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Electronic and magnetic properties of SnSe monolayer doped by Ga, In, As, and Sb: a first-principles study

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Abstract: SnSe monolayer with orthorhombic *Pnma* GeS structure is an important two-dimensional (2D) indirect band gap material at room temperature. Based on first-principles density functional theory calculations, we present systematic studies on the electronic and magnetic properties of X (X = Ga, In, As, Sb) atoms doped SnSe monolayer. The calculated electronic structures show that Ga-doped system maintains semiconducting property while In-doped SnSe monolayer is half-metal. The As- and Sb- doped SnSe systems present the characteristics of *n*-type semiconductor. Moreover, all considered substitutional doping cases induce magnetic ground states with the magnetic moment of $\sim 1 \mu_B$. In addition, the calculated formation energies also show that four types of doped systems are thermodynamic stable. These results provide a new route for the potential applications of doped SnSe monolayer in 2D photoelectronic and magnetic semiconductor devices.

Keywords: SnSe monolayer, substitutional doping, electronic properties, magnetism

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1. Introduction

Along with the discovery of graphene, many new two-dimensional (2D) atomic layered systems have attracted special attention for future electronics applications.¹⁻⁵ Recently, more and more researchers devote themselves on 2D atomic-layer materials, such as silicene, germanene, stanene, phosphorene, and so on.⁶⁻¹⁰ Just as the scope of group IV semiconductors, such as graphene silicene and germanene have been broadened significantly by introducing isoelectronic III-V compounds,^{1,8,9} phosphorene arsenene, and antimonene have been broadened by introducing isoelectronic IV-VI compounds.^{6,11-14} IV-VI group semiconductors have layered structures which are similar to phosphorene.^{15,16} For bulk Tin selenium (SnSe), it has two most common crystal structures: one is cubic NaCl (rock salt) and the other is orthorhombic GeS structure with an orthorhombic *Pnma* space group at room temperature.^{17,18} Furthermore, bulk SnSe is an important double layered binary IV-VI semiconductor with structural orthorhombic symmetry and weak van der Waals force between double layers. In addition, bulk SnSe has both a direct band gap of 1.30 eV and an indirect band gap of 0.90 eV, just falling into the optimum band gap for solar cells. Therefore, bulk SnSe is also considered as the most promising candidates for solar cells.¹⁹⁻²¹ Especially, with the successfully synthesizing of 2D SnSe experimentally, SnSe monolayer has attracted more and more attention in monolayer IV-VI semiconductor.²² SnSe monolayer is comprised of zigzag double-layered planes and exhibits strong anisotropic properties.^{19,23,24} As material of earth-abundance, environment friendly and good chemical stability, SnSe can be applied in a wide range of potential applications, e.g. optical devices, memory switching devices, infrared op-

toelectronic devices and anode materials for rechargeable lithium batteries.²⁵⁻²⁹

SnSe monolayer has the graphene-analogous structure. Sn and Se atoms present a puckered surface due to the sp^2 hybridization.³⁰ Each Sn atom forms three covalent bonds with Se, and the same as Se atom. As we know, 2D material have many special properties due to their unique dimension-dependent properties comparing with 3D material,³¹ and graphene-like structure have already shown exceptional properties.^{32,33} The synthesis and properties of SnSe monolayer have attracted much attention.^{19,22} Whereas there is few literature about 2D SnSe monolayer,¹⁴ the electronic and magnetic properties of substitutional doping of SnSe monolayer have not been done. In this work, using first-principles density functional theory (DFT) calculations, we present a systematic study of the electronic and magnetic properties of Ga-, In-, As-, and Sb- doped SnSe monolayer. These atoms are from group III and V, which are around Sn atom and common in semiconductor composition. Furthermore, they have the similar electronic configuration, which can avoid of lattice distortion. Firstly, we calculate the electronic and magnetic properties of the doped systems. And then, we calculate the formation energy E_f and find that the formation energy of As-doped system is lowest than the other three systems, indicating that As-doped system is apt to be realized in experiment.

2. Computational Details

The present first-principles DFT³⁴ calculations are performed using Perdew-Burke-Ernzerh (PBE)³⁵ in the projector augmented wave (PAW)³⁶ within Vienna *ab initio* Simulation Package (VASP).³⁷ The reciprocal space is sampled with a fine grid of $3 \times 3 \times 3$ *k*-points in the Brillouin zone of the primitive unit cell for bulk SnSe,

and $1 \times 3 \times 3$ k -points for the SnSe monolayer and the doped systems. The wave functions are expanded in a plane-wave basis with an energy cutoff of 500 eV. The maximum force of each atom is less than 0.01 eV/Å. The geometrical structure is employed with a 3×3 supercell including 36 atoms with doping concentration of 2.78%. A vacuum spacing perpendicular to the plane is employed to be at least 15Å in the unit cell to avoid the coupling between neighboring cells. The spin-polarized method is employed to analyze the magnetism of the doped systems.

