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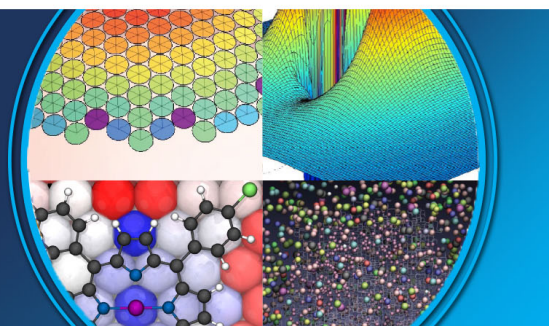
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PERSPECTIVES



Dirac cone in two dimensional bilayer graphene by intercalation with V, Nb, and Ta transition metals

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Bilayer graphene (BLG) is a semiconductor whose band gap and properties can be tuned by various methods such as doping or applying gate voltage. Here, we show how to tune electronic properties of BLG by intercalation of transition metal (TM) atoms between two monolayer graphene (MLG) using a novel dispersion-corrected first-principle density functional theory (DFT) approach. We intercalated V, Nb, and Ta atoms between two MLG. We found that the symmetry, the spin, and the concentration of TM atoms in BLG-intercalated materials are the important parameters to control and to obtain a Dirac cone in their band structures. Our study reveals that the BLG intercalated with one vanadium (V) atom, BLG-1V, has a Dirac cone at the K-point. In all the cases, the present DFT calculations show that the $2p_z$ sub-shells of C atoms in graphene and the $3d_{yz}$ sub-shells of the TM atoms provide the electron density near the Fermi energy level (E_F) which controls the material properties. Thus, we show that out-of-plane atoms can influence in-plane electronic densities in BLG and enumerate the conditions necessary to control the Dirac point. This study offers insight into the physical properties of 2D BLG intercalated materials and presents a new strategy for controlling the electronic properties of BLG through TM intercalation by varying the concentration and spin arrangement of the metals resulting in various conducting properties, which include: metal, semi-metal and semiconducting states. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5008996>

I. INTRODUCTION

In modern science and technology, there has been a tremendous amount of theoretical and experimental interest in the low-energy electronic properties of ultrathin graphite films including graphene monolayer and graphene bilayer materials.^{1–6} Graphene is a 2D honeycomb sheet of carbon, just one atom thick, with hybridized sp^2 bonded orbitals between carbon atoms.^{7,8} Graphene is an ideal material for making nanoelectronic and photonic devices because it is a very good electrical conductor as well as the thinnest 2D material known. Graphene has a unique linear band structure around the Fermi level (E_F) forming a Dirac cone at the K-points of its Brillouin zone. This has led to fascinating phenomena, exemplified by massless Dirac fermion physics.^{9–12} This emergent behavior of Dirac fermions in condensed matter systems defines the unifying framework for a class of materials called Dirac materials.

Monolayer graphene (MLG) or simply graphene has an electronic structure that can be controlled by an electrical field.¹³ However, MLG has the well-known zero-gap issue¹⁴ which makes a high on-off ratio difficult, deeming it unsuitable

for transistors which are the foundation of all modern electronic devices. Therefore, opening the band gap of graphene still remains a challenging task to date. Bilayer graphene (BLG) can be used instead of MLG to overcome the zero-gap problem, with a gap opening simply by applying an electric field.^{15,16} BLG has an entirely different band structure though it is equally interesting.^{17,18} Since the band gap of the BLG can be modulated from zero to a few eV by using different methods, such as doping and applying an external electric field. In addition, BLG holds the potential for electronics and nano-technological applications, particularly, because of the possibility of controlling both carrier density and the energy band gap through doping or gating.^{9,10,18–20} The most remarkable property of BLG is that the inversion symmetric AB-stacked BLG is a zero-band gap semiconductor in its pristine form, but a non-zero band gap can be induced by breaking the inversion symmetry of the two graphene monolayers to form AA-stacked BLG.^{18–20} When two graphene monolayers are stacked (in both the cases AA- and AB-stacked), the monolayer features are lost and dispersion effects become quadratic and more effective.¹⁹ Thus, BLG acts as a semiconductor and exhibits an induced electric field and a broadly tunable band gap.^{10,21} By tuning the band gap, BLG can transform from a semiconductor into a metal or semi-metal, which means that a single millimeter-square sheet of BLG could potentially hold millions of differently tuned electronic devices that can be

