First-Principles Study of Electronic Properties of Substitutionally Doped Monolayer SnP$_3$

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Abstract: SnP$_3$ has a great prospect in electronic and thermoelectric device applications due to its moderate band gap, high carrier mobility, optical and chemical characteristics. Doping in two-dimensional semiconductors is likely to display various anomalous behaviors when compared to doping in bulk semiconductors due to the significant electron confinement effect. By introducing foreign atoms from group III to VI, we can successfully modify the electronic properties of two-dimensional SnP$_3$. The interaction mechanism between the dopants and atoms nearby is also different from the type of doped atom. Both Sn$_7$BP$_{24}$ and Sn$_7$NP$_{24}$ systems are indirect bandgap semiconductors, while the Sn$_7$AlP$_{24}$, Sn$_7$GaP$_{24}$, Sn$_7$PP$_{24}$, and Sn$_7$AsP$_{24}$ systems are metallic due to the contribution of doped atoms intersecting the Fermi level. For all substitutionally doped 2D SnP$_3$ systems considered here, all metallic systems are nonmagnetic states. In addition, the Sn$_7$XP$_{24}$ and Sn$_7$P$_{24}$Y may have long-range and local magnetic moments, respectively, because of the degree of hybridization between the dopant and its adjacent atoms. The results complement theoretical knowledge and reveal prospective applications of SnP$_3$-based electrical nanodevices for the future.

Keywords: first-principles; two-dimensional materials; substitutional doping; monolayer SnP$_3$

1. Introduction

In 2004, single-atom-thick sheets of graphene were successfully prepared by mechanical stripping [1]. Since then, two-dimensional materials have attracted much attention because of their intrinsic excellent physical and chemical characteristics [2–13]. The exploration of the ultra-thin two-dimensional system is also inspired by the latest experimental progress of controlled fabrication of nanomaterials. However, monolayer 2D materials are always limited by their inherent electronic properties. For example, the zero band gap of graphene restricts it from being used in practical electrical devices [3]. For 2D MoS$_2$ with the direct band gap of 1.79 eV, abundant internal defects seriously reduce the mobility of carriers [4,14]. On the other hand, the boron nitride monomolecule is not an ideal candidate material for optoelectronic components or electronic devices because of its wide band gap. Therefore, it is significant to find an effective solution to improve their electronic properties. To further improve the performance of 2D materials, there are many methods such as adsorption, doping, and constructing heterogeneous junctions by stacking different materials, which have shown excellent effects in different fields [15,16]. In this research, doping is used to improve the performance of SnP$_3$, which has been demonstrated as an effective and simple approach to modify the magnetic and electrical characteristics of 2D materials [5–9,17–19]. By doping heteroatoms, carbon-based materials exhibit exceptional electrochemical properties in lithium-ion and sodium-ion batteries [20]. Atomic metal ion-doped graphene offers strong conductivity and stability to the materials, resulting in good pseudocapacitance performance [21]. By inserting small BN domains, the band gap...
of graphene could well be efficiently expanded near K as well as K' points [7]. MoS$_2$ is usually stated as natively n-type while dopants quench the n-type, allowing it to perform as a single-photon emitter [22]. Doping various elements with even or odd amounts of valence electrons causes an oscillating behavior in black phosphorene [23].

Very recently, a 2D monolayer SnP$_3$, one of the representative layered group-IV-based triphosphide family materials, has been theoretically proposed by Sun et al. [24]. The cleavage energy of monolayer SnP$_3$ [24] is close to the cleavage energy of graphene. The cleavage energy of monolayer SnP$_3$ [22] is comparable to that of graphene [25]. In its monolayer form, SnP$_3$ exhibits semiconducting behavior, with the indirect bandgap determined as 0.42 eV by the PBE function [26] and 0.72 eV by the HSE06 function [27]. Furthermore, with a higher affinity to the NH$_3$, NO, and NO$_2$, the SnP$_3$ monolayer has been described as a promising sensing material for tiny gas molecules [28,29]. Because of its high areal capacity and good stability, SnP$_3$ is also widely employed in Na- and Li-ion batteries [30,31]. SnP$_3$ has also been predicted with a high light absorption coefficient and carrier mobility [32] and has been found as an excellent p-type thermoelectric material [33]. The thermoelectric effect, as an essential part of the solution to today’s energy challenges, by reducing adverse effects on the environment, makes the application of SnP$_3$ more extensive [35].