3. Results and discussion

Fig. 1 presents the geometrical structure and electronic band structure of bulk SnSe. The calculated optimal lattice parameters of bulk SnSe are $a=11.50 \text{Å}$, $b=4.16 \text{Å}$, and $c=4.45 \text{Å}$, which are in agreement with the experiment values³⁸ and previous theoretical values^{39,40}. The bond lengths of Sn-Se are $d_1=2.81 \text{Å}$ and $d_2=2.78 \text{Å}$, which are in line with the previous reported values,¹⁷ as seen in Fig. 1 (a). The calculated band gap is 0.50 eV, which is smaller than experimental value and the previous theoretical calculation,⁴⁰ on account of the DFT-PBE method which underestimates the band gap of semiconductor. Even though the fundamental band gaps are typically underestimated in DFT-PBE approach, the prediction of the indirect semiconductor system is correct.^{41–44} In Fig. 1 (b), we can see that the valence band maximum (VBM) of bulk SnSe is at M point, while conduction band minimum (CBM) is located at the middle of Γ -M, indicating an indirect band gap. Moreover, the bulk SnSe has no magnetism according to our calculation.

The structure of SnSe monolayer is displayed in Fig. 2. As seen in Fig. 2 (a), Sn and Se atoms form three covalent bonds with each other in a puckered surface. To investigate the electronic and magnetic properties of substitutional doping in SnSe monolayer, the band structure, total density of states (DOS) and partial density of states (PDOS) of the doping systems $\text{Sn}_{17}\text{Se}_{18}\text{X}_{\text{Sn}}$ ($\text{X}=\text{Ga}, \text{In}, \text{As}, \text{Sb}$) with 3×3 supercell are calculated, along with the pure SnSe monolayer for comparison. In addition, we would like to point out that in our calculation, we also investigate the electronic structures of Ga-, In-, As-, Sb-doped systems with different doping concentration of 1.56%, corresponding to 4×4 supercell. We find that there are no obvious differences of magnetisms and band structures comparing to 3×3 supercell. Moreover, the 3×3 supercell is large enough to avoid of interaction between dopant atoms. Thus, we only focus on the electronic properties of the doped systems with 3×3 supercell in detail.

Firstly, band structures, DOS and PDOS of SnSe monolayer are calculated in Fig. 2. As shown in Fig. 2 (b), the indirect band gap is 0.78 eV, which is bigger than that of bulk SnSe ($E_g=0.50$ eV). From the PDOS of SnSe monolayer, as shown in Fig. 2 (c), we can clearly see that it is $5s$ -orbitals of Sn and $4p$ -orbitals of Se that contribute mostly to the total DOS below Fer-

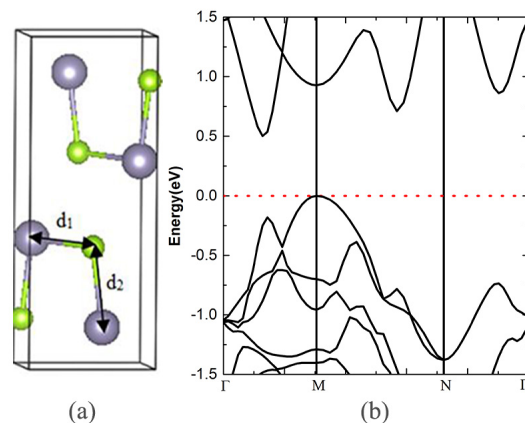


FIG. 1: (a) The geometry and (b) electronic structure of bulk SnSe.

mi level from -1.50 eV to -0.11 eV. While above Fermi level, $5p$ -orbitals of Sn and $4s$ -orbitals of Se contribute mostly to the total DOS. In detail, it is the hybridization of $5s$ -orbital of Sn and $4p$ -orbital of Se that forms the valence band, and $5p$ -orbital of Sn and $4s$ -orbital of Se hybridize to comprise the conduction band. The spin-polarized calculations show that pristine SnSe monolayer is of non-magnetism.

Now we turn to investigate the doping effects on electronic structures of SnSe monolayer. As we know that the outer electron valence configuration of Sn is $4d^{10}5s^25p^2$, two $5p^2$ electrons joining in bonding, and two $5s^2$ electrons forming a lone pair.¹⁸ As a result, the electronic structure of SnSe monolayer can be tuned in a widely range by substitutional doping. In the doped system $\text{Sn}_{17}\text{Se}_{18}\text{X}_{\text{Sn}}$ ($\text{X}=\text{Ga}, \text{In}, \text{As}, \text{Sb}$), X dopant atom is neighborhood with Sn in the periodic table of elements, which can avoid of lattice distortion. The dopant atom can form states either above valence band or below conduction band, or the middle of band gap. To explore the underlying electronic and magnetic properties of the doped monolayer $\text{Sn}_{17}\text{Se}_{18}\text{X}_{\text{Sn}}$ ($\text{X}=\text{Ga}, \text{In}, \text{As}, \text{Sb}$), we divide the related figures into two parts: spin up and spin down, which make us to have a clear insight to the substitutional doping systems.

