Magnetic and Electronic Switch in Metal Intercalated Two-Dimensional GeP₃

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Intercalation of foreign atoms in two dimensional hosts has been considered a quite promising route in order to engineer the electronic, and magnetic properties in 2D platforms. In the present study, we performed a first-principles theoretical investigation of the energetic stability, and the magnetic/electronic properties of 2D GeP₃ doped by Cr atoms. Our total energy results reveal the formation of thermodynamically stable Cr doped GeP₃ bilayer [(GeP₃)ₓBL], characterized by interstitial Cr atoms lying in the van der Waals (vdW) gap between (GeP₃)ₓBL [(GeP₃)ₓBL]. We show that the ground state row-wise antiferromagnetic (RW-AFM) phase of (GeP₃)ₓBL can be tuned to a ferromagnetic (FM) configuration upon compressive mechanical strain (ε), Cr⁺⁺⁺ ↔ Cr⁺⁺. By considering its stacked counterparts, (GeP₃)ₓBL/(GeP₃)ₓBL and (GeP₃)ₓBL/Cr/(GeP₃)ₓBL, we found that such a magnetic tuning is dictated by a combination of intralayer and interlayer couplings, where the RW-AFM phase change to layer-by-layer FM (Cr⁺⁺⁺/Cr⁺⁺) and AFM (Cr⁺⁺⁺/Cr⁺⁺/Cr⁺⁺) phases, respectively. Further electronic band structure calculations show that these Cr doped systems are metallic, characterized by the emergence of strain induced spin polarized channels at the Fermi level. These findings reveal that the atomic intercalation, indeed, offers a new set of degree of freedom for the design and control the magnetic/electronic properties in 2D systems.

I. INTRODUCTION

Many efforts have been devoted in the last years for the development of two-dimensional (2D) materials. The combination of quantum confinement and surface effects leads to novel physical properties, which are not present in their bulk counterparts. Since graphene was first isolated and characterized ¹¹, many others 2D materials with graphene-like structures have been synthesized or theoretically predicted ², such as silicene, germanene, phosphorene, among others ³, layered transition metal dichalcogenides ⁴, transition metal carbides ⁵. These materials are envisioned to have a wide range of technological applications.

Over recent years, it has been reported the structural stability of various 2D triphosphides. They all present moderate band gaps (adjustable through strain engineering), high carrier mobility and strong light absorption in the visible and ultraviolet regions. These features show promising applications as anode materials for Li-ion and Na-ion batteries ¹² ¹³, and also in electronic, spintronic, and photovoltaic devices. Moreover, Yao et al. ¹⁴ showed that SbP₃ and GaP₃ monolayers are also stable, and present larger band gaps than the other 2D triphosphides structures mentioned so far, and are suggested to be potential candidates for watersplitting photocatalysts.

In particular, the bulk phase of germanium triphosphate (GeP₃) has long been synthesized ¹⁵ ¹⁶, which consist of planes stacked through van der Waals interactions along the perpendicular direction. This material presents metallic behavior. Recently, Jing et al. ¹⁷ have shown that few layers GeP₃ are chemically, mechanically and dynamically stable, by means of first principles calculations. The monolayer and bilayer GeP₃ have a small indirect band gap (0.55 and 0.43 eV respectively) while the trilayer becomes metallic. Moreover, the monolayer GeP₃ presents high carrier mobility and solar absorption. The combination of these remarkable properties with the prediction of experimentally accessible cleavage energies have motivated a large number of theoretical works proposing possible applications and new features of monolayer GeP₃. For example, Li et al. ¹⁸ have proposed another stable phase of monolayer GeP₃, and demonstrated that this system shows a ferromagnetic ground state through hole doping the material beyond a critical value. Monolayer GeP₃ has been shown to have high capacity, favorable ion hopping barrier, and robust structural stability, thus being a strong candidate for applications in electrodes of Li-ion ¹⁹ and non-Li ion ²⁰ batteries. Further investigations on strain engineering has also been recently carried out ²¹. In Refs. ²² and ²³ the electronic and transport properties of GeP₃ nanoribbons were investigated. GeP₃ monolayer may also find
applications as gas sensors. It is verified that GeP$_3$ monolayer is highly active for hydrogen evolution reaction, where the effect of a graphene substrate is also considered. Meanwhile, in a recent study, Zhang et al. performed a detailed study of the electronic properties, and the energetic stability of GeP$_3$ monolayer doped by elemental impurities.

