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Magnetism in phosphorene: Interplay between vacancy and strain

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First-principles calculations based on the density functional theory were carried out to investigate the magnetic property of phosphorene. It is found that vacancy or external strain alone does not result in magnetism in phosphorene. However, an interplay between vacancy and external strain can lead to magnetism. When either a biaxial strain or a uniaxial strain along the zigzag direction of phosphorene containing P vacancies reaches 4%, the system favors a spin-polarized state with a magnetic moment of $\sim 1 \mu_B$ per vacancy site. This is due to spin-polarized p states of under-coordinated P atoms next to the vacancy, which are bonded in the absence of the external strain or when phosphorene is subjected to a low strain. © 2015 AIP Publishing LLC.

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Two dimensional (2D) layered materials have drawn great attention in recent years due to their potential applications in future nano-electronics.^{1–6} Graphene and MoS₂, in particular, have shown exceptional electronic and transport properties. Recently, another 2D layered material, phosphorene, attracted much attention due to its potential in various applications.^{7–11} The observation of high mobility of up to 1000 cm²/V s and on/off ratio of 10⁴ makes phosphorene⁸ an attractive material for electronic applications. The chemically inert nature of phosphorene has opened up possible applications in transport.^{7,8} Moreover, the existence of a direct band gap at the Γ point of phosphorene is expected to be useful for optoelectronic applications.¹² Recently, a sustenance of phosphorene with high tensile strain up to 30% has been reported,¹³ which indicates that phosphorene is highly flexible and has exceptional mechanical properties.

The unique properties of these 2D materials in nano electronics further suggest their potential applications in spintronic devices.^{14–18} The peculiar vacancy induced magnetism in 2D layered materials has generated a lot of interest in recent years.^{19–21} The crucial role played by vacancies in the magnetism of graphene has been noticed in several studies.^{15,22–24} Meanwhile, tuning of magnetism by tensile strain has been reported in different 2D layered materials.^{25,26} In pristine VS₂ and VSe₂ monolayers,²⁵ the strain dependent magnetism is related to the ionic and covalent interactions between atoms. In contrast to these 2D materials, vacancies or strain alone does not produce any magnetism in MoS₂ monolayer, due to strong chemical bonding between Mo atoms surrounding the vacancy. However, magnetism can be produced in MoS₂ monolayer by an interplay between defect and strain.^{20,21} The tensile strain applied to the defected MoS₂ helps to weaken the chemical bonding between Mo atoms surrounding the vacancy which results in a magnetic moment.²¹

Similar to graphene and MoS₂, phosphorene has already emerged as a potential material for various applications. It is noted that some of its unique properties are attractive for spintronic applications. Therefore, it would be scientifically interesting and practically important to explore its magnetic properties. To date, only limited studies reported magnetism in phosphorene.²⁷ It is noted that in case of graphene, vacancy alone can introduce the magnetism, and on the other hand, vacancy or strain alone does not introduce the magnetism in MoS₂. Since magnetism induced by defects and strain was found in other 2D materials, it is quite interesting to see whether vacancy and/or strain is able to provoke magnetism in phosphorene. In the present work, we investigate the prospect of magnetism in phosphorene due to the interplay between strain and vacancies.

The electronic and magnetic nature of phosphorene with vacancy and/or strain were analyzed using first principle density functional theory (DFT) based calculations using the Vienna *ab-initio* simulation package (VASP).^{28–30} Projection augmented wave method is used to describe the ion-electron interaction. Generalized gradient approximation in the Perdew-Burke-Ernzerof (PBE) form³¹ is adopted for the exchange-correlation potential. The electron wave function is expanded using plane waves with a cutoff energy of 500 eV. A Γ centered $6 \times 6 \times 1$ k -point mesh is used to sample the irreducible Brillouin zone. The structure containing a single vacancy with in-plane biaxial or uniaxial strain is modeled using a supercell of 4×4 units of monolayer phosphorene (Figure 1(a) shows 4 times of the supercell). A vacuum space of 15 Å is used to avoid the interaction between adjacent monolayers in neighboring supercells. In all cases, positions of all atoms in the monolayer are fully relaxed using the conjugate gradient algorithm³² until the maximum force on a single atom is less than 0.01 eV/Å.