We have performed systematic investigations of the substitutionally doped SnP$_3$ monolayer. The structural characteristics (including the optimized geometries, lattice constants, distortion) and electronic properties (including the energy band structures, density of states, and the charge densities) are systematically discussed. The doping atoms replaced Sn, including group III (B, Al, Ga) and group V (N, P, As), while dopants substituted for P are from group IV (C, Si, Ge) and group VI (O, S, Se). The electronic properties of doped 2D systems are strongly affected by the number of outer electrons in the dopants and the doping sites. Since each layer of bulk SnP$_3$ is mainly connected by weak van der Waals forces, our study has guiding significance for understanding bulk SnP$_3$ and also provides direction for future SnP$_3$-based nanoscale applications.

2. Computational Details

The Vienna ab initio simulation software (VASP) is performed to do the first principle calculations, which are based on the functional theory (DFT) of plane wave density and the projector augmented wave (PAW) approach [36,37]. In the Perdew-Burke-Ernzerhof (PBE) parameterization, the generalized gradient approximation (GGA) was used to describe the exchange-correlation interactions [38]. PBE functionals are related to semi-local functionals where the exchange-correlation energy is given by a function that depends on the electron density and the derivative of the electron density at each point of space. At the same time, SnP$_3$ material is a layered structure with van der Waals (vdW) forces binding between layers. Since the DFT-GGA calculation lacks a prediction of the interlayer spacing of layer structures, we also take the van der Waals interaction (vdW) into consideration [39] by inserting a semi-empirical dispersion potential to the usual Kohn-Sham DFT energy (PBE-D2 computations). The plane wave function is used to create the electronic wave function, and the Monkhorst–Pack unique K-point sampling method is used to integrate the Brillouin zone (BZ) [40]. The vdW-D2 correction by Grimme is used to describe the interaction between SnP$_3$ and dopant atoms over large distances. To eliminate the artificial contact between the neighboring periodic sheets, a $2 \times 2 \times 1$ supercell with a vacuum layer of 20 Å in ‘z’ axis is utilized. A total of 500 eV was set as cut-off energy of the plane wave expansion. The Brillouin zone sampling was carried out using a $13 \times 13 \times 1$ Γ-centered Monkhorst–Pack K-point mesh. All structures were completely relaxed until the total change in energy between two self-consistent steps was smaller than $1 \times 10^{-4}$ eV.
3. Result and Discussion

We established a 1 × 1 SnP3 cell (contains eight atoms) to determine the basic structural parameters of the 2D SnP3 system. After relaxation, the optimal lattice constant of the SnP3 supercell is 7.17 Å, which agrees well with the existing theoretical calculations [24,27,28]. The system was modeled based on a 2×2 SnP3 supercell (containing 32 atoms) for substitutionally doped SnP3 (shown in Figure 1) to minimize the influence of electrons states neighboring atoms. We first removed one Sn (or P) atom from the 2 × 2 SnP3 supercell and then replaced it with the one doped atom, which is labeled as X (or Y). The substitutionally doped SnP3 system is labeled as Sn7XP24 (or Sn8P23Y). Since the number of valence electrons in dopants has a great impact on the electronic characteristics of low dimensional materials, we select atom B, Al, and Ga from group III and atom N, P, As from group V as dopants for Sn atoms due to the one more or one less electron than Sn atoms. Similarly, we choose the atoms in group IV (C, Si, Ge), which has one less electron than P, and group VI (O, S, Se), which has one more electron as dopants for the P atom. The substitutional atoms are selected from the two adjacent groups of the Sn or P atom, each of which differs from the substituted atom by one outer electron.

![Figure 1. Top and side views of 2 × 2 substitutionally doped SnP3 supercell.](image)

After full relaxation, the lattice constant of 2 × 2 SnP3 is 14.32 Å. Table 1 displays the parameters of the Sn7XP24 and Sn8P23Y systems in which doped atoms have been replaced. We can see that the lattice constants of the doped systems are not much different from that before doping. Within the same group, the lattice constants rise as the atomic number increases. This is owed to the influence of the ionic radius’s effect upon the length of bonds. Although the insertion of doping atoms breaks the symmetry of the defect-free SnP3, the structure of the doping system typically retains the original hexagonal frame structure.