To broaden the application possibilities of 2D crystals there is nowadays an increasing interest to obtain 2D materials with magnetic properties. Recently, two chromium compounds have been verified to be ferromagnetic: Cr$_2$Ge$_2$Te$_6$ and CrI$_3$. Currently, many others 2D magnetic crystals have been obtained. Control of the magnetic properties in 2D systems has been pursued based on the proximity effects. For instance, in vdW stacking of CrI$_3$ bilayers where the magnetic coupling between the stacked layers depends on the CrI$_3$/CrI$_3$ interface geometry. Further studies examined the tuning of the magnetic phases in CrI$_3$ monolayer and bilayers as a function of an external electric field.

In the present study, we show that magnetic and electronic properties of few layers of GeP$_3$ doped by Cr atoms can be tuned by mechanical strain. Based on first-principles calculations, we investigate the energetic stability, magnetic, and electronic properties of the GeP$_3$ bilayer (GeP$_3$)$_{BL}$ doped with interstitial Cr atoms (GeP$_3$)$_{BL}$$^{Cr}$ and its stacked counterparts, namely (GeP$_3$)$_{BL}$$^{Cr}$/Cr/(GeP$_3$)$_{BL}$$^{Cr}$, and the Cr intercalated (GeP$_3$)$_{BL}$/$Cr$/(GeP$_3$)$_{BL}$ structure. We show that these systems present tunable magnetic phases, characterized by an intralayer AFM to FM transition and interlayer FM and AFM couplings, respectively. Further electronic band structure calculations reveal the emergence of strain induced spin polarized channels at the Fermi level, suggesting that (GeP$_3$)$_{BL}$$^{Cr}$ is an interesting building block to the design 2D spintronic devices.

II. METHODS

The calculations were performed by using the Density Functional Theory (DFT) as implemented in the QUANTUM ESPRESSO code. The exchange correlation energy was described within the spin-polarized generalized gradient approximation, as proposed by Perdew, Burke and Ernzerhof (GGA-PPE). The electron-ion interactions were described using the projector augmented wave potential (PAW). The Kohn-Sham wave functions were expanded in a plane-wave basis set with an energy cutoff of 48 Ry for the single particle wave functions, and 457 Ry for the total charge density. The atomic positions and lattice vectors were fully optimized by including van der Waals (vdW) interactions by using the vdW-DF approach, where we have considered a force convergence criterion of 1 mRy/bohr and $10^{-5}$ eV for the total energy. We have checked the convergence of our results by increasing the energy cutoffs to 60 Ry (plane basis-set) and 480 Ry (total charge density), and reducing the force convergence criterion to 0.2 mRy/bohr. The few layers GeP$_3$ systems were described within the supercell approach, where we have employed a vacuum region of (at least) 20 Å between neighboring slabs, that is, normal to the GeP$_3$ layers. The Brillouin zone sampling was performed by using a $3 \times 3 \times 1$ Monkhorst-Pack mesh. Due to the nature of d orbitals, we have used the GGA+U method for simulating the doped structures; where we set an effective interaction parameter $U_{eff} = 2$ eV of Cr(3d) electrons. In addition, some key results were further confirmed by using the Vienna Ab initio Simulation Package (VASP).

