

Magnetic Properties of Edge Hydrogenated Zigzag Black Phosphorene Nanoribbon by Fe Doping

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Abstract: Using first-principles based on density functional theory within the GGA+U framework, we investigated the structural states, energy, and magnetic properties of edge hydrogenated Zigzag black Phosphorene Nanoribbon (H-ZPNR) with P atom substituted by Fe atom in different site. Undoped Edge hydrogenated ZPNR has no magnetic moment, however our results show that the magnetic moment of doped systems varied from 1 μ B to 4 μ B, and the coupling between the Fe atom and adjacent P atoms is either ferromagnetic or anti-ferromagnetic.

1 INTRODUCTION

Two-dimensional(2D) material displayed great potential applications in optoelectronic devices, spintronic, lithium batteries and gas sensors (Liu et al., 2017; Sun et al., 2016). Single layer black phosphorus is a two-dimensional structure followed by graphene and transition metal dichalcogenides (MoS₂), stanene and germanene, which had attracted extensive research efforts. Many two-dimensional materials are composed of nonmagnetic atoms, and no magnetic state appeared in the 2D system. Studies has shown that magnetic properties of two-dimensional materials can be induced by doping, vacancy defects, and edge effects (Cao et al., 2018; Sharma et al., 2018; Son, 2006). For example, magnetic properties are induced by doping transition metal atom for MoS₂, germanene, and graphene. Phosphorene monolayer exhibits pleated structure and is semiconductor with a direct band gap of 0.91eV (Luan et al., 2017). The field effect transistor fabricated with phosphorene exhibits a high-speed carrier mobility ($\sim 1000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) and gives a high switching ratio of $\sim 10^5$ at room temperature (Li et al., 2014), indicating the great potential application to micro-electronic devices. So we explore the physical properties of edge hydrogenated zigzag black phosphorene nanoribbon (H-ZPNR) using first-principles calculation. Latest studies indicated

H-ZPNR does not show edge magnetism and the system is a direct band gap semiconductor (Zhou et al., 2017). Moreover, due to the quantum confinement effect, the band gap of H-ZPNR varies greatly with the width of the nanoribbon (Peng et al., 2014). Compare with other transitional atom Co and Ni, the Fe atom has smaller mass so it can be easily cooperated into ZPNR and the magnetic configuration is simple compared with the Mn atom. In this paper, we explore the electronic structure for H-ZPNR doped with Fe atom, especially in magnetic properties.

2 CALCULATION MODEL AND PARAMETERS

The bare edge zigzag black phosphorus nanoribbon (ZPNR) show either semiconductor or metallic behavior in dependence on their edge chemical groups (Peng et al., 2014), and edge hydrogenated ZPNR transformed into a direct band gap semiconductor (Zhu et al., 2014). H-ZPNR are more stable than the ZPNR, and it is found that the ZPNR band gap decreases with the increase of the nanoribbon width (Zhu et al., 2014), we consider the effect of inequivalent dopant position from the centre of the nanoribbon to the margin, so we choose 8 as the width of ZPNR (H-8ZPNR) as

narrow as possible. We have employed the method of projector augmented wave based on density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996), and selected the projection augmented wave (PAW) to describe the mutual interaction between the ions. Meanwhile, we use the generalized Gradient Approximation (GGA) of the Perdew Burke Ernzerhof (PBE) functional form to process the exchange-correlation energy between electrons (Perdew et al., 1996a; Perdew et al., 1996b). Considering that the localized d orbital electrons will have a significant electron correlation effect on the transition metal magnetism, correction method GGA+U is applied to the doping system (Dudarev et al., 1998). $U=2.5\text{eV}$ is used as the available value for obtaining the magnetic moment of the transition metal atom in the study of transition metal doped in single layer black phosphorus (Zhai et al., 2017). We selected GGA+U ($U=2.5\text{eV}$) framework to check the magnetic states of doped systems.

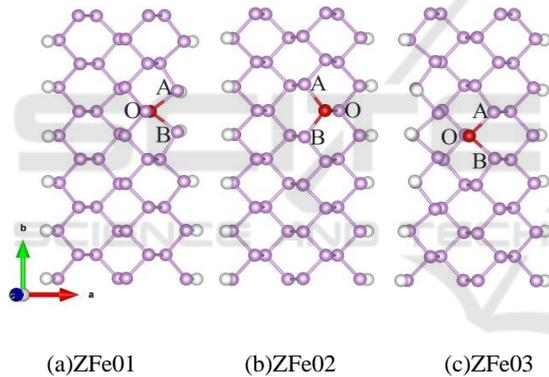


Figure 1: Schematic illustration: (a) ZFe01, (b) ZFe02, (c) ZFe03. The Fe, P and H atoms are represented by the red, purple and white color. O, B and A represent P atoms adjacent to Fe atom.