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reconfigured. Recently, lasers have been used to get BLG to act as a conductor, a Dirac material, or a semiconductor. This is an important step toward the invention of computer chips made of a 2D material.²²

Metals interacting with graphite, MLG, and BLG have been investigated both experimentally as well as theoretically by first principles computational methods. Graphite intercalation compounds (GICs), formed by insertion of atomic or molecular layers of different chemical species between the layers of carbon in graphite, have been also investigated both experimentally and computationally.^{23–27} Novoselov and co-workers experimentally investigated detailed surface

interactions between MLG and three metals (Au, Fe, and Cr) using scanning transmission electron microscopy.²⁸ Intercalation occurs when metal atoms are inserted between two graphene monolayers, e.g., BLG. Accordingly, Takahashi and co-workers²⁹ experimentally fabricated Li-intercalated BLG on a SiC(0001) substrate and characterized the crystallographic and electronic properties by low-energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES). They predicted that the Li-intercalation in BLG would open a way to develop a nano-scale ion battery. Wang *et al.*³⁰ studied the energetics of the intercalation of alkali metal atoms (Li, Na, and K) in graphite by van

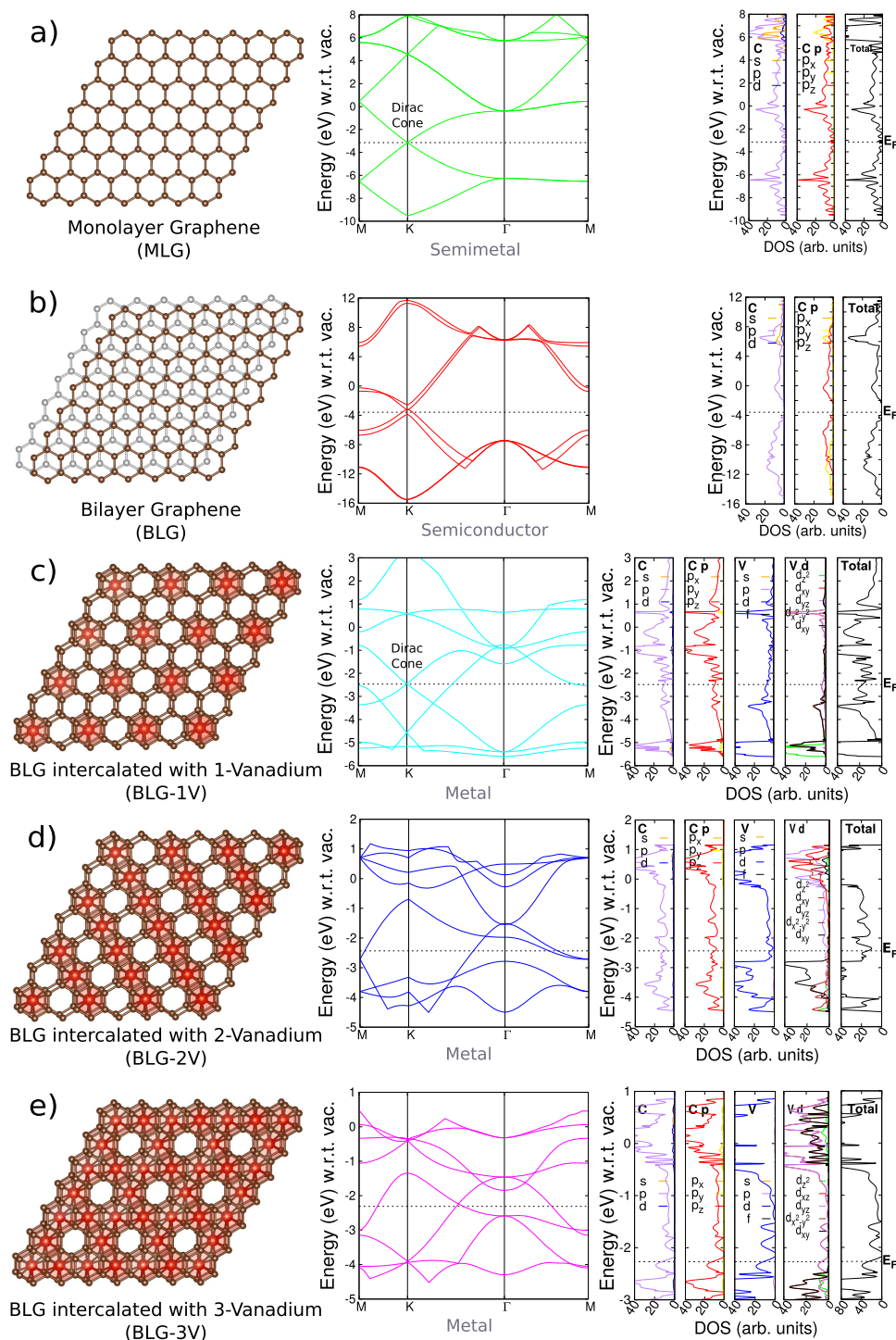


FIG. 1. The optimized structures, band structures, and density of states (DOSs) are shown: (a) MLG, (b) BLG, (c) BLG-1V, (d) BLG-2V, and (e) BLG-3V. The individual components of the DOSs of the C and V atoms and total DOSs (depicted by "Total") are also presented in here. The energy for the band structures and DOSs is reported with respect to vacuum (i.e., w.r.t. vac.).

der Waals density functionals. They found that the intercalation induces only a subtle increase of in-plane C–C bond lengths, with longer C–C bonds in the vicinity of the alkali metals. Additionally, intercalation was accomplished but without breaking the hexagonal symmetry. Very recently, Hasegawa and co-workers found direct evidence for superconductivity in Ca-intercalated BLG using *in situ* electrical transport measurements.