The structure of phosphorene is shown in Fig. 1. Each P atom is covalently bonded to three other P atoms. Since all P atoms are equivalent, we remove a P atom in the upper plane

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FIG. 1. (a) Schematic illustration of magnetism induced by strain on a monolayer phosphorene with phosphorous vacancies. A phosphorous atom is removed from the monolayer to create the vacancy and the phosphorous sheet is subjected to biaxial or uniaxial strain. The magnetic moment is mainly contributed by p orbitals of phosphorous atoms which are closest to the vacancy site. (b) Top view of local structure around the vacancy site. The atom to be removed is indicated by the light color and is labeled P0. Its three nearest neighbors are labeled P1, P2, and P3, respectively. P4 and P5 are next nearest neighbors of P0.

in Fig. 1 to create the vacancy. For convenience of discussion, we label the P atom to be removed as P0 or V, its three neighbors as P1, P2, and P3, and its next nearest neighbor bonded to P3 as P4, as shown in Fig. 1(b). It is noted that P1 and P2 are in the same (upper) plane as P0, while P3 and P4 are in the lower plane. For ideal phosphorene, the optimized lattice constants are $a = 3.30 \text{ \AA}$ and $b = 4.63 \text{ \AA}$, which are in close agreement with the results of previous studies.¹³ The bond length between P0 and P1 (or P2) is $2.22 \text{ \AA}$ and that between P0 and P3 is $2.259 \text{ \AA}$, which are also consistent with the values obtained in previous calculations.¹³ As expected, the ideal phosphorene is non-magnetic, which is confirmed by the symmetric density of states (DOS) for spin-up and spin-down states, shown in Fig. 2(a).

Motivated by vacancy and/or strain induced magnetism in some other 2D systems,^{15,20,21,23–26} we have systematically done the following to explore magnetism in phosphorene of a similar origin. (1) A P vacancy is introduced in the 4×4 supercell of phosphorene. (2) A biaxial tensile strain is applied to the ideal phosphorene. (3) A uniaxial strain is applied in x - (armchair) or y -direction (zigzag) of the ideal phosphorene. (4) A biaxial tensile strain is applied to phosphorene with a P vacancy. (5) A uniaxial strain is applied in x - or y -direction of phosphorene with a P vacancy. The calculated total DOS for all above cases are shown in Fig. 2. In the case of uniaxial strain, we only show the results of strain applied in the y -direction. Uniaxial strain applied in x -direction does not induce magnetism (see discussion below) and the DOS is not shown here. As already mentioned above, the ideal phosphorene is non-magnetic. Figure 2(b) shows that the P vacancy alone in phosphorene does not produce any magnetism, since the DOS for spin-up and spin-down states are symmetric. Similar to the case of single vacancy, our calculations showed that P di-vacancy alone does not result in a magnetic ground state. Furthermore, a tensile strain, either uniaxial or biaxial, up to 15% applied to the ideal phosphorene also does not result in magnetism. For example, the DOS of defect-free phosphorene at 5% of biaxial tensile strain is shown in Fig. 2(c). The symmetric DOS for spin-up and spin-down states indicates its non-magnetic behavior. Moreover, Figure 2(d) shows the DOS of defect-free phosphorene with 5% of uniaxial strain applied along the y -direction. Again, the system does not show any spin-polarization.

FIG. 2. Calculated total DOS for (a) ideal phosphorous, (b) phosphorous with P vacancy only, (c) ideal phosphorous subjected to 5% of biaxial strain, (d) ideal phosphorous subjected to 5% of uniaxial strain applied along the y -direction (zigzag direction), (e) phosphorous with a P vacancy subjected to 5% of biaxial strain, and (f) phosphorous with a P vacancy subjected to 5% of uniaxial strain along the y -direction. The Fermi level is set at 0 eV.

