Intercalated Phosphorene for Improved Spintronic Applications

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In this work, we study the intercalation of monolayer phosphorene with nitrogen, lithium, and calcium for exploring prospects of spintronic applications. The electronic and the magnetic properties of the intercalated structure are investigated via density functional theory to obtain the band structure and the spin-polarized density of states (DOS). Albeit the band structure data show vanishing bandgap, a noticeable difference emerges in the densities of the up and the down spin states induced by the intercalants. To evaluate the performance of the intercalated phosphorene, the spintronic order parameter, measuring the asymmetry among the up and the down spin DOSs, is computed, which clearly shows the evolution of improved spintronic properties at large intercalant densities. Furthermore, larger atomic numbers of the intercalants seem to aid the performance of phosphorene as a spintronic material.

Index Terms—2D Material, Spintronics.

I. INTRODUCTION

MODERN civilization is based on integrated circuits (ICs) made of silicon chips. According to Moore’s law, the efficiency of transistors in IC will double every two years. However, due to the limit of the transistor size that could fit on silicon chips, the semiconductor industry continuously tries to shrink the sizes of the electronic components on ICs, thereby enhancing the performance of the computers. Furthermore, to overcome the hurdle related to the miniaturization of the components, new methods and novel materials are being discovered, which can dramatically transform the electronics industry. Thus, search for new suitable materials that can replace silicon in IC constitutes new motivation for materials research [1]. The quest for new and nontraditional materials whose properties can be controlled easily and the spins can be made to carry information instead of the charges has contributed to the development of a field called spintronics. Here, the spins make the electrons act like tiny magnets where the “up” and the “down” states behave similar to the positive and the negative charges, which can store information in a binary format [2]. The necessary properties of these spintronic materials are tunable bandgap in both the up-spin and the down-spin channels and large magnetization values that are computed using $m = (n^↑ - n^↓)\mu_B$, where $m$ is the total magnetization and $n^↑$ and $n^↓$ are the average occupation densities for the spin-up and spin-down states, respectively, of the carriers [3]. Therefore, the magnetic semiconductors with a relatively large bandgap between the up-spin and the down-spin channels fall into this category. Intercalated phosphorene is possibly one such material and hence is studied here.

A lot of bulk and monolayer semiconductors, such as bismuthene, GaAs, and ZnO, have large bandgaps and doping-induced magnetic properties can also be achieved, but nonetheless, the values of magnetization remain insignificant for any practical applications [4], [5]. Recent interest in monolayer materials, such as graphene, MoS$_2$, silicene, borophene, and phosphorene, has drawn attention in the search of spintronic materials. Among them, graphene has no (or vanishingly small) bandgap; however, pristine phosphorene and MoS$_2$ have bandgaps [6]–[8]. Not only these monolayer materials but also the study of spintronics include a diverse area of ferromagnetic, antiferromagnetic, half-metallic, topological insulators, magnetic semiconductors, and spin gapless semiconductors [9]. Conceptualizing spintronics started with another important discovery of giant magnetoresistance (GMR) [2], [10] where the GMR effect is employed to make two-state memory cells and switches. Despite the advantages, construction of spintronics materials has a great deal of challenges, such as having fully spin-polarized materials, the manipulation of spin orientation of the carriers, spin transport and modeling of spin injected devices, and mismatch of Fermi energies at the junction of two dissimilar materials.

To solve these issues, a lot of materials have been devised with distinct electronic and magnetic properties of matter, and monolayer materials are one among them. Since the discovery of graphene, attention is drawn toward other materials with the same structure leading to renewed interest in phosphorene: monolayer black phosphorus [11]. Experimental and theoretical studies of phosphorene show a direct bandgap and high carrier mobility. However, the nature of the bandgap is not beyond debate, where the valence band maximum is theoretically found to be shifted from the zone center [12], [14]. Furthermore, both the mobility and the bandgap can be controlled via tuning the layer thickness of phosphorene. The bandgap in a single layer of phosphorene yields a large ON-OFF current ratio ($\sim 10^5$), which should be relevant for device applications [15].
Phosphorene in its stable form contains four P molecules, and these four atoms form a tetrahedron with each P atom having three neighbors. All the \( \text{P}_4 \) units are joined to set up continuous layers. Comparing the structure with graphene, the \( y \)-axis is named the zigzag direction and \( x \)-axis the armchair direction. Earlier studies have shown that foreign materials can induce magnetization when doped in monolayer materials, such as phosphorene, silicene, borophene, and bismuthene [16]–[29]. In phosphorene, the 3D-transition metal dopants induce strong magnetic character [29]; in particular, Mn doping yields large magnetization. Besides, some of the studies show the emergence of dilute magnetic semiconducting properties as well upon doping with other elements. Earlier research has also proof of magnetization in doping with nonmetals, which results in semiconductors without a spin gap. Since parent phosphorene has high carrier mobility, it is possible to tune the magnetization using intercalation and hence create a better spintronic material.