³¹ To date, only a few computational studies have examined the electronic properties of BLG intercalated with transition metals (TMs). For example, intercalation of BLG with Cr^{32,33} and Mn³⁴ is predicted for spintronic applications. A theoretical investigation of BLG intercalated with Cr was carried out using density functional theory (DFT), which found that the BLG–Cr layer material is ferromagnetic (FM).³² Using first-principles calculations, Liao *et al.*³⁵ investigated various stable BLG structures intercalated with Sc and Ti. They found that the strain was important for the stability of high-coverage TM in BLG. The effect of TM on the electronic and magnetic properties of defective BLG was investigated using DFT.³⁶ In spite of these reports, the structures and electronic properties are not well studied yet for BLG intercalated with TM from the same group column in the periodic table, specifically V, Nb, and Ta.

In this work, we apply first-principles calculations to search for new BLG intercalated with V, Nb, and Ta atoms. Here, we show that the Dirac cone in the band structure of BLG can be controlled by adding TM atoms between two graphene layers (where TM = V, Nb, and Ta) so that the electronic band gap between the valence and conduction bands can be tuned, thus resulting in the appearance of a Dirac cone only in BLG-1V. We found that intercalation of TM atoms, and their spin arrangement, causes a surprisingly diverse array of electronic properties. Additionally, the band gap depends on the coupling between the two graphene layers and symmetry of the BLG system, i.e., AB stacking vs AA stacking. We have also performed a theoretical investigation of the electronic properties such as band structure, density of states (DOSs), spin arrangements, and structural stability for MLG, BLG, and BLG intercalated with one, two, and three vanadium atoms, BLG-1V, BLG-2V, and BLG-3V, as shown in Fig. 1. Other intercalated materials presented here include BLG intercalated with Nb and Ta. A few sophisticated theoretical or computational studies have been conducted to understand the intercalation behavior under graphene covers in a quantitative way. A 2D microenvironment formed under 2D material can provide an ideal and practical model system to explore the fundamental material properties of the confined TM-intercalated BLG. Confined microenvironments formed by TM-intercalated 2D materials may be an interesting study in 2D materials science and nano technology.

