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Tailoring magnetism of black phosphorene doped with B, C, N, O, F, S and Se atom: A DFT calculation

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ABSTRACT

We calculate the electronic structure and magnetism of monolayer phosphorene doped by nonmagnetic atoms. O, S and Se impurities can induce the magnetic moment. O doping makes it become a spin-gapless semiconductor, but S and Se doping induces a half-metallic characteristic. The *p* orbital of dopant has a strong hybridization with P around impurities, which induces spin splitting of P and impurities. C induces a metallic character. B acts as *n*-type dopant and F results in *p*-type dopant. The magnetism of phosphorene doped by two O atoms strongly depends on the doping sites and distance between two O atoms.

1. Introduction

Recently, two-dimensional (2D) materials become a hot topic due to its excellent electronic structure. Black phosphorene (BP), a new candidate of 2D semiconductor, is potential to be applied in electric circuit, due to a direct band gap of 0.7–2.0 eV, high carrier mobility of ~10^3 cm^2/V, and on/off ratio of ~10^4 [1–4]. However, its ferromagnetism limits its application in spintronic devices. Few results about magnetism in phosphorene are reported, thus introducing magnetism in BP is valuable in academic and application research.

The influence of different strains can transform phosphorene from semiconductor to metal [5,6]. Vacancies in phosphorene induce a magnetic moment of 1.0 μ_B and change the band gap [7]. Doped or adsorbed 3*d* metals (Mn, Fe, Co, Ni and so on) on graphene, MoS_2 or Si can make it become diluted magnetic semiconductor and change its carrier type [8–10]. Phosphorene absorbed metal atoms also exhibits the magnetic and half-metal characters [11]. Spin-polarized semiconductors are realized in phosphorene by substitutional doping of Ti, Cr, and Mn, and a half-metallic state is obtained by doping V and Fe [12]. Except for the magnetic metal atoms doping, the nonmagnetic atoms are also considered. The properties of phosphorene doped by Si, S, and Cl were studied and some doped systems presents magnetic moments [13]. Pan et al. previously reported the ferromagnetism in C-doped ZnO [14]. Shen et al. observed a Dirac gap of 82 meV and a magnetic moment in C-doped Bi_2Se_3 [15]. Therefore, doping nonmagnetic atoms in phosphorene may also induce the magnetic moment and spin polarization.

In this paper, we selected B, C, N, O, F, S and Se to substitute P in phosphorene. The influence of impurities on its electronic structure and magnetism is studied. O, S and Se can induce a magnetic moment in phosphorene, and F acts as a *p*-type doping. B induces *n*-type doping. O-doped system is a spin-gapless semiconductor; S and Se induce a half-metallic characteristic. The magnetism in two O atoms doped phosphorene strongly depends on the dopant site and distance.

2. Calculation details and models

The calculations are performed by Vienna *ab initio* simulation package Code [16] by using projector augmented wave [17] potentials and Perdew–Burke–Ernzerhof exchange correlation function [18]. The structure is fully relaxed until the residual force on each atom is less than 0.01 eV/Å and the total energy is converged to 10^{-5} eV. The kinetic energy cutoff is 500 eV and a 64-atom

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$4 \times 1 \times 4$ supercell with a Γ-centered $5 \times 1 \times 5$ is used. A 15 Å vacuum space is used to separate the interaction between periodic images. The calculated lattice constants ($a = 3.308$ Å, $c = 4.549$ Å) and a direct band gap of 0.91 eV for monolayer BP are consistent with previous reports [4,6]. A dopant substitutes P on X site with a concentration of 1.56% (see Fig. 1). We found that no experiment could prove that if black phosphorus doped by O, S, Se, B, C, N, F show its different properties, such as magnetism. However, Khan et al. [13] reported that magnetism produced in phosphorene doped S, while there is no magnetism in Ref.19. It is relatively accurate that initial magnetic moment is slightly larger than experiment value in calculations. In order to ensure accuracy of the calculations, we use the initial magnetic moment for 0, 1 and 2 μ_B to calculate phosphorene doped by S. We found there is no magnetism when 0 is set, while almost the same magnetism occurs when 1 and 2 μ_B are set, respectively. Importantly, the energy of magnetic system is less than the nomagnetic system, which means the magnetic system is more stable. Therefore, we use the initial magnetic moment 1 μ_B to carry out all of our calculations.

The binding energy is defined as $E_b = (E_{\text{BP-vacany}} + E_{\text{dopant}} - E_{\text{dop-system}})$, where $E_{\text{BP-vacany}}$ is the energy of phosphorene with a single vacancy, E_{dopant} is the energy of dopant, and $E_{\text{dop-system}}$ is the energy of doped phosphorene. The positive E_b indicates that dopant is favor to bonding with phosphorene.

3. Results and discussion

The pristine phospherene has sp^3 hybridization, where P bonds with three adjacent P, with a lone pair of electrons, resulting in a puckered structure. Table 1 shows the lattice constants, bond length and distance between two atoms in pristine and doped systems. The lattice constants almost do not change because the radius of dopant is similar with P, and the atom radius is Se > P > S > B > C > N > O > F. Herewith, we called P on A, B, C, D, E, b, c, d and e sites as P_A, P_B, P_C, P_D, P_E, P_b, P_c, P_d and P_e, respectively. In pristine phosphorene, d_{XA} and $d_{XB/C}$ is 2.26 and 2.22 Å, respectively. In O, S and Se-doped systems, the distance between P_A and dopant is about 3.00 Å. The length is too large to form a strong bond, confirmed by the charge density difference distribution (see Fig. 2).