III. RESULTS AND DISCUSSIONS

A. Pristine (GeP$_3$)$_{BL}$

Firstly, as a benchmark, we compare our results of equilibrium geometry and total energies of (GeP$_3$)$_{BL}$ with the ones presented in the seminal work on 2D GeP$_3$ performed by Jing et al. The pristine GeP$_3$ bilayer presents a puckered hexagonal structure, in each layer the Ge atoms bonds to three neighboring P atoms, and each P atom forms two P–P bond and one Ge–P bond. At the equilibrium geometry, we found optimized lattice constants of $a = b = 7.08$ Å, $P$–$P$ and $P$–$P$ bond lengths of 2.25 and 2.50 Å, respectively. The GeP$_3$ MLs are separated by $d = 2.00$ Å, and the vertical distance between the topmost and bottommost Ge atoms ($h$) is equal to 5.05 Å, as shown in Fig. 1(a). In order to verify the energetic stability of the bilayer system, we compare the total energies of GeP$_3$ BL ($E_{BL}$) and ML ($E_{ML}$), $\Delta E_{BL} = E_{ML} - E_{BL}/2$. We found that the formation of (GeP$_3$)$_{BL}$ is an exothermic process, $\Delta E_{BL} = 52$ meV/Å$^2$. These findings are in good agreement with the ones in Refs. 15, 16.

B. Cr-doped GeP$_3$ bilayer

The electronic and magnetic properties in 2D systems have been engineered upon the atomic intercalation processes. For instance, by the incorporation of foreign atoms, or taking advantage of the symmetry resulting from the stacked layers, giving rise to 2D atomic self assemblies. Here, we examine the energetic stability, the magnetic/electronic properties of (GeP$_3$)$_{BL}$ doped by Cr atoms, and the control of these properties by external pressure.

Firstly, we have considered a number of plausible configurations for Cr atoms in (GeP$_3$)$_{BL}$. In Fig. 1(c) we present the lowest energy configuration, where we find the Cr atoms occupying the rhombohedral room between the GeP$_3$ MLs [(GeP$_3$)$_{BL}$$^{Cr}$]. The energetic stability of such a structural model was examined through the cal-
The formation energy \( E_f[X] \) of a system containing \( n_{\text{ML}} \) GeP\(_3\) MLs, \( n_{\text{Cr}} \) Cr atoms, and \( E_{\text{ML}} \) is given by:

\[
E_f[X] = n_{\text{ML}} (E_X - n_{\text{ML}} \times E_{\text{ML}}) - n_{\text{Cr}} \times \mu_{\text{Cr}},
\]

where \( E_X \) is the total energy of the final system, \( X = (\text{GeP}_3)_{\text{BL}} \), \( n_{\text{ML}} \) and \( n_{\text{Cr}} \) are the number of GeP\(_3\) MLs and Cr atoms within our supercell approach, and \( \mu_{\text{Cr}} \) is the chemical potential of Cr atoms. The upper limit of \( \mu_{\text{Cr}} \) is the chemical potential of its elemental (bcc bulk) phase, \( \mu_{\text{Cr}} \leq \mu_{\text{bulk}} \).

By considering the upper limit of \( \mu_{\text{Cr}} \), \( \mu_{\text{Cr}} = \mu_{\text{bulk}} \) (Cr-rich condition), we found that (GeP\(_3\))\(_{\text{BL}}\)Cr is an energetically stable structure with \( E_f = -20 \) meV/\( \text{Å}^2 \). Further structural stability was confirmed by performing \textit{ab initio} molecular dynamics (AIMD) simulations at 300 K. We have considered time steps of 5 fs, and we observe that the (GeP\(_3\))\(_{\text{BL}}\)Cr structure has been preserved up to 10 ps.

In Fig. 1, we present the total energy fluctuation as a function of the simulation time.

The interstitial Cr atoms embedded between the GeP\(_3\) layers form a triangular lattice [Fig. 1(d)], giving rise to a \( \delta \)-doping like structure. We found that the lattice constants, \( a = b = 7.05 \) Å, and the interlayer distance, \( d = 2.11 \) Å, of (GeP\(_3\))\(_{\text{BL}}\)Cr are practically the same compared with those of pristine (GeP\(_3\))\(_{\text{BL}}\), \( a = b = 7.08 \) Å, and \( d = 2.09 \) Å, thus indicating that the local atomic structure of (GeP\(_3\))\(_{\text{BL}}\)Cr is weakly perturbed by the presence of interstitial Cr atom. At the equilibrium geometry, we found Cr–P and Cr–Ge bond lengths of 2.59 and 3.17 Å, respectively, which are slightly larger than the sum of their covalent radii, increasing the vertical distance \( h \) from 5.05 to 6.34 Å, Figs. 1(a) and (c).

In Fig. 2, we present the total energy fluctuation as a function of the simulation time.