II. COMPUTATIONAL DETAILS

The geometry of the 2D layer structures MLG, BLG, and BLG-intercalated materials (BLG-1V, BLG-2V, BLG-3V, BLG-1Nb, and BLG-1Ta) were optimized using dispersion-corrected unrestricted hybrid density functional theory,^{37–43} i.e., unrestricted Becke, 3-parameter, Lee–Yang–Parr with -D2 dispersion correction (UB3LYP-D2) which has been shown

to give correct electronic properties for 2D materials.^{40,44–47} The semi-empirical Grimme-D2 dispersion corrections were added in the present calculations in order to incorporate van der Waals dispersion effects on the system.^{40–42,48} For simplicity, this UB3LYP-D2 method is termed as DFT-D throughout this work. The symmetry operation was considered in the calculations. MLG, AA-stacked BLG, AB-stacked BLG, BLG-1V, BLG-2V, BLG-3V, BLG-1Nb, and BLG-1Ta have high $P6/mmm$, $P6/mmm$, $P-3m1$, $P6/mmm$, $Cmm2$, $P6/mmm$, $P6/mmm$, and $P6/mmm$ hexagonal symmetry (except BLG-2V which has rectangular symmetry), which were constrained during the optimization of these materials. The CRYSTAL14⁴⁹ suite code, which makes use of localized Gaussian basis sets, was used to perform all of the first-principles computations. During the optimization and single point energy calculations, “SPIN” and “SPINLOCK” keywords were used to specify the unrestricted wave functions and the total spin of the BLG-intercalated materials, respectively. The “ATOMSPIN” keyword was also used to specify the individual spins of the TM atoms in the BLG-intercalated materials. The ferromagnetic (FM) and anti-ferromagnetic (AFM) spin alignment was studied by using the equivalent spin polarized wave function for Gaussian basis sets. The bilayer graphene intercalated 2D materials (BLG-1V, BLG-2V, BLG-3V, and BLG-1Nb and BLG-1Ta) have been prepared by adding the V, Nb, and Ta atoms in one unit cell of the crystal structures. In the present computation, triple-zeta valence with polarization (TZVP) quality Gaussian basis sets were used for both C and V,⁵⁰ and HAYWSC effective core potentials (ECPs) were used for both Nb and Ta.⁵¹ The threshold used for evaluating the convergence of the energy, forces, and electron density was 10^{-7} a.u. for each parameter. The height of the cell was formally set to 500 Å, i.e., the vacuum region of approximately 500 Å was considered in the present calculations. The DFT exchange-correlation contribution was evaluated by numerical integration over the unit cell volume. Radial and angular points of the integration grid were generated through the Gauss-Legendre radial quadrature and Lebedev two-dimensional angular point distributions.

Integration inside of the first Brillouin zone was sampled on $15 \times 15 \times 1$ k-mesh grids in all the materials for both the optimization and material properties (band structures and density of states) calculations with a resolution of around $2\pi \times (1/60) \text{ \AA}^{-1}$ for all bilayer graphene intercalated materials and $2\pi \times (1/40) \text{ \AA}^{-1}$ for the MLG. In this work, we used a shrinking factor (the number of points along each reciprocal lattice vector at which the Fock matrix is diagonalized) of 30. We have plotted the bands along a high symmetric k-direction, $M-K-\Gamma-M$, in the first Brillouin zone. Electrostatic potential calculations have been included in the present computation, i.e., the energy for the band structures and DOSs is reported with respect to vacuum (i.e., w.r.t. vac.).

III. RESULTS AND DISCUSSION

In this section, we