Fig. 3 (a) presents the split band structure of Ga-doped system. The impurity state is split into spin-up and spin-down cases, and the impurity energy level appears either above valence band (spin-up) or below conduction bands (spin-down). Furthermore, the band gap is 0.66 eV for spin-up and 0.43 eV for spin-down, indicating semiconductor properties. The band gaps of spin-up and spin-down are both smaller than that of pure SnSe monolayer. Since Ga is the acceptor, the band gap decreases for both spin-up and spin-down. When Ga atom is doped, the doped system has a red shift, giving rise to a relatively wide application in electron devices. However, for In-doped system, it is exceptive that the VBM rises for spin-up, while the CBM goes down across the Fermi level for spin-down, which lead to a half-metal

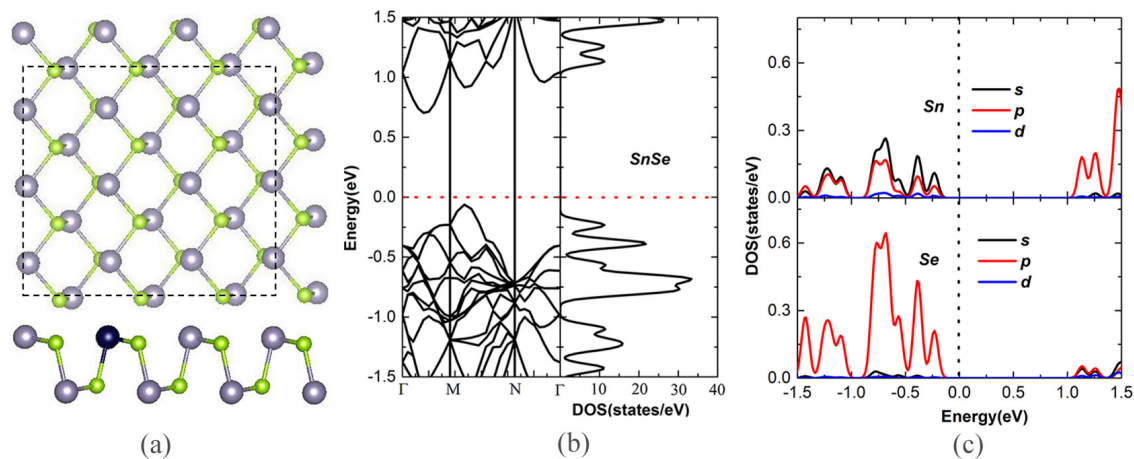


FIG. 2: (a) Top and side views of SnSe monolayer with 3×3 supercell cell, indicating the black dashed rectangle. The dark atom denotes Sn atom substituted by a dopant atom, and navy balls denote Sn atoms and prasinous balls denote Se atoms. (b) Electronic band structure along Γ -M-N- Γ direction and corresponding total DOS and (c) PDOS of SnSe monolayer. The energy zero represents the Fermi level.

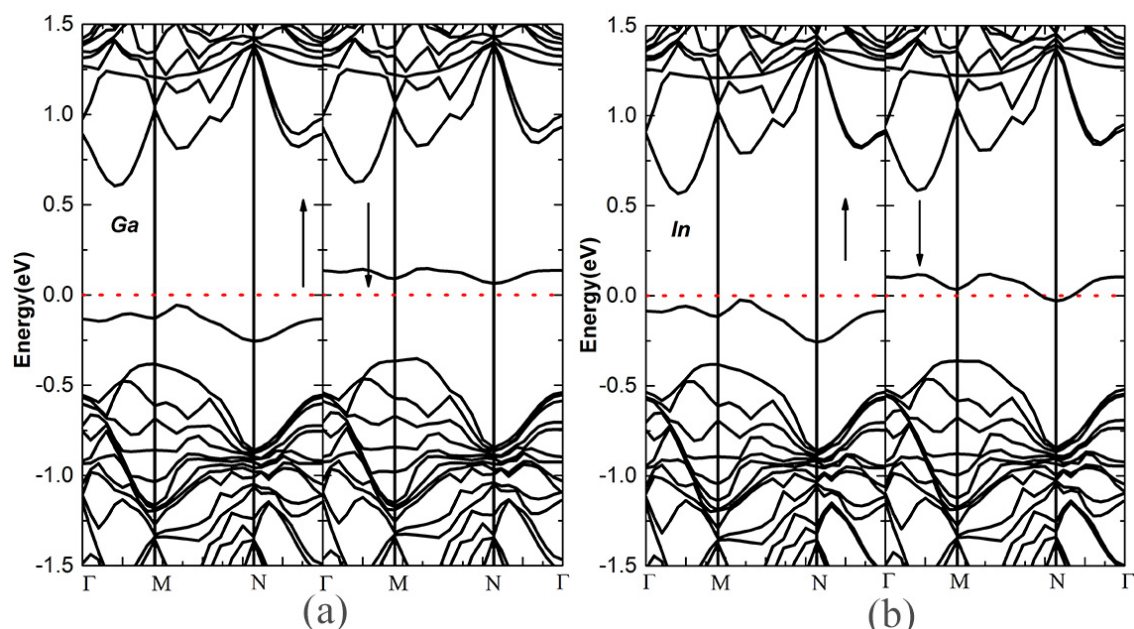


FIG. 3: Calculated band structures of (a) Ga- and (b) In-doped systems, along Γ -M-N- Γ direction. The energy zero represents the Fermi level.

property, as shown in Fig. 3 (b). For the Ga- and In-doped systems, although Ga and In belong to the same group IIIA, they present different properties. The intriguing phenomenon can be explained by the nearly equal electronegativity (Ga \sim 1.81, Sn \sim 1.96, In \sim 1.78), and we know that the difference between Sn and In is slightly bigger than that between Sn and Ga. To have a further insight into the underlying mechanism of the dopant systems, the total DOS and PDOS of Ga- and In-doped system are shown in Fig. 4.