To evaluate the stability and feasibility of substitutionally doped SnP3 monolayer, the formation energy (E_f) of the system is given as follows:

$$ E_f = E_{\text{total}} + E_{\text{replaced}} - E_{\text{pristine}} - E_D $$

where $E_{\text{total}}$ stands for the total energy of the SnP3 monolayer after doping (Sn7XP24 or Sn8P23Y), $E_{\text{pristine}}$ denotes the total energy of the pure Sn8P24. The chemical potentials of single X (or Y) and Sn (or P) atoms are symbolized by $E_D$ and $E_{\text{replaced}}$, respectively. With the exception of Sn7BP24 and Sn8P23C, the formation energies of all of these doping systems are quite low. Particularly, the formation energies of Sn7BP24, Sn7PP24, Sn7AsP24, Sn8P23C, Sn8P23Si, and Sn8P23O systems are negative. The positive or negative formation energy...
can reflect the stability of the systems. The results implied that the substitutional doping processes of these systems are stable and exothermal. The lengths of bond P-X/P-Y and bond Sn-P/Sn-Y are listed in Table 1 to study the structural deformation in the Sn$_7$XP$_{24}$ or Sn$_8$P$_{23}$Y systems. In comparison to the length of the Sn-P bond (2.71 Å) in pristine monolayer Sn$_3$, the d has pronounced change. Although the doped atoms from the same main group have similar electronic configurations, the larger ionic radius could promote sp$^3$ hybridization. For the doped atoms in the same main group, the atomic radius increase with the atomic number. This would explain why P-X/P-Y and Sn-Y bond lengths increase as the number of protons increases. However, sheet thickness did not vary much because the configuration distortions generated by a single dopant atom are highly localized.

Table 1. Calculated Structural Geometry of substitutionally doped Sn$_7$XP$_{24}$ and Sn$_8$P$_{23}$Y system, including the lattice constants ($a = b$), P-X/P-Y bond length ($d_1$), Sn-P/Sn-Y bond length ($d_2$), band gap ($E_g$), Sn$_3$ thickness ($h$) and total magnetic moment of the system in units of Bohr magneton (M) calculated by using PBE-D2.

| System    | $a = b$ (Å) | $E_g$ (eV) | $d_1$ (Å) | $d_2$ (Å) | $h$ (Å) | $E_g$ (eV) | M (µg) |
|-----------|-------------|-----------|-----------|-----------|--------|-----------|--------|
| Sn$_3$    | 14.32       | /         | 2.71      | 2.71      | 2.81   | 0.42      | 0.00   |
| Sn$_7$BP$_{24}$ | 14.30 | −5.662   | 1.93      | 2.71      | 2.72   | 0.09      | 1.00   |
| Sn$_7$AlP$_{24}$ | 14.32 | −3.918   | 2.32      | 2.71      | 2.85   | /         | 0.00   |
| Sn$_7$GaP$_{24}$ | 14.32 | 0.592    | 2.33      | 2.71      | 2.85   | /         | 0.00   |
| Sn$_7$NP$_{24}$ | 14.25 | 0.333    | 1.86      | 2.71      | 2.74   | 0.08      | 1.00   |
| Sn$_7$PP$_{24}$ | 14.25 | −1.184   | 2.32      | 2.71      | 2.76   | /         | 0.00   |
| Sn$_7$AsP$_{24}$ | 14.26 | −0.699   | 2.44      | 2.71      | 2.77   | /         | 0.00   |
| Sn$_8$P$_{23}$C | 14.22 | −6.609   | 1.74      | 2.35      | 2.72   | 0.21      | 1.00   |
| Sn$_8$P$_{23}$Si | 14.37 | −0.206   | 2.19      | 2.67      | 2.69   | 0.26      | 1.00   |
| Sn$_8$P$_{23}$Ge | 14.41 | 0.579    | 2.28      | 2.72      | 2.65   | 0.27      | 1.00   |
| Sn$_8$P$_{23}$O | 14.20 | −0.636   | 1.75      | 2.69      | 2.80   | /         | 0.00   |
| Sn$_8$P$_{23}$S | 14.29 | 0.756    | 2.20      | 2.74      | 2.75   | 0.12      | 1.00   |
| Sn$_8$P$_{23}$Se | 14.37 | 0.661    | 2.35      | 2.83      | 2.72   | 0.16      | 1.00   |