The interstitial Cr atoms present a net magnetic moment of 3.4 \( \mu_B \), which are coupled mediated by the P atoms. We have compared the energetic stability of four magnetic phases [51], as shown in Figs. 2(a1)–(a4). At the equilibrium geometry, we found the row-wise antiferromagnetic (RW-AFM) phase [Fig. 2(a1), hereafter labeled as Cr\(_{\uparrow\downarrow}\)] as the most stable spin-configuration, and the ferromagnetic (FM) phase [Fig. 2(a4), hereafter labeled as Cr\(_{\uparrow\uparrow}\)] as the least stable one by \( E_{\text{RW-AFM}} - E_{\text{FM}} = -59 \) meV/Cr-atom. On the other hand, we found that such a energetic preference for the RW-AFM alignment in (GeP\(_3\))\(_{\text{BL}}\)Cr can be tuned by mechanical compressive strain (\( \varepsilon \)). In Fig. 2(b) we present our results of \( E_{\text{RW-AFM}} - E_{\text{FM}} \) as a function of the vertical distance \( h \). It is noticeable a Cr\(_{\uparrow\downarrow} \rightleftharpoons \text{Cr}\(_{\uparrow\uparrow}\) magnetic transition for \( h \) between 5.32
and 5.19 Å, and upon further compression to \( h = 5.07 \text{ Å} \), which corresponds to an external pressure of 2.30 GPa, the FM phase become more stable by \( E_{\text{RW-AFM}} - E_{\text{FM}} = +21 \text{ meV/Cr} \).

The orbital projected electronic band structure of the RW-AFM \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\), Fig. 2(c), reveals the formation of metallic bands mostly ruled by the P(3p), while the Cr atoms give rise to localized states resonant with the Fermi level along the KM direction. In contrast, the spin-up and -down energy bands are no longer degenerated upon compression, Figs. 2(d) and (e). The spin-up channel presents a larger density of states near the Fermi level compared with that of the spin-down channel. The former can be characterized by Cr(3d) bands along the KM direction, one dispersionless and the other with nearly linear dispersion crossing the Fermi level. Meanwhile, both spin-channels present nearly parabolic metallic bands.

along the ΓM and ΓK directions, which are projected on the Ge(4p) and P(3p) orbitals. These findings allow us to infer the emergence of mechanically tuneable spin bands dictated by the spin-polarized Cr(3d) states near the Fermi level.

### C. \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) interfaces

Stacking of 2D magnetic system is a quite interesting option aiming the search of new phenomena ruled by interlayer interactions. For instance, magnetic phases in few layers CrI\(_2\) as a function of the stacking geometry [35], that in turn can be tuned by external agents like electric field [36] or mechanical pressure [32, 33]. Here, we investigate the tuning of the magnetic properties of \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) bilayers mediated by vertical compressive strain. Firstly we have considered a pristine bilayer system, \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\), and then the intercalation of Cr atoms, \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}/\text{Cr}/(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\). It is worth noting that such a compression will promote two concurrent magnetic interactions, (i) the intralayer RW-AFM → FM transition discussed above; and (ii) proximity effects at the \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}/(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) interface.

In Fig. 3(a) we present the structural model of \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}/(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\), where the GeP\(_3\) layers are stacked following the conventional ABC stacking order of its bulk phase [17]. At the equilibrium geometry, the structural properties of each \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) are mostly preserved, for instance the vertical distances \(d_1\) and \(h\) of 2.06 and 6.44 Å, respectively. The interlayer spacing between the two \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) layers, \(d_2 = 2.07 \text{ Å}\), also is practically the same compared with that of pristine \((\text{GeP}_3)_{\text{BL}}\). There are no chemical bonds connecting the \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) layers, indicating that the energetic stability of the stacked system is ruled by vdW interactions. The energetic stability of the bilayer system was verified by the calculation of the formation energy. For \(X=(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}/(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) in eq. (1), we obtained \(E_f = -25 \text{ meV/Å}^2\).