From the PDOS of Ga-doped system, as seen in Fig. 4 (a), we can see that it is obvious that $4s$ -, $4p$ -orbital of Ga

and $4p$ -orbital of Se play an important role for the VBM and CBM, and make the main contribution to the total DOS. Similarly, the In-doped system presents the almost same phenomenon: $5s$ -, $5p$ -orbital of In and $4p$ -orbital of Se play an important role for VBM, CBM, and the total DOS. Comparing to the semiconductor property of Ga-doped system, it is obvious that the $5p$ -orbitals of In atom presents hybridization at the Fermi level. Consequently, the doping system presents a half-metallic property, which is in line with the band structure. Moreover, we find that the total DOS is asymmetric at the Fermi level, indicating that Ga- and In-doped system present mag-

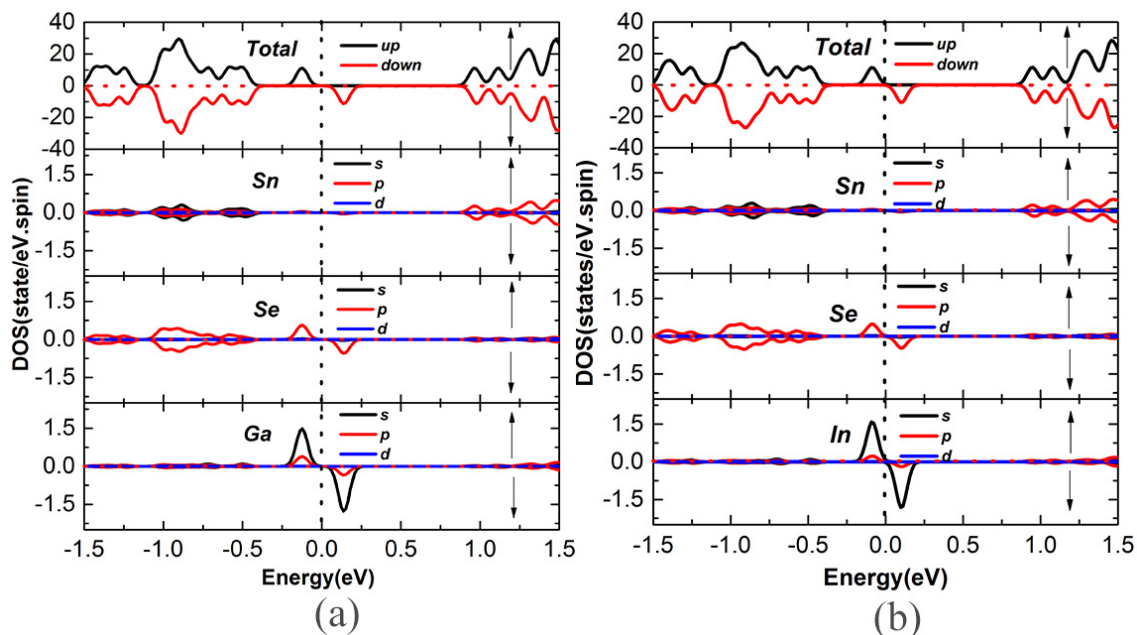


FIG. 4: DOS and PDOS of (a) Ga-doped and (b) In-doped systems. The energy zero represents the Fermi level.

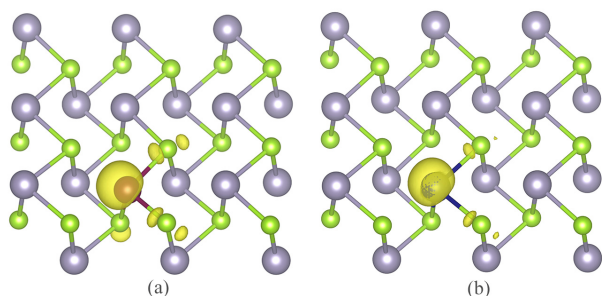


FIG. 5: Spin charge density ($\rho_{up}-\rho_{down}$) of (a) Ga- and (b) In-doped system, respectively. The value of isosurfaces is $0.03 e/\text{\AA}^3$.

netism with the values about $1.00 \mu_B$ and $0.99 \mu_B$, respectively, which are close to their free atoms ($\text{Ga} \sim 1.00 \mu_B$; $\text{In} \sim 1.00 \mu_B$). Furthermore, from Fig. 4 (a), it is obvious that the majority of magnetism is induced by Ga atom while Se atom contributes minority to the magnetism. But in In-doped system, the magnetism is mainly induced by the In dopant, as seen in Fig. 4 (b).

