rev. Lett.*, vol. 45, no. 7, pp. 566-59, 1980, doi: 10.1103/PhysRevLett.45.566.
- [16] M. Cococcioni, S. De Gironcoli, “Linear response approach to the calculation of the effective interaction parameters in the LDA+U method,” *Phys. Rev. B*, vol. 71, no. 3, pp. 035105-1-16, 2005, doi: 10.1103/PhysRevB.71.035105 .
- [17] V.N. Jafarova, “Ab-initio calculation of structural and electronic properties of ZnO and ZnSe compounds with wurtzite structure,” *Intern. J. Modern Phys. B*, vol. 36, no. 24, pp. 2250156-1-12, 2022, doi: 10.1142/S0217979222501569 .
- [18] V.N. Jafarova, M.A. Musaev, “First-principles study of structural and electronic properties of ZnSe with wurtzite structure,” *Technium: Romanian Journal of Applied Sciences and Technology*, vol. 6, pp. 42-46, 2023, doi: 10.47577/technium.v6i.8487.
- [19] R.W.G. Wyckoff, “Second Edition. Interscience Publishers, New York Note,” *Crystal Structures* vol. 1, pp. 239-444, 1963, doi: 10.1107/S0365110X65000361.
- [20] V.N. Jafarova, H.S. Orudzhev, “Structural and electronic properties of ZnO: A first-principles density-functional theory study within LDA(GGA) and LDA(GGA)+ U methods,” *Sol. State Commun.*, vol. 325, pp. 114166-1-5, 2021, doi: 10.1016/j.ssc.2020.114166.
- [21] X.-L. Chen, B.-J. Huang, Y. Feng, P.-J. Wang, C.-W. Zhang, P. Li, “Electronic structures and optical properties of TM (Cr, Mn, Fe or Co) atom doped ZnSe nanosheets,” *RSC Adv.*, vol. 5, pp. 106227-106233, 2015, doi: 10.1039/C5RA20223J.
- [22] X.-T. Yang, J.-H. Lin, M.SH. Khan, B.-S. Zou, L.-J. Shi, “Interstitial Zn-modulated ferromagnetism in Co-doped ZnSe,” *Mater. Res. Express*, vol. 6, no.10, pp. 106121-1-7, 2019, doi: 10.1088/2053-1591/ab20de.
- [23] N. Ahmed, A. Nabi, J. Nisar, M. Tariq, M.A. Javid, M.H. Nasim, “First principle calculations of electronic and magnetic properties of Mn-doped CdS (zinc blende), a theoretical study,” *Materials Science-Poland*, vol. 35, no. 3, pp. 479-485, 2017, doi: 10.1515/msp-2017-0084.
- [24] J. Blinowski, P. Kacman, J.A. Majewski, “Ferromagnetism in Cr-based diluted magnetic semiconductors,” *Cryst. Growth*, vol. 159, no. 1-4, pp. 972-975, 1996, doi: 10.1016/0022-0248(95)00719-9.