Next, we apply a strain to phosphorene with a P vacancy. We consider first a tensile biaxial strain. Interestingly, even though the system is non-magnetic at zero or low strain, it becomes magnetic when the tensile strain reaches a critical value (about 4%). The calculated total DOS of the defected phosphorene at a strain of 5% is shown in Fig. 2(e). The imbalance between the occupied spin-up and spin-down states implies a net magnetic moment, and the different spin-up and spin-down density of states at the Fermi level (set to 0 eV) indicates that conducting charges are spin-polarized. The magnetic moment is estimated to be close to $1 \mu_B$ per vacancy site. For a uniaxial strain applied to the defected phosphorene along the y -direction, similar results are obtained, as shown in Fig. 2(f). Our results therefore confirm that it is possible to generate magnetism by strain in phosphorene with P vacancies, similar to MoS_2 .^{21,22}

However, to produce a reasonable magnetic state, there must be a sufficient concentration of P vacancies in phosphorene. To assess the probability of vacancy generation, we estimated the vacancy formation energy which is obtained from Ref. 33 $E_{\text{form}} = E_{\text{defect}} - E_{\text{ideal}} - n\mu_P$, where E_{defect} and E_{ideal} are the total energies of defected and ideal phosphorene, respectively, at a given strain, μ_P is the chemical potential of phosphorous which is taken from the total energy per single atom in bulk phosphorous, and n is the number of P atoms removed which is one for a single phosphorous vacancy. The calculated vacancy formation energy is shown in Fig. 3(a) for the case of biaxial strain. The formation energy is relatively high and the vacancy concentration is, therefore, expected to be low in equilibrium condition. However, vacancy can always be created during sample growth. Furthermore, if the magnetic property of P vacancy is promising for applications, other methods such as ion irradiation can be used to create vacancies in phosphorene. The results for uniaxial strain applied in y -direction are similar and are

FIG. 3. Variations of (a) vacancy formation energy and magnetic moment with applied biaxial strain. (b) Relative changes in bond lengths or distances between concerned atoms with applied biaxial strain. (c) Contour plot of charge density in plane passing through atoms P1, P2, and P3, at zero (left panel) and 5% (right panel) of biaxial strain, respectively. (d) DOS projected to nearest neighbor P atoms of the vacancy at zero (upper panel) and 5% (lower panel) of biaxial strain, respectively. The Fermi level is set to 0 eV. Inset in Fig. 3(d) shows the spin-density. Yellow and blue colors indicate spin-up and spin-down isosurface, respectively.

not shown. The formation energy initially increases with the applied strain and reaches a maximum at $\sim 4\%$ of strain, and then decreases with further increase in strain. At the same time, the system is non-magnetic until the strain reaches a critical value of about 4% which coincides with the strain at which the vacancy formation energy is the maximum. Beyond this value, the magnetic moment increases slowly with the strain and eventually saturates to $1 \mu_B$ at higher strains, as shown in Fig. 3(a).

To understand the origin of the magnetism, we consider first the structural changes induced by the vacancy and strain. The variations of bond lengths or distances between concerned atoms in the defected phosphorene are shown as a function of applied biaxial strain in Fig. 3(b), in percentage changes relative to that in ideal phosphorene at zero strain. It is interesting to note that at low (below 4%) or no strain, the distance between atoms P1 and P3, d_{P1-P3} (the distance between P2 and P3 is the same), is significantly reduced upon the relaxation. Similarly, the distances between atoms P1 and P2 (d_{P1-P2}), between atoms P1 and P5 (d_{P1-P5}), and between atoms P4 and P5 (d_{P4-P5}) also shrink, but to a lesser degree. In contrast, the bond P3-P4 (d_{P3-P4}) is elongated. This suggests that when a P atom is removed to create the vacancy, its nearest neighbor P atoms relax towards the vacancy, to form a bonding state. This is confirmed by the calculated electron density. As shown in the left panel in Fig. 3(c), the electron density between atoms P1 and P3 and between P2 and P3 is relatively high, which clearly indicates that bonds are formed between these pairs of atoms. The relaxation of atoms P1, P2, and P3 towards the vacancy site is also clearly visible in the figure. Atoms P1 and P2 also come closer, and d_{P1-P2} is reduced by about 10% compared to that in ideal phosphorene, which, however, is not enough

to form a bond between them. Due to the formation of this bonding state, the electronic structure of the system does not show any spin-polarization which is further confirmed by the calculated partial DOS (PDOS) of atoms P1, P2, and P3, shown in the upper panel of Fig. 3(d), in addition to the total DOS given in Fig. 2(b).