In order to get a clear explanation of magnetism, the spin charge density of Ga- and In- doped systems are calculated in Fig. 5. From Fig. 5 (a) and (b), we can obviously see that the magnetism is induced by the dopant Ga atom and In atom, respectively. The phenomena are consistent well with the results of DOS and PDOS. And in the Ga-doped system, the majority of magnetism distributes around the Ga atom while the minority scatters around Se atom. Comparing to Ga-doped system, the magnetism is mainly induced by the dopant atom in In-doped system. The magnetism is induced by the dopant

Ga and In atoms. As a result, both Ga and In dopant atoms lead to an acceptor level which gives rise to *p*-type doping systems with band gap decreasing.

In addition, we calculate the electronic band structure of As- and Sb-doped systems in Fig. 6. From Fig. 6, we can see that the impurity level appears in valence bands leading to the VBM rise for spin-up, while in conduction bands resulting in the CBM declining for spin-down. However, the impurity level does not cross the Fermi level, so the system maintains the semiconductor property for As- and Sb-doped systems. In detail, for the As-doped system, as seen in Fig. 6 (a), the band gap is divided into two parts: 0.48 eV for spin-up and 0.88 eV for spin-down. At the same time the band gap of Sb-doped system is 0.26 eV for spin-up and 0.84 eV for spin-down, as seen in Fig. 6 (b). Otherwise, comparing to the band gap of SnSe monolayer, we find that the value of Sb-doped system has a less change than that of As-doped system. This phenomenon can be explained by electronegativity ($\text{As} \sim 2.18$; $\text{Sn} \sim 1.96$; $\text{Sb} \sim 2.05$). It is visible that the electronegativity difference between Sn and As is larger than that between Sn and Sb. In order to have a further penetration into the electronic property of dopant systems, the total DOS and PDOS of As- and Sb-doped are shown in Fig. 7.

From Fig. 7 (a) we can obviously see that *4p*-orbitals of As make the contribution to not only VBM and CBM, but also the total DOS. In other words, the main contribution is from *4p*-orbitals of the dopant As, which is corresponding with the explanation by band structure. Furthermore, there is a flat-level for the band structure in spin-up, leading to a large density of states in that region, as shown in PDOS of As. In addition, we find that the system is assymetry at the Fermi level in total DOS,

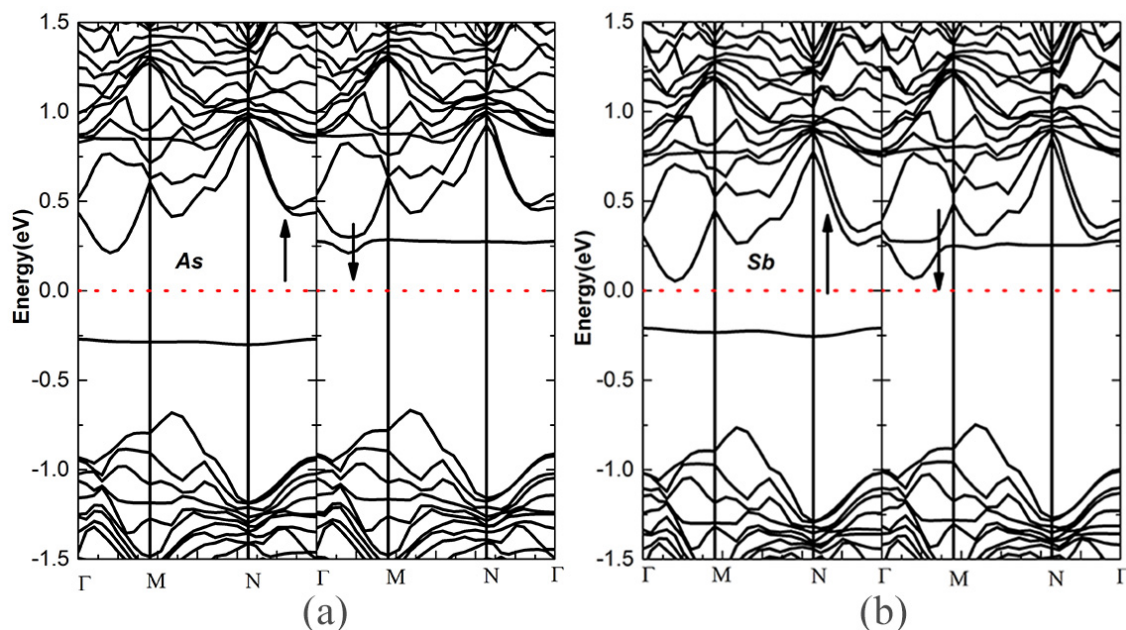


FIG. 6: Calculated band structures of (a) As- and (b) Sb-doped systems, along Γ -M-N- Γ direction. The energy zero represents the Fermi level.