The above findings have inspired us to study the spintronic properties of intercalated phosphorene and compare them to the earlier studies on phosphorene since doping-induced magnetization is already established. We further show that the intercalation induced changes for other intercalant atoms, such as lithium and calcium. It may be noted that doped phosphorene has already been shown to be a promising candidate for spintronics [23]. Here, we investigate intercalation with nitrogen, lithium, and calcium, and in particular, large concentration of lithium and nitrogen yields effective spintronic materials. To the best of our knowledge, studies on the intercalation-induced spintronic property have not been reported in the literature.

In this article, we use density functional theory (DFT) to investigate the electronic and magnetic properties of intercalated phosphorene. Subsequently, we show that though phosphorene has a bandgap, the process of intercalation reduces the bandgap and it induces magnetic properties. In the following, we first describe our methodology for calculating the band structures and the density of states (DOS). Hence, we analyze and discuss the results for each of the intercalants and their contribution to spintronic properties. A brief summary finally follows.

II. COMPUTATIONAL DETAILS

We studied intercalation of phosphorene with nitrogen, lithium, and calcium and varied the intercalation densities to evaluate their density and the atomic number dependences on the electronic and the magnetic properties. The percentage of intercalation is defined as the ratio of the number of atoms intercalated in a supercell to the total number of atoms present in the supercell. The interlayer van der Waals interaction is the dominant interaction in this case. We have compared our results on the phosphorene with the earlier pristine phosphorene results [34]. First-principle methods based on DFT [30] are employed for this purpose. The computations are performed using WIEN2K full-potential linearized augmented plane wave (FP-LAPW) [33] \textit{ab initio} package within the DFT formalism to get the electronic band structures and corresponding total DOS. A generalized gradient approximation Perdew–Burke–Ernzerhof (GGA-PBE) exchange-correlation potential is used here. In order to find the magnetic properties, spin-polarized calculations are implemented on the intercalated phosphorene. For pristine phosphorene, we have used a unit cell of four P atoms, and for the intercalation, we have used a \( 2 \times 2 \) supercell of this material. It is important to note that the size of the supercell has been kept fixed, while we have varied the intercalation density. The intercalant elements are placed in the space between the two layers, which has an interlayer distance of 5 Å without affecting the energy convergence limit of 0.0001 eV, and thus, we obtained an energy minimized structure for each intercalant.
The parent crystal structure and the intercalated structural are shown in Fig. 1. The corresponding lattice constants, namely, \( a = 3.31 \, \text{Å} \), \( b = 10.47 \, \text{Å} \), and \( c = 4.37 \, \text{Å} \), are in agreement with the existing literature \[34\] and are calculated with the abovementioned energy convergence limit. For the band structure of monolayer phosphorene, a vacant space of 20 Å is introduced in the \( b \)-direction. The muffin-tin radii, \( R_{MT} \), is chosen as 2.09 for phosphorus, 1.92 for nitrogen, 1.56 for lithium, and 2.45 for calcium atoms. With the choice of \( R_k \text{max} \) \( (R_k \text{max} \) stands for the product of the smallest atomic sphere radius, \( R_{MT} \) times the largest \( k \)-vector \( k_{\text{max}} \)) as 7.0 and a \( 10 \times 10 \) \( k \)-mesh, the total energy is calculated while relaxing all the atoms so that the maximum force is smaller than 0.01 eV/Å. Then, the band structure, the DOS, and the total magnetization are calculated from the converged spin-polarized self-consistent field (scf) calculations.