When a small tensile strain is applied, the bonding state is undisturbed and the system remains non-magnetic. However, as the strain increases, the P1-P3 and P2-P3 bonds are stretched and become weakened. It is noted that the vacancy formation energy increases slightly under a tensile strain. Finally, when the applied strain reaches 4%, the P1-P3 and P2-P3 bonds are broken, as indicated by the sudden increases in d_{P1-P3} , d_{P1-P5} , d_{P4-P5} and sudden decrease in d_{P3-P4} . The calculated electron density, shown in the right panel of Fig. 3(c), confirms that atom P3 is no longer bonded to P1 and P2 at 5% of biaxial strain. In contrast, d_{P1-P2} increases gradually, in response to the increasing strain, since no bond was formed between atoms P1 and P2. Once the bonds are broken, the p -orbitals of atoms P1, P2, and P3 spin-split, as shown by the calculated PDOS of the defected phosphorene under a biaxial strain of 5% (lower panel of Fig. 3(d)). The spin-up p -orbitals of P1 and P2 are occupied but the spin-down p -orbitals are empty, resulting in a spin-polarized ground state and a magnetic moment of $1 \mu_B$ per vacancy site. The inset in Fig. 3(d) shows that the magnetic moment is mainly localized on P1 and P2, and a small amount on P3, in opposite direction.

Due to the anisotropic structure of phosphorene, one can expect that a uniaxial strain applied along the y -direction would produce the same effect, while a uniaxial strain applied in the x -direction would be less effective. Results of our calculations carried out on defected phosphorene

subjected to different uniaxial strains confirm that this is indeed the case. The total DOS (Fig. 2(f)) of the defected phosphorene at 5% of tensile strain along the y -direction is very similar to that at 5% biaxial strain (Fig. 2(e)). The spin density is also similar to that obtained in the case of biaxial strain (inset in Fig. 3(d)). Furthermore, other calculated quantities such as variations of distances between the concerned atoms also show similar trends. On the other hand, the system does not show any magnetism when the uniaxial strain is applied along the x -direction, in the given range of strain. The results are, therefore, not presented here.

Therefore, magnetism in monolayer phosphorene can be provoked effectively by applying a sufficient biaxial or uniaxial strain along the zigzag direction. The latter shows the anisotropic nature of magnetism which could be explored for certain applications. The origin of magnetism in both cases is due to the hole states derived from the p orbitals of P atoms next to the vacancy. The magnetic moments are mainly contributed by the p_y and p_z orbitals of the two P atoms which are in the same plane as the vacancy, while little comes from the third neighbor P atom of the vacancy. We repeated our calculations using larger supercells, i.e., 4×4 , 5×5 , and 6×4 , and the main conclusion remains the same. That is, vacancy alone does not result in a magnetic ground state but interplay of vacancy and strain stabilizes the magnetic ground state, with a magnetic moment of $1 \mu_B$ per vacancy site. This indicates that the magnetic property of a single vacancy is independent of vacancy concentration in the dilution limit. Magnetic coupling and concentration dependence of magnetism require further study. The effect of a compressive strain is not considered in the present study. Since a compressive strain increases the strength of bonding, it is not expected to produce any magnetism in monolayer phosphorene with P vacancies. On the other hand, phosphorene is able to sustain up to 30% of tensile strain, it is highly possible that the predicted magnetism can be realized experimentally which may find applications in spintronic devices. This would complement magnetism found in graphene and MoS_2 .

In conclusion, we have carried out DFT-based first-principles calculations to investigate the magnetic property of monolayer phosphorene. Results of calculations indicate that ideal phosphorene is non-magnetic. Furthermore, neither P vacancy nor strain alone induces magnetism in phosphorene. However, when a biaxial strain or a uniaxial strain applied along the zigzag direction of phosphorene containing P vacancies reaches a critical value (4%), the system becomes magnetic, with a magnetic moment of $1 \mu_B$ per vacancy site. On the other hand, a uniaxial strain applied along the arm-chair direction is not effective in producing magnetism. Without the external strain or before the external strain reaches the critical value, the P atoms next to the vacancy come together and form a bonding state. An external strain with sufficient strength breaks the bonds and left behind spin-polarized states localized on the under-coordinated P

atoms which is the origin of the magnetism. In both cases of biaxial strain and uniaxial strain applied along the y -direction, the magnetic moment is mainly contributed by p orbitals of these under-coordinated P atoms.

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