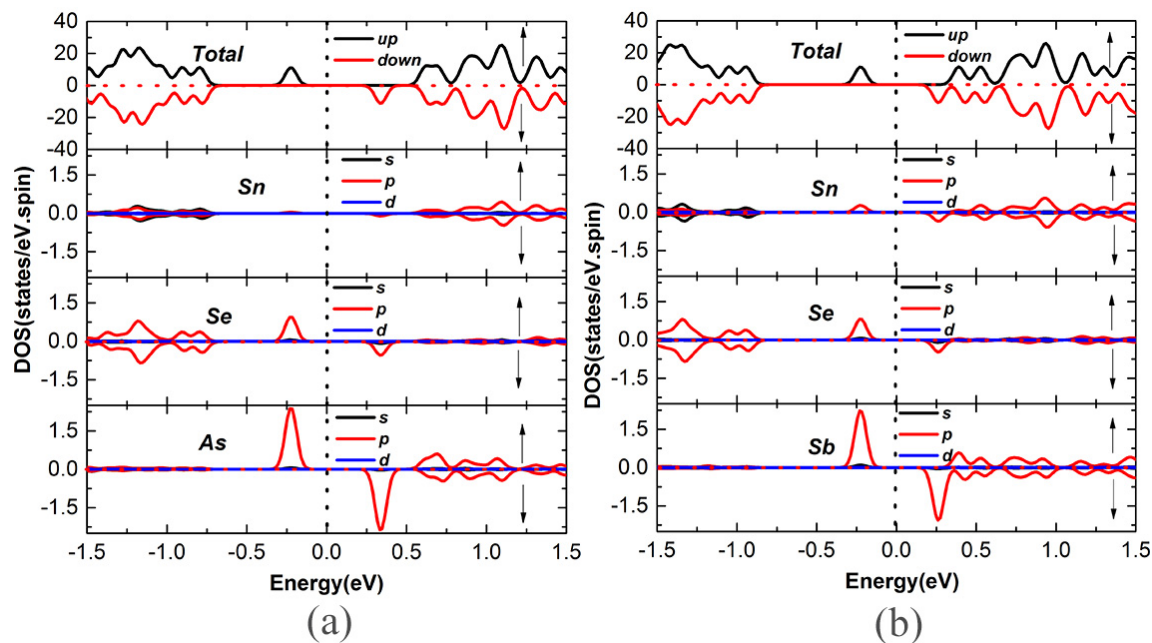


FIG. 7: DOS and PDOS of (a) As- and (b) Sb-doped systems. The energy zero represents the Fermi level.

which exhibits the system is of magnetism. Obviously, the magnetism is mainly induced by As atom. Then we calculated the magnetic value ($1.00 \mu_B$), which is smaller than its free atom ($\text{As} \sim 3.00 \mu_B$). On the other hand, for Sb-doped system, as seen in Fig. 7 (b), it shows up the similar properties to As-doped system that $4p$ -orbitals of Sb play an important role for VBM, CBM and total DOS. The total DOS appears asymmetry at the Fermi level, indicating the Sb-doped system is of magnetism.

Obviously, the magnetism is mainly derived from the S-b atom, and the value of calculated magnetism is $1.00 \mu_B$, which is also smaller than its free atom ($\text{Sb} \sim 3.00 \mu_B$). From Fig. 7, we obtain the same explanation with that of the band structures. Finally, in order to explain the magnetic mechanism, we calculated the spin charge density of As- and Sb-doped systems as shown in Fig. 8.

From Fig. 8 (a) and (b), we can distinctly see that the magnetism is mainly induced by As atom and Sb atom

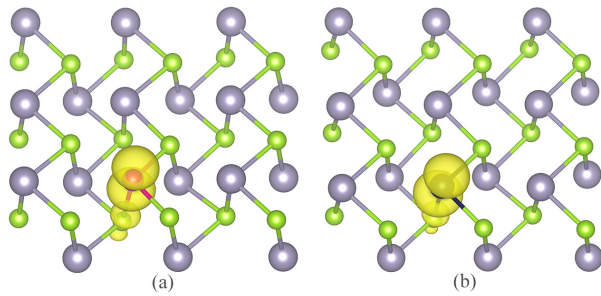


FIG. 8: Spin charge density ($\rho_{up}-\rho_{down}$) of (a) As- and (b) Sb-doped system, respectively. The value of isosurface is $0.03 e/\text{\AA}^3$.

TABLE I: Calculated structural and magnetic properties for single atoms doping on SnSe monolayer. Formation energy (E_f); the magnetic moments (μ); minimum dopants-Se (D-Se) distance (d_2).

Dopant	E_f (eV/atom)	μ (μ_B)	d_2 (D-Se) (\AA)
SnSe	-4.13	0	2.78
Ga	-0.39	1.00	2.55
In	-0.44	0.99	2.79
As	-0.88	1.00	3.08
Sb	-0.61	1.00	3.17

for As- and Sb-doped systems, respectively. For the As-doped system, the magnetism mainly gathers around the As atom, and minority scatters around Se atoms. Similarly, the magnetism is mainly induced by the dopant atom in Sb-doped system. The phenomena are consistent with the results of DOS and PDOS. The reason of the magnetism is that when As and Sb replaced Sn in SnSe monolayer, the system will exist an extra electron. Hence, the extra electron will induce the magnetism. As a result, both As and Sb dopant atoms lead to an donor level resulting in n -type doped systems.