### III. Results and Discussion

The band structure of parent black phosphorus shows a bandgap and nearly a Dirac-like feature along the \( Z-\Gamma \) direction of the Brillouin zone. Here, we plot the band structure along the high symmetry \( k \)-points in the first Brillouin zone of the reciprocal space along the \( \Gamma-X-L-Z-\Gamma \) direction. The results are shown in Fig. 2(a). The corresponding DFT DOS is presented in Fig. 2(c), which shows the presence of a gap at the Fermi energy. In Fig. 2(b) and (d), we have shown the band structure and the DOS of monolayer phosphorus, which shows a gap of 0.91 eV that matches with earlier GGA-PBE calculation \[34\]. The band structures of the pristine black phosphorus also agree with the existing results \[34\]. We have performed spin-polarized calculations for the intercalated materials and the corresponding band structure for the up and the down spins are obtained. The results appear in Fig. 3(a)–(f) for the nitrogen intercalation, while those for the lithium and the calcium intercalation are shown in Fig. 4(a)–(e).

Let us focus on Fig. 3, which shows the band structure of nitrogen intercalated phosphorene. The results for the up and the down spin DOSs appear in three columns for three different nitrogen concentrations, namely, 20%, 30%, and 40%. When compared with the corresponding results for pristine phosphorene, it may be concluded that the intercalation changes the band structure considerably both quantitatively and qualitatively. The intercalation induces lowering of the overall gap, while differences between the up-spin and the down-spin channels evolve.

To further check for the concentration dependence of different elements on its spintronic properties, we have used lithium and calcium as intercalants. In both cases, the band structures and the DOSs are calculated to enumerate their features. For lithium, we have used 20% and 30% as the intercalation concentration, and for calcium, we have used only 20% as higher concentrations are found to be energetically unfavorable; more particularly, the energy convergence in our computation could not be achieved after a significantly large number of iterations. We have observed that for 20% lithium intercalation, the spin-polarized band structure shows no gap between the up and down spins, while upon increasing the concentration, a gap emerges. Thus, we have presented the band structure for one type of spin in Fig. 4(a), whereas in Fig. 4(b) and (c), we present the band structures for both the up and the down spins, respectively, at higher value of the intercalation density, namely, for 30% lithium concentration. It is evident that there is a considerable change between the up- and down-spin densities. Therefore, intercalating with lithium needs larger concentration in order to obtain pronounced spintronic properties. Interestingly, intercalation has also changed the band structure considerably compared with the DFT band structure, which implies that the impurity bands have more pronounced effects near the Fermi level, and the bandgap diminishes with intercalation.

In contrast to lithium and nitrogen, 20% of calcium intercalation in phosphorene makes a large change in the band structure and the difference between the up and the down spins is also high for this material. In the band structure, it can be observed that, though there is no gap at the Fermi level, the bands near the Fermi level do not overlap with each other for the up spin, which carries a signature that tuning the Fermi level with external voltage can make the system a gapped one. However, higher concentration of calcium intercalation is energetically forbidden due to the size mismatch of the calcium atoms with that of the pristine phosphorus, which constitutes a major drawback of calcium intercalation at large densities.

Spin polarization induces a feature around the \( \Gamma \) point. The Dirac-like property along the \( Z-\Gamma \) direction vanishes with intercalation. The difference in the band structures for the up and the down spins indicates that the intercalated phosphorene is a promising candidate for spintronics applications. To get a better understanding of the difference between the up- and down-spin DOSs, we present here the spin-polarized DOS for the intercalated phosphorene in Fig. 5(a)–(c) for...
Fig. 3. Spin-polarized DFT band structures for nitrogen intercalation. (a)–(c) Up spin and others are for the down spin. The six plots are for intercalation concentration of (a) and (d) 20% (up and down spins, respectively), (b) and (e) 30% (up and down spins, respectively), and (c) and (f) 40% (up and down spins, respectively).

nitrogen intercalation with different values of concentration and Fig. 6(a)–(c) for lithium and calcium intercalation, respectively. As indicated from the band structure, the DOS also shows the gapless feature in the up- and down-spin channels, while there is a sharp difference between the DOS for the up and the down spins for three different nitrogen densities. For low lithium intercalation, the up and the down spins show similar structures as predicted also from the band structure plots. However, with increased concentration, there is a difference between the up- and down-spin DOSs. Similarly, the calcium intercalation also shows a large difference in the DOSs for the two spins. In these spin-polarized systems, we found that the source of polarization is from the intercalation and the major contribution to the magnetic moment is due to the intercalating material since pure phosphorene has no spin polarization and with increasing intercalation polarization increases. These results agree with the calculated band structures and the data for the spin densities.