Focusing on the magnetic properties, we have examined three plausible magnetic configurations, namely, (i) each \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) layer presents RW-AFM alignment \(\text{Cr}^{\uparrow\uparrow}/\text{Cr}^{\uparrow\downarrow}\), (ii) the \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) layers present intralayer FM coupling, and interlayer AFM coupling \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}\), and (iii) the \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) layers present intralayer and interlayer FM coupling \(\text{Cr}^{\uparrow\uparrow}/\text{Cr}^{\uparrow\downarrow}\). These spin configurations are schematically shown in Figs. 3(b1)–(b3). Our total energy results reveal the former configuration, \(\text{Cr}^{\uparrow\uparrow}/\text{Cr}^{\uparrow\downarrow}\), as the most stable one, followed by \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}\) and \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}\) by 51 and 67 meV/Cr, respectively. The energy difference of 16 meV between these two intralayer FM phases indicates the presence of magnetic coupling between the FM \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) layers, favoring the former one.

**TABLE I.** Total energy differences (in meV/Cr-atom) with respect to the energetically more stable spin configuration of the free \(\Delta E_{\text{Free}}\) and compressed \(\Delta E_{\text{Compress}}\) \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}/(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) and \((\text{GeP}_3)_{\text{BL}}^{\text{Cr}}/\text{Cr}/(\text{GeP}_3)_{\text{BL}}^{\text{Cr}}\) systems.

| structure       | \(\Delta E_{\text{Free}}\) | \(\Delta E_{\text{Compress}}\) |
|-----------------|-----------------------------|-------------------------------|
| \(\text{Cr}^{\uparrow\uparrow}/\text{Cr}^{\uparrow\downarrow}\) | 0                           | 4                             |
| \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}\) | 51                          | 39                            |
| \(\text{Cr}^{\uparrow\uparrow}/\text{Cr}^{\uparrow\uparrow}\) | 67                          | 0                             |
| \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}\) | 0                           | 38                            |
| \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}/\text{Cr}^{\uparrow\uparrow}\) | 60                          | 0                             |
| \(\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\downarrow}/\text{Cr}^{\uparrow\uparrow}\) | 20                          | 33                            |

Such a magnetic coupling can be strengthened by a compressive strain normal to the stacking direction. In
FIG. 4. (a) Structural model of (GeP$_3$)$_{BL}$/Cr/(GeP$_3$)$_{BL}$ and the spin configurations Cr$^{↑↑}$/Cr$^{↑↓}$ (b1), Cr$^{↑↑}$/Cr$^{↑↓}$ (b2), and Cr$^{↑↑}$/Cr$^{↑↑}$/Cr$^{↑↑}$ (b3). The localization and the spin-polarization of the Cr-atom are indicated by arrows. Planar averaged spin-density along the z-axis of the compressed (GeP$_3$)$_{BL}$/Cr/(GeP$_3$)$_{BL}$ system, Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ (c) and Cr$^{↑↑}$/Cr$^{↑↑}$/Cr$^{↑↑}$ (d). The interface distances are indicated by $d_1$ and $d_2$ in (a).

In this case, concomitantly with the reduction of the vertical interlayer distance $d_2$, the reduction of $d_1$ will favor the intralayer FM interaction between the Cr atoms, Cr$^{↑↑}$ $\rightarrow$ Cr$^{↑↑}$. Indeed, for a compressive strain of $\varepsilon = 26\%$, which corresponds to an external pressure ($P$) of 3.82 GPa, we found energetic preference for the intralayer and interlayer FM configuration [Fig. 3(b3)], thus characterizing a Cr$^{↑↑}$/Cr$^{↑↓}$ $\rightarrow$ Cr$^{↑↑}$/Cr$^{↑↑}$ magnetic transition tuned by a mechanical strain. Our total energy results are summarized in Table I. These results, in addition to the spin-polarization of the Ge and P atoms at the interface region, suggest an indirect magnetic interaction between the (GeP$_3$)$_{BL}$ layers.