Generally, the X-doped (X=Ga, In, As, Sb) systems with either half-metal or semiconductor properties can be explained by the sp^2 bonding character of Sn atoms with a lone pair of valence electrons and their strong hybridizations with the sp orbitals of dopants. We can conclude that the doped systems $Sn_{17}Se_{18}X_{Sn}$ (X=Ga, In, As, Sb) are ferromagnetic states from the spin charge density. Although the Ga-, As-, and Sb-doped systems present semiconductor properties, the band gaps are different with 0.12, 0.48, and 0.28 eV, respectively. Considering our work, we are aware that the electronic properties can be tuned by substitutional doping.

Finally, we calculate the formation energy of the substitutional system in order to verify the stability of X-

doped SnSe monolayer. The formation energy (E_f) is defined as $E_f=[E_{tot}-(E_{pure}-E_{atom}^{Sn}+E_{atom}^X)]/n$, where E_{tot} , E_{pure} , E_{atom}^{Sn} , and E_{atom}^X are the total energies of the doped system $Sn_{17}Se_{18}X_{Sn}$ (X=Ga, In, As, Sb), the energy of pure SnSe monolayer, the energies of single Sn atom and isolated X atoms, respectively. n presents the number of atoms in supercell. From our definition, the negative value of E_f shows that a system is stable. The large absolute value of E_f energy means strong interaction between dopants and Sn. A summary of the results is shown in Table 1. From Table 1, we find that the formation energy of Ga-doped system is minimum, which demonstrates Ga atom is easy to be doped and the Ga-doped system is the most stable than other three systems. Although the formation energy of doping system is somewhat larger than that of SnSe monolayer, the doped systems may be synthesized by chemical-vapor deposition (CVD) or molecular-beam epitaxy (MBE) experimentally.

4. Conclusions

In summary, using first-principles calculations, we present the geometrical structure, electronic and magnetic properties of monolayer SnSe substitutionally doped by Ga, In, As, and Sb atoms, respectively. We find that the electron structure can be tuned by substitutional doping. For Ga- or In-doped system, it presents semiconductor and half-metal properties, respectively; while As or Sb substitute Sn, the systems display semiconductor properties. In Ga-doped system, due to the band gap declining, the system exhibits red shift, which makes the system to have a wide application in optoelectronic devices. When Sn atom is replaced by Ga atom or In atom, inducing a hole, so the systems belong to p -type doping; on the other hand, if As or Sb replace Sn, the system has an unpaired electron, resulting n -type doping. No matter whether Ga and In as dopant atoms, or As and Sb, there is an unpaired electron which can induce about $1\mu_B$ magnetism. Finally, comparing to the formation energy of $Sn_{17}Se_{18}X_{Sn}$ (X=Ga, In, As, Sb), we find that As is easy to be doped and the As-doped system of is the most stable, whereas the four types of doped systems are thermodynamic stable. The results of substitutional doping make the application of SnSe monolayer more extensive.

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¹ K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y.

Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, *Science*, 2004, **306**, 666.

² A.K. Geim and K.S. Novoselov, *Nat Mater.*, 2007, **6**, 183.