Figure 2 illustrates the substitutionally doped 2D Sn$_3$ band structures obtained by the PBE-D2, the band gap values of different systems are shown in Table 1. The orange and blue dots represent the contributions of dopant atoms in spin-up and spin-down states, respectively. As presented in Figure 2, the pure Sn$_3$ is a semiconductor with an indirect band gap of 0.42 eV, which agrees well with previous results [28,34,41]. The valence band maximum (VBM) is located at K-point, whereas the conduction band minimum (CBM) is found at Γ-point. When one Sn or P atom is removed from the $2 \times 2$ Sn$_3$ monolayer, the system transforms into a metal. All B- and N-doped Sn$_7$XP$_{24}$ systems are indirect bandgap semiconductors. The band gaps of Sn$_7$BP$_{24}$ and Sn$_7$NP$_{24}$ are 0.08 and 0.09 eV, respectively. The band configurations of them are quite similar to the pristine monolayer Sn$_3$. While the Sn$_7$AlP$_{24}$, Sn$_7$GaP$_{24}$, Sn$_7$PP$_{24}$, and Sn$_7$AsP$_{24}$ systems are metallic due to the contribution of doped atoms intersecting the Fermi level. This means the Al-, Ga-, P-, and As-doping of Sn atom in Sn$_3$ could increase its conductivity. In the case of substitutional doping of the P atom in Sn$_3$, however, only the Sn$_8$P$_{23}$O system appears to be metallic. For systems with dopants from group IV (C, Si, Ge) and group VI (S, Se), the doped Sn$_8$P$_{23}$Y systems could retain semiconducting properties. In our research, the contributions of dopants are mainly around the Fermi level. Thus, for all doped semiconductor systems, the addition of doped atoms reduces the band gap value. Compared with the P-vacancy system, the Fermi level moves up in Sn$_8$P$_{23}$O, Sn$_8$P$_{23}$S, and Sn$_8$P$_{23}$Se systems. Among Sn$_7$XP$_{24}$ systems, the doped atoms contribute significantly near the Fermi level for the magnetic Sn$_7$BP$_{24}$ and Sn$_7$NP$_{24}$ systems, while for Al-, Ga-, P- and As-doped systems, the dopants contribute more in deep level. Within each main group, the band gap value of the substitutionally doped Sn$_3$ also increases with the increasing atomic number (shown in Table 1).
To illustrate the intrinsic mechanism of the substitutionally doped system, the densities of states of the substitutionally doped Sn₇XP₂₄ and Sn₈P₂₃Y systems are presented in Figures 3 and 4, respectively. The partial density of states (PDOS) of the dopant atom and its adjacent atoms is also displayed in addition to the total density of states (TDOS). The locations of these atoms have been marked in Figure 1. As can be found in the PDOS, near the Fermi level, the impurity atom has a larger contribution to the doped system. For substitutional doping on the Sn site of Sn₃P₃ monolayer, only the Sn₇BP₂₄ and Sn₇NP₂₄ systems are semiconductors. We can see that the spin-up (fully occupied) and spin-down (unoccupied) states are totally different near the Fermi level. The unevenness occupation between spin-up and spin-down leads to magnetic moments in the doped system. However, among all considered Sn₇XP₂₄ Y systems, the occupation situations of the spin-up and spin-down states are very uneven except for Sn₇P₂₄O. For systems with unevenness DOS, the spin-up states are fully occupied, and spin-down states are unoccupied. For all Sn₇XP₂₄ systems considered here, no matter the SnP₃ monolayer has magnetic moments or not, there is strong hybridization between the X atom and its nearest (atom 1) and second nearest neighbor (atom 2) P atoms. What is more, the same degrees of hybridization are found between the X atom and its third nearest Sn atoms (atom 3). This would lead to a long-range magnetic moment in the systems. However, for the substitutionally doped Sn₈P₂₃Y systems, there is only strong hybridization between the Y atom and its nearest (atom 4) Sn atoms. On the other hand, the Sn₇AlP₂₄, Sn₇GaP₂₄, Sn₇PP₂₄, and Sn₇AsP₂₄ systems are found to be metallic. Different from the substitutional doping on the Sn site, the semiconducting characteristics of the pure SnP₃ monolayer are retained in the majority of Sn₈P₂₃Y systems. All group IV atoms-doped Sn₈P₂₃Y systems are semiconductors. The lowest unoccupied states fall below the Fermi level after substitutional doping of the O atom on the Sn site, showing n-type doping of the SnP₃ monolayer.