Such a magnetic coupling between the (GeP$_3$)$_{BL}$ layers can be strengthened by the intercalation of Cr atoms, (GeP$_3$)$_{BL}$/Cr/(GeP$_3$)$_{BL}$. The Cr-atoms lie in the rhombohedral room between the (GeP$_3$)$_{BL}$ layers [Fig. 4(a)], that is, the same geometry as obtained for the isolated (GeP$_3$)$_{BL}$. By using the eq.(1), for X=(GeP$_3$)$_{BL}$/Cr/(GeP$_3$)$_{BL}$, we found $E^f$ of $-21$ meV/$\AA^2$, thus supporting the energetic stability of the Cr $\delta$-doped GeP$_3$ quadrilaterals [(GeP$_3$)$_{QL}$]. At the optimized geometry, (GeP$_3$)$_{QL}$ presents interlayer distances of $d_1 = 2.00$ Å, and $d_2 = 2.04$ Å, while the undoped pristine GeP$_3$ quadrilateral presents equally spaced interlayer distances of 1.97 Å.

Next we investigate the magnetic couplings between the Cr atoms. We have considered the spin configurations presented in Figs. 4(b1)–(b3), hereafter labeled as Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$, Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$, and Cr$^{↑↑}$/Cr$^{↑↑}$/Cr$^{↑↑}$. At the equilibrium geometry, we found the former spin configuration, where each (GeP$_3$)$_{QL}$ is characterized by the RW-AFM alignment, more stable than the other ones by 20 and 60 meV/Cr-atom, respectively. However, for $\varepsilon$ of 22% ($P = 4.09$ GPa), Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ [Fig. 4(b2)] becomes more stable than Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ and Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ by 33 and 38 meV/Cr-atom, as presented in Table I. Thus, revealing that (GeP$_3$)$_{BL}$/Cr/(GeP$_3$)$_{BL}$ also presents a tunable spin configuration, Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$. However, differently from its (GeP$_3$)$_{BL}$/Cr/(GeP$_3$)$_{BL}$ counterpart, the spin-polarizations are alternated along the stacked layers.

In order to provide a more complete picture of the interlayer coupling in (GeP$_3$)$_{QL}$, we have examined the planar averaged spin-density $\Delta \rho^{z}(z)$ along the stacking direction (z),

$$\Delta \rho^{z}(z) = \frac{1}{S} \int_{S} [\rho^{↑}(x, y, z) - \rho^{↓}(x, y, z)] dx dy,$$

(2)

where $S$ represents the surface area in the $xy$-plane, and $\rho^{↑}/\rho^{↓}$ are the spin-polarized total charge densities. Our results of $\Delta \rho^{z}(z)$ for the spin configurations Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ and Cr$^{↑↑}$/Cr$^{↑↑}$/Cr$^{↑↑}$ at $\varepsilon = 22\%$ are shown in Figs. 4(c) and (d). The net magnetic moments are mostly localized in the layers containing Cr atoms, however in the Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ configuration, the interface P atoms also become spin polarized. The energetic advantage of Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$, in the compressed system, comes from a combination of (i) the Cr$^{↑↑}$$\rightarrow$ Cr$^{↑↑}$ transition within the (GeP$_3$)$_{QL}$ units, and (ii) the lowering of the kinetic energy ruled by a super-exchange interaction mediated by the interface P atoms [Figs. 4(c) and (d)]. As shown in Figs. 4(d), such (kinetic) energy gain is not allowed in Cr$^{↑↑}$/Cr$^{↑↑}$/Cr$^{↑↑}$.

Finally, focusing on the electronic properties, in Fig. 5(a) we present the orbital projected electronic band structure of the uncompressed (GeP$_3$)$_{QL}$. The projec-
tion on the edge (GeP$_3$)$_{BL}^{−}$ layers present the same band structures [Figs. 5(a1) and (a3)], where we find the formation of metallic bands, mostly composed by Cr(3d) and P(3p) hybridized states. Meanwhile, the electronic bands projected in the central layer are characterized by the strengthening of dispersionless Cr(3d) bands near the Fermi level, Fig. 5(a2). Since we have considered the lowest energy configuration, Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$, of the uncompresssed system ($\varepsilon = 0$), the spin-up and -down channels are degenerated. In contrast, such a degeneracy has been removed for $\varepsilon = 22\%$, where the Cr$^{↑↑}$/Cr$^{↑↓}$/Cr$^{↑↑}$ configuration becomes more stable. As shown in Figs. 5(b1) and (b3), the hybridization of Cr(3d) and P(3p) orbitals gives rise to metallic bands along the edge (GeP$_3$)$_{BL}^{−}$/Cr/(GeP$_3$)$_{BL}^{−}$ layers. In contrast, the density of metallic states has been reduced in the central layer, with no projection of the Cr(3d) orbitals, Fig. 5(b2). The spin-down energy bands present a somewhat opposite picture, namely the Cr(3d) and P(3p) hybridized bands localized in the central (GeP$_3$)$_{BL}^{−}$ layer [Fig. 5(c2)], and no Cr(3d) orbital projection on the spin-down channels at the edge layers [Figs. 5(c1) and (c3)]. These findings reveal that, in addition to the spin configurations, the rise and (layer) localization of the spin-polarized metallic bands can also be tuned by mechanical strain in Cr intercalated GeP$_3$ systems.