- ³ A.S. Rodin, A. Carvalho and A.H. Castro Neto, *Phys. Rev. Lett.*, 2014, **12**, 176801.
- ⁴ T. Brumme, M. Calandra and F. Mauri, *Phys. Rev. B.*, 2015, **91**, 155636.
- ⁵ J. Sivek, H. Sahin, B. Partoens and F.M. Peeters, *Phys. Rev. B.*, 2013, **87**, 085444.
- ⁶ W.Y. Yu, Z.L. Zhu, C.Y. Niu, C. Li, J.H. Cho and Y. Jia, *Phys. Chem. Chem. Phys.*, 2015, **17**, 16351.
- ⁷ Z.L. Zhu, C. Li, W.Y. Yu, D.H. Chang, Q. Sun and Y. Jia, *Appl. Phys. Lett.*, 2014, **105**, 113105.
- ⁸ P. Vogt, P.D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio, A. Resta, B. Ealet and G.L. Le, *Phys. Rev. Lett.*, 2012, **108**, 155501.
- ⁹ W.Q. Xia, W. Hu, Z.Y. Li and J. L. Yang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22495.
- ¹⁰ F.F. Zhu, W.J. Chen, Y. Xu, C.L. Gao, D.D. Guan, C.H. Liu, D. Qian, S.C. Zhang and J.F. Jia, *Nat. Mater.*, 2015, **14**, 1020.
- ¹¹ H.J. Zhang, Y.D. Ma and Z.F. Chen, *Nanoscal.*, 2015, **7**, 19152
- ¹² S.L. Zhang, Z. Yan, Y.F. Li, Z.F. Chen and H.B. Zeng, *Angew. Chem. Int. Ed.*, 2015, **54**, 3112
- ¹³ S.L. Zhang, M.Q. Xie, F.Y. Li, Z. Yan, Y.F. Li, E.J. Kan, W. Liu, Z.F. Chen and H.B. Zeng, *Angew. Chem. Int. Ed.*, 2016, **55**, 1666
- ¹⁴ Z. Zhu; J. Guan; D. Liu; D. Tomnek, *ACS Nano.*, 2015, **9**, 8284.
- ¹⁵ M. Rarenteau and C. Carlone, *Phys. Rev. B: Condens. Matter.*, 1990, **41**, 5227.
- ¹⁶ J. Choi, J. Jin, I.G. Jung, J.M. Kim, H.J. Kim and S.U. Son, *Chem. Commun.*, 2011, **47**, 5241.
- ¹⁷ I. Lefebvre, M.A. Szymanski, J. Olivier-Fourcade, J.C. Jumas, *Phys. Rev. B.*, 1998, **58**, 1896.
- ¹⁸ J.M. Chamberlain and M. Merdan, *J. Phys. C: Solid State Phys.*, 1977, **10**, L571.
- ¹⁹ P.D. Antunez, J.J. Buckley, R.L. Brutchey, *Nano scale.*, 2011, **3**, 2399.
- ²⁰ S. Liu, X. Guo, M.H. Zhang, X. Liu and C. Li, *Angew. Chem., Int. Ed.*, 2011, **50**, 12050.
- ²¹ W.J. Baumgardner, J.J. Choi, Y.F. Lim, T. Hanrath, *J. Am. Chem. Soc.*, 2010, **132**, 9519.
- ²² L. Li, Z. Chen, Y. Hu, X.W. Wang, T. Zhang, W. Chen and Q.B. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 1213.
- ²³ B. Pejova, I. Grozdanov, *Thin Solid Films.*, 2007, **515**, 5203.
- ²⁴ D.J. Xue, J. Tan, J.S. Hu, W. Hu. Y.G. Guo. L.J. Wan, *Adv. Mater.*, 2012, **24**, 4528.
- ²⁵ D. Chun, R.M. Walser, R.W. Bene and T.H. Courtney, *Appl. Phys. Lett.*, 1974, **24**, 479.
- ²⁶ Z. Zhang, G. Du, Q. Meng, Z. Guo, X. Yu, Z. Chen, T. Guo and R. Zeng, *RSC Adv.*, 2011, **1**, 1834.
- ²⁷ G.J. Xiao, Y.N. Wang, J.T. Ning, Y.J. Wei, B.B. Liu, W.W. Yu, G.T. Zou and B. Zou, *RSC Adv.*, 2013, **3**, 8104.
- ²⁸ M.Z. Xue, J. Yao, S.C. Cheng and Z.W. Fu, *J. Electrochem. Soc.*, 2006, **153**, A270.
- ²⁹ Z. Zhang, C. Shao, X. Li, L. Zhang, H. Xue, C. Wang and Y. Liu, *J. Phys. Chem. C.*, 2010, **114**, 7920.
- ³⁰ S.S. Li, C.W. Zhang, W.X. Ji, F. Li, P.J. Wang, S.J. Hu, S.S. Yan and Y.S. Yu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15968.
- ³¹ J.A. Rogers, M.G. Lagally and R.G. Nuzzo, *Nature*, 2011, **477**, 45.
- ³² Q. Tang, Z. Zhou and Z.F. Chen, *WIREs Comput. Mol. Sci.*, 2015, **5**, 360.
- ³³ Q. Tang and Z. Zhou, *Prog. Mater. Sci.*, 2013, **58**, 1244.
- ³⁴ W. Kohn and L.J. Sham, *Phys. Rev.*, 1965, **140**, A1133.
- ³⁵ J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- ³⁶ P.E. Blochl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
- ³⁷ G. Kresse and J. Frthmuller, *Phys. Rev. B: Condens. Matter.*, 1996, **54**, 11169.
- ³⁸ M.A. Franzman, C.W. Schlenker, M.E. Thompson and R.L. Brutchey, *J. Am. Chem. Soc.*, 2010, **132**, 4060.
- ³⁹ K. Kutorasinski, B. Wlondlocha, S. Kaprzyk and J. Toboła, *Phys. Rev. B.*, 2015, **91**, 205201.
- ⁴⁰ Y.C. Huang, C.Y. Ling, H. Liu and S.F. Wang, *RSC Adv.*, 2014, **4**, 6933.
- ⁴¹ P. Lu, X. Wu, W. Guo, C. Niu, Y. Zhu and B. Huang, *ACS Nano*, 2012, **6**, 1695.
- ⁴² A.V. Krashenninikov, P.O. Lehtinen, A.S. Foster, P.Pyykko and R.M. Nieminen, *Phys. Rev. Lett.*, 2009, **102**, 126807.
- ⁴³ A. Ramasubramaniam, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **87**, 195201.
- ⁴⁴ Y.C. Cheng, Z.Y. Zhu, W.B. Mi, Z.B. Guo and U. Schwingenschlogl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **87**, 100401.