To understand the mechanisms inherent in these low dimensional structures, which are necessary for the dynamics of material formation [42], the deformation charge density ($\Delta \rho$) is also discussed in this work. The density of deformation charge is described as:

$$\Delta \rho(r) = \rho(r) - \sum_{\mu} \rho_{\text{atom}}(r - R_{\mu})$$  \hspace{1cm} (2)
where the $\rho(r)$ stands for the total charge density of the system and the $\sum_{\mu} \rho_{\text{atom}}(r - R_{\mu})$ denotes the superposition of atomic charge densities. The extent of charge transfer between the dopant and the monolayer SnP$_3$ could be measured through $\rho(r)$. The deformation charge density of planes slicing across the dopant atoms is shown in Figure 5. The electron accumulation ($\Delta \rho > 0$) and electron depletion ($\Delta \rho < 0$) are depicted by red and blue lines, respectively. For the Sn$_7$BP$_{24}$ and Sn$_7$NP$_{24}$ systems, there is obvious charge transfer from adjacent P atoms to dopant atoms. On the other hand, the electrons are apparently converging around the dopant atoms Sn$_8$P$_{23}$O and Sn$_8$P$_{23}$C systems. For doped atoms in the same main group, the properties of the bonds between dopant and its nearby atoms change with the atomic number of doped atoms. With the increase in dopants’ proton, the ionic component decreases, and the covalent component increases. At the same time, the electron transfer between atoms and the electron-accepting ability decreases as the atomic number increases. It can be explained by that electron-accepting ability decreases as the atomic number increases. Due to the strongest electron-accepting ability of the O atom, among all the substitutionally doped systems studied here, the most obvious electron transfer is found in the Sn$_8$P$_{23}$O system. Furthermore, when the covalent bonding ratio increases, the P-X and P-Y bond lengths of the substitutionally doped SnP$_3$ monolayer also become longer. Thus, the distribution of electrons in the systems is significantly affected by the introduction of doping atoms.

Figure 3. Total and partial densities of states of the substitutionally doped Sn$_7$XP$_{24}$ system.
To understand the mechanisms inherent in these low dimensional structures, which are necessary for the dynamics of material formation [42], the deformation charge density \( \Delta \rho(r) \) is also discussed in this work. The density of deformation charge is described as:

\[
\Delta \rho(r) = \rho(r) - \sum \rho_{\text{atom}} - R \mu \mu
\]

where the \( \rho(r) \) stands for the total charge density of the system and the \( \sum \rho_{\text{atom}} - R \mu \mu \) denotes the superposition of atomic charge densities. The extent of charge transfer between the dopant and the monolayer SnP3 could be measured through \( \rho(r) \). The deformation charge density of planes slicing across the dopant atoms is shown in Figure 5. The electron accumulation \( (\Delta \rho > 0) \) and electron depletion \( (\Delta \rho < 0) \) are depicted by red and blue lines, respectively. For the Sn7BP24 and Sn7NP24 systems, there is obvious charge transfer from adjacent P atoms to dopant atoms. On the other hand, the electrons are apparently converging around the dopant atoms Sn8P23O and Sn8P23C systems. For doped atoms in the same main group, the properties of the bonds between dopant and its nearby atoms change with the atomic number of doped atoms. With the increase in dopants’ proton, the ionic component decreases, and the covalent component increases. At the same time, the electron transfer between atoms and the electron-accepting ability decreases as the atomic number increases. Due to the strongest electron-accepting ability of the O atom, among all the substitutionally doped systems studied here, the most obvious electron transfer is found in the Sn8P23O system. Furthermore, when the covalent bonding ratio increases, the P-X and P-Y bond lengths of the substitutionally doped SnP3 monolayer also become longer. Thus, the distribution of electrons in the systems is significantly affected by the introduction of doping atoms.