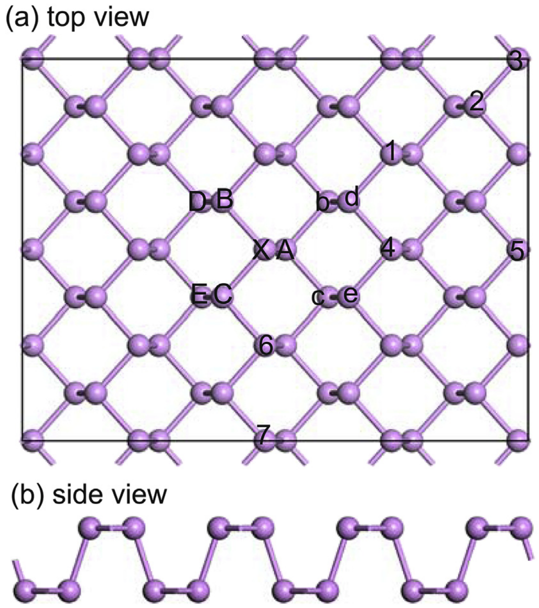

Fig. 1. The top and side view of phosphorene doped by impurity atom. The X site is the substitutional dopant atom.

Table 1
The calculated constants, the bond lengths and binding energy of pristine and doped phosphorene.

System	a(Å)	c(Å)	α(deg)	β(deg)	γ(deg)	E_b (eV)	d_{XA}(Å)	$d_{XB(C)}$ (Å)
pristine	13.19	18.52	90	90	90	–	2.26	2.22
B	13.18	18.57	89.95	90	90	7.57	1.85	1.94
C	13.15	18.47	90.18	90	90	7.98	1.80	1.80
N	13.12	18.45	90.27	90	90	9.22	1.81	1.78
F	13.11	18.64	89.23	90	90	3.93	1.66	2.95
O	13.09	18.50	89.21	90	90	5.97	3.13	1.71
S	13.16	18.50	89.91	90	90	4.27	2.94	2.16
Se	13.18	18.49	89.74	90	90	3.63	2.96	2.31

No charge accumulation appears between dopant and P_A, which means that the dopant only bonds with P_B and P_C. The bond length is 1.71, 2.16 and 2.31 Å in O, S and Se-doped systems, respectively. The shortest bond length implies that the O–P bonds are the strongest. The O-doped system is more stable due to its largest binding energy of 3.13 eV.

In B, C and N-doped systems, the dopant bonds with three P, and all of the bond lengths are smaller than 2.22 Å, revealing that P atoms around impurity carry one lone pair of electrons and thus these atoms still form sp^3 bonds, like the structure of pure phosphorene. N-doped system is the most stable with the largest binding energy among B, C and N-doped systems since N has the same valence electron distribution with P. Therefore, similar charge accumulation appears between N and P (see Fig. 2). In F-doped system, F just bonds with P_A, and no charge accumulation exists between F and $P_{B/C}$ (see Fig. 2). Among all of the systems, the bond length between dopant and P_A in F-doped system is the shortest due to the largest electronegativity. Among B, C and N, a larger electronegativity also results in a shorter bond length. Similarly, the phenomenon is also demonstrated in bond length between dopant and $P_{B/C}$.

The magnetic moment is 0.457, 0.441 and 0.422 μ_B in O, S and Se-doped systems, respectively (see Table 2). The presence of magnetism is related to the bonding nature and nonbonding electron states are easily modified by the valence electrons of impurity. The PDOS of 2p orbital of dopant and P shows similar patterns ranging widely from −0.37–0.53 eV, especially the PDOS of S and Se p orbital nearly overlapping with P. Meanwhile, sharp peaks appear at −0.13 and 0.24 eV in O, S and Se-doped phosphorene. In Fig. 3, O 2p orbital (S 3p and Se 4p) splits obviously near Fermi level (E_F), and the adjacent P 2p that splits near E_F has a strong hybridization with O (S and Se). P_A has the strongest hybridization with O 2p (S 3p and Se 4p), as shown in Fig. 3. P on other sites has a weaker hybridization with further distance away from dopant. This performance comes from spin splitting, resulting in a magnetic moment. We see O, S and Se bond with two P atoms, remaining one unpaired electron on 2p orbital of P_A, which possibly causes the net magnetic moments.

Furthermore, the magnetic moment is primarily from P_A whose 2p orbital has the strongest hybridization with p orbital of dopant. Other P atoms have minor contribution relatively, and the magnetic moment depends on the hybridization with dopant. Unexpectedly, the dopant itself has a spin splitting near E_F, especially S and Se. Therefore, the local O magnetic moment is smaller than S and Se. In different systems, the longer distance away from dopant leads to a weaker hybridization and smaller P magnetic moment. Among O, S and Se-doped systems, with the increase of atomic number and radius, the bonds with adjacent P become longer, resulting in a weaker interaction and slightly decreased magnetic moment. In Fig. 3, the impurity level locates near E_F, which is flat and corresponds to the relatively sharp peak of PDOS, especially for S and Se.