IV. CONCLUSIONS

We have performed an ab initio investigation of few layer systems of GeP$_3$ doped by Cr atoms. The energetic and structural stabilities of Cr atoms lying in the rhombohedral room of between GeP$_3$ layers, (GeP$_3$)$_{BL}^{−}$, have been verified through formation energy calculations and first-principles molecular dynamic simulations. We show that (GeP$_3$)$_{BL}^{−}$, as well as its stacked counterparts are quite interesting platforms for tuneable magnetism in 2D systems. We found that the ground state row wise antiferromagnetic configuration in (GeP$_3$)$_{BL}^{−}$, Cr$^{↑↓}$, can be tuned to a ferromagnetic phase mediated by compressive mechanical strain ($\varepsilon$), Cr$^{↑↓} \rightarrow$ Cr$^{↑↑}$. Meanwhile, in the stacked systems, (GeP$_3$)$_{BL}^{−}$/Cr/(GeP$_3$)$_{BL}^{−}$, and (GeP$_3$)$_{BL}^{−}$/Cr/(GeP$_3$)$_{BL}^{−}$, the combination of intralayer and interlayer interactions gives rise to the following strain induced changes in the magnetic configurations, Cr$^{↑↓} \rightarrow$ Cr$^{↑↑}$ and Cr$^{↑↑} \rightarrow$ Cr$^{↑↓}$, respectively. Concomitantly with such a magnetic tuning, further electronic structure calculations revealed the emergence of spin polarized channels near the Fermi level. These findings indicate that mechanical tuning of the electronic and magnetic properties, in two dimensional platforms, can be engineered throughout synergic combinations between the foreign atoms and the 2D-hosts.

V. APPENDIX

In order to provide further support to the energetic stability of the Cr intercalated (GeP$_3$)$_{BL}^{−}$ structure, we performed ab-initio molecular dynamics (AIMD) simulations of the (GeP$_3$)$_{BL}^{−}$ system, in order to verify its thermal stability at room temperature. We have considered the ground state row-wise antiferromagnetic RW-AFM phase by using a 2x1 surface periodicity, containing two formula units. The AIMD simulations were carried out using Nosé thermostat method at a temperature of 300 K for a total of 10 ps, with a time step of 5 fs. There is no bond breaking between Ge and P atoms during the AIMD simulation, after heating the (GeP$_3$)$_{BL}^{−}$ for 10 ps. Likewise, the individual layers of GeP$_3$ remained coupled via the Cr atoms during the simulation, as can be seen in the initial and final configuration of the structure [inset of Fig. 6], thus ensuring that it is stable at room temperature. The calculated total magnetic moment per (GeP$_3$)$_{BL}^{−}$ supercell varied between $\pm 0.22 \mu_B$/unit-cell during the AIMD simulation, showing that the RW-AFM spin configuration also keeps practically unchanged during the MD process. From an energetic point of view, the total energy at 0 ps and after 10 ps has changed from -11.3 to 10.8 meV/unit-cell, Fig. 6, showing that the structural properties are maintained even at 300 K, enabling future experimental applications.
FIG. 6. The total energy fluctuations as a function of time step (5 fs) for the AIMD simulation at 300 K, of the RW-AFM (GeP$_3$)$_{BL}$ Cr. The inset figures represent snapshots of atomic structures of (GeP$_3$)$_{BL}$ Cr at 0 ps (initial configuration) and 10 ps (final configuration).

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