For a long time, the magnetism of 2D materials has attracted a great deal of academic attention. The difference in charge density between the spin-up \( (\rho^\uparrow) \) and spin-down \( (\rho^\downarrow) \) states of substitutionally doped 2D SnP3 systems are presented in Figure 6. Table 1 also shows the total magnetic moments of the doped systems determined with PBE-D2. For substitutionally doped 2D SnP3 systems considered here, all metallic systems are nonmagnetic states. As mentioned above in Table 1, the magnetic moments of about 1.00 µB in doped systems were caused by the dopant atoms in the SnP3 monolayer. We found that the long-range magnetic moments can be found in the Sn7BP24 and Sn7NP24 systems, resulting from the strong hybridization between the B (or N) atom and its nearest P atoms, second nearest P atoms, and its third nearest Sn atoms. However, the magnetic Sn8P23Y (Y = C, Si, Ge, S, Se) systems only show local magnetic moments through the substitutional doping process. Thus, the 2D indirect bandgap SnP3 monolayer can attain local or long-range magnetic moments through the substitutional doping, resulting from the different interaction mechanisms between the doping atom and its neighboring atoms, which make the SnP3 sheet a promising material for nanoscale technological application in spintronic.
states ($\rho_i$) of substitutionally doped 2D SnP$_3$ systems are presented in Figure 6. Table 1 also shows the total magnetic moments of the doped systems determined with PBE-D2. For substitutionally doped 2D SnP$_3$ systems considered here, all metallic systems are nonmagnetic states. As mentioned above in Table 1, the magnetic moments of about 1.00 $\mu_B$ in doped systems were caused by the dopant atoms in the SnP$_3$ monolayer. We found that the long-range magnetic moments can be found in the Sn$_7$BP$_{24}$ and Sn$_7$NP$_{24}$ systems, resulting from the strong hybridization between the B (or N) atom and its nearest P atoms, second nearest P atoms, and its third nearest Sn atoms. However, the magnetic Sn$_8$P$_{23}$Y ($Y = C, Si, Ge, S, Se$) systems only show local magnetic moments through the substitutional doping process. Thus, the 2D indirect bandgap SnP$_3$ monolayer can attain local or long-range magnetic moments through the substitutional doping, resulting from the different interaction mechanisms between the doping atom and its neighboring atoms, which make the SnP$_3$ sheet a promising material for nanoscale technological application in spintronic.

![Figure 6. The spin densities of magnetic substitutionally doped Sn$_7$XP$_{24}$ and Sn$_8$P$_{23}$Y system.](image)

4. Conclusions

In summary, we investigated the electronic characteristics of substitutionally doped 2D SnP$_3$ systems using first-principles calculations. One Sn atom is replaced with a dopant from group III (B, Al, Ga) and group V (N, P, As), while the P atom is replaced with an atom from group IV (C, Si, Ge) and group VI (O, S, Se). The substitutional atoms are selected from the two adjacent groups of the Sn or P atom due to one less or more electron. Our results show that the impurity atoms have a significant impact on the electronic characteristics of whole substitutionally doped systems. SnP$_3$ monolayers can exhibit metallic or semiconducting behavior depending on the dopant type. All semiconductive systems are indirect band gap semiconductors with the introduced magnetic moments of about 1.00 $\mu_B$. Within the same main group, the band gap and structural parameters increase as the atomic number of dopant rise. In addition, monolayer SnP$_3$ may have local or long-range magnetic moments because of the degree of hybridization between the dopant and its adjacent atoms. This allows SnP$_3$ monolayers to be widely used at the nanoscale in the field of spintronics. Since the doped atoms have a significant impact on the properties of the material, SnP$_3$ is suitable for various functionalization processes.

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