We wish to reiterate that cases of large intercalation densities are permissible due to the stability of the structures at high values of the intercalant densities, except for calcium. We ensure this by plotting the energy as a function of the number of iterations used in our scf method. Clearly, a stable minimum in each of the plots shown in Fig. 1(c) is a testimony of that. In addition to providing the structural stability of the intercalated compounds, it allows devising more efficient spintronic materials for reasons we elaborate next.

The performance of a spintronic material is determined by the degree of spin polarization of the carriers of a system. To firmly establish the degree of polarization of the charge carriers in these materials, we have computed the spintronic order parameter \( \lambda \), which is defined by

\[
\lambda = \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}}
\]

where \( n_{\uparrow} \) and \( n_{\downarrow} \) are the occupation densities of the up and the down spins, respectively. Larger values of \( \lambda \) imply larger spin polarization and, hence, a better candidate for

| Intercalant | Atomic No | \( \lambda \) |
|------------|-----------|-------------|
| lithium    | 3         | 0.0004588   |
| nitrogen   | 7         | 0.01715     |
| calcium    | 20        | 0.12        |
Fig. 4. Spin-polarized DFT band structures for lithium intercalation. (a)–(d) Up spin and others are for the down spin. The plots are for intercalation concentration of (a) 20% (up spin), (b) and (c) 30% of lithium (up and down spins, respectively), and (d) and (e) 20% of calcium (up and down spins, respectively).

Fig. 5. DFT DOS with nitrogen intercalation. Top: up spin. Bottom: down spin. down spin DOS is multiplied by $-1$. The three plots are for intercalation concentration of (a) 20%, (b) 30%, and (c) 40%.

a spintronic material. Here, we show that $\lambda$ increases with increasing the intercalation density for nitrogen and lithium [see Fig. 7(a)]. Similar features emerge for $\lambda$ parameter as a function of the atomic number of the intercalants, thereby signaling emergence of improved spintronic properties upon intercalation with elements having a larger atomic number. The results are shown in Table I, which indicates that as lithium is replaced by calcium, there is an enhancement of the value of $\lambda$ by three orders of magnitude. While we find this result remarkable and the study probably warrants intercalation with elements having larger atomic number, however, more work is required to validate this claim as some of the larger elements may not yield an energetically favorable scenario. Even pristine phosphorene is believed to be a promising candidate for spintronic applications; however, intercalation certainly enhances the prospects of its applicability [35].

In comparison with other spintronic materials, the intercalated phosphorene does not possess any gap in its band structure, and however, there is a difference between the densities of the up- and down-spin states, which, in effect, induces magnetic properties in the system. The results are shown in Fig. 7(b) where the magnetization, $m = (n_\uparrow - n_\downarrow)\mu_B$, **
It is by and large established that an enhanced spin–orbit coupling (SOC) is key to the phenomenon of spin polarization and hence to the performance of the spintronic materials. First-principle calculations [37], [38] indicate a highly anisotropic intrinsic Rashba SOC (RSOC) which is an artifact of the anisotropic band structure. It is possible to tune the strength of RSOC using an external gate voltage, which breaks the inversion symmetry (thereby reducing the symmetry from $D_{2h}$ to $C_{2v}$) leading to lifting of the spin degeneracy. While such an engineered SOC also shows strong directional anisotropy in the Brillouin zone, the magnitude is only a few tens of $\mu eV$, which is insufficient to contribute to the efficiency of phosphorene as a spintronic device. However, the prospects of using proximity effects, such as phosphorene on transition metal dichalcogenides or other topological insulators, may yield larger SOC and aid toward achieving larger spin-polarized transport properties for technological applications [28].

In conclusion, we have observed that the phosphorene monolayer, which is an anisotropic direct gap semiconductor with high carrier mobility, exhibits strong magnetic properties, which scales with the intercalation density and the choice of the intercalant. These properties make them exceptional materials for zero bandgap spintronic devices. The density dependence of the magnetic properties indicates flexible control on the magnetization of phosphorene. This opens up new possibilities for engineering room-temperature magnetic and spintronic devices.

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