As shown in Figure 1, the width is defined by the number of P atoms along the x-axis. We construct H-8ZPNR with periodic boundary, the vacuum region of 15\AA along the z-axis to avoid the influence of interaction between the periodic nanoribbons. And the 6\AA vacuum region along the edge of the hydrogenated nanoribbon to avoid interaction between H atoms, lattice constant of $a = 15.00\text{\AA}$, $b = 19.80\text{\AA}$ and $c = 15.0\text{\AA}$ are used. H-8ZPNR contains 48 P atoms, the doping concentration of Fe atom is 2.83%. These inequivalent doping sites were chosen to research the effect on nanoribbon, three doped systems substituted Fe atom for original P atom are defined ZFe01, ZFe02 and ZFe03 from

margin to centre of nanoribbon respectively. The kinetic energy cutoff of 450eV for the plane wave expansion, and the structure relaxation was executed until force on each atom less than 0.01 eV/\AA , and the energy convergence criterion of the each electron was kept 10^{-5}eV . The spin is considered in the calculation performance. The Monkhorst-Pack k-point sampling with a $1\times 7\times 1$ k-mesh is used in the Brillouin zone integration. And $1\times 31\times 1$ k-mesh is used for density of the state.

3 CALCULATION MODEL

Structural States and Energy. The top view of the ZFe01, ZFe02 and ZFe03 are listed in Figure 1, P-P bond transforms into Fe-P bond after doping. Three P atoms adjacent to Fe atom are denoted as ‘O’, ‘A’ and ‘B’. Table 1 shows bond length and energy of doped system, focus on position ‘O’ in ZFe01, the P-P(O) bond length is 2.255\AA , the bond length of Fe-P(O) is 2.222\AA after doping, the difference is 0.033\AA , the difference in ‘B’ and ‘A’ are 0.042\AA and 0.041\AA respectively. The total bond length difference is 0.116\AA , 0.105\AA and 0.129\AA for ZFe01 ZFe02 and ZFe03, and ZFe02 has the smallest change of bond length indicating that the bond length is likely to be impacted by doping position. By comparing the energy difference of the system, ZFe03 has the lowest energy of -299.280eV . Results indicated that ZFe03 is the most stable.

Table 1: Optimized Bond Lengths ((P-P and Fe-P) in \AA), Energy (in eV).

		P(O)	P(B)	P(A)	Energy
ZFe01	P	2.255	2.259	2.26	-297.225
	Fe	2.222	2.301	2.301	
ZFe02	P	2.255	2.224	2.224	-296.737
	Fe	2.311	2.247	2.25	
ZFe03	P	2.25	2.224	2.224	-299.280
	Fe	2.26	2.28	2.287	

Table 2: Magnetic moment of the Fe doped system under GGA+U (in μB).

	Fe	P(O)	P(B)	P(A)	total
ZFe01	2.701	0.09	-0.077	-0.077	2.781
ZFe02	3.426	0.109	0.12	0.118	4.034
ZFe03	1.154	-0.028	-0.042	-0.026	1.07

Magnetic Properties: Charge Analysis and Density of States. The total magnetic moments of ZFe01, ZFe02 and ZFe03 are $2.78\mu_B$, $4.034\mu_B$ and $1.070\mu_B$ respectively, ZFe02 has the largest total magnetic moment, as shown in Table 2. The magnetic moments of the three doped systems are mainly arised from the Fe atom. The three P atoms adjacent to the Fe atom in ZFe02 exhibit spin-up magnetic moment, indicates that the three adjacent P atoms are ferromagnetic coupling. In contrast, the three P atoms adjacent to the Fe atom in the ZFe01 and ZFe03 exhibit spin-down status as a whole in Figure 2, indicating antiferromagnetic coupling between Fe atom and adjacent P atoms. The average magnetic moment of adjacent P atoms and second nearest P atom's are $0.081\mu_B$ and $0.013\mu_B$ for ZFe01, $0.116\mu_B$ and $0.018\mu_B$ for ZFe02, and $0.032\mu_B$, $0.013\mu_B$ for ZFe03. So the most magnetic moment are mainly from the Fe and adjacent P atoms and we can take the magnetic moment of doped system are localized. The magnetic moment is relavent to the bond length, with the shorter Fe-P bond length in ZFe02, the wave function overlapped more compared with the others, so the magnetic moment of ZFe02 is larger than others. Especially the coupling between the Fe atom and the adjacent P atoms can be either ferromagnetic or antiferromagnetic indicates the coupling is intricate, which need further research like multi-dopant investigation.

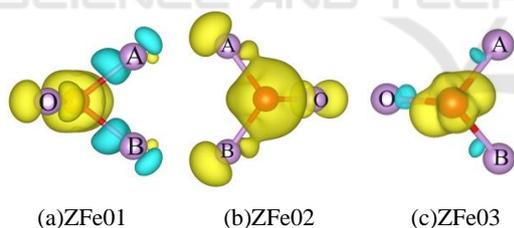


Figure 2: Spin charge density for Fe-doped system within the GGA+U framework. The gold and cyan color have iso-values of $\pm 0.005 e/\text{\AA}^3$.

The Bader charge analysis has used to investigate properties of the magnetic moment between Fe and adjacent P atoms. The localized spin charge density of the Fe atoms and three adjacent P atoms were listed, gold color represents the spin-up density, and cyan color represents the spin-down density. In ZFe01 and ZFe03, the gold areas are mainly accumulated around the Fe atom, the cyan areas are small and concentrated in P atoms adjacent to the Fe atom. Therefore, the adjacent P atoms of Fe atoms in ZFe01 and ZFe03 are antiferromagnetic

coupling. However, ferromagnetic coupling is exhibited in the ZFe02, which is consistent with the conclusion from magnetic moment analysis. Thus the spin charge density of the system is mainly concentrated around the Fe atom, there are only a few spin charge densities around the adjacent P atoms, and there are almost no spin charge densities in the adjacent position and locations far away from the Fe atom. It also shows that the magnetic properties in the doped system are mainly from the Fe atom. Bader charge analysis also illustrate the charge transfer, the Fe atom in three doped systems are all electronegative, and electrons transfer from the d orbital of the Fe atom to the p orbital of the P atoms, and the charge transfer electrons are $0.37e$, $0.44e$, and $0.33e$, respectively.

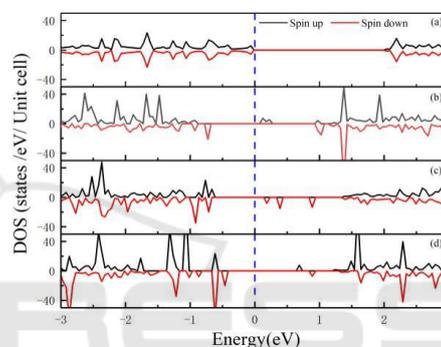


Figure 3: DOS illustration: (a) ZPNR, (b) ZFe01, (c) ZFe02, (d) ZFe03.

Density of states (DOS) for ZFe01, ZFe02 and ZFe03 are listed in Figure 3. In H-8ZPNR, the band gap is $2eV$. However, dopant energy state appeared in ZFe01, ZFe02 and ZFe03 so reduce the band gap, their band gap is $0.76eV$, $0.74eV$ and $1.04eV$ respectively. The majority spin density of state and the minority spin density of state are asymmetric, Compared with the width of band gap, central doped is greater than the edge doped. As shown in Figure 4, the partial wave hybridization between d orbital of the Fe atom and the p orbital of P atoms make most contribution to density of states (PDOS) clearly indicate the influence of electron orbital of the atom on the magnetic properties. The magnetic moment is derived from d orbital of the Fe atom, p-d orbital the total magnetic moment and this coupling is localized.

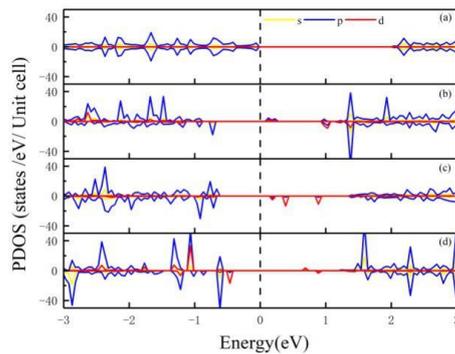


Figure 4: PDOS illustration: (a) ZPNR, (b) ZFe01, (c) ZFe02, (d) ZFe03.

4 CONCLUSIONS

In summary, based on the density functional calculations, we have explored the structure and magnetic properties of doped black phosphorene nanoribbon. The result show that doped nanoribbon had lattice distortion but the structure is stable. The substitution of Fe for P induce magnetic moment and this moment is localized. The coupling between the Fe atoms and adjacent P atoms can be either ferromagnetic or anti-ferromagnetic coupling, relavent to the magnetic value of Fe atom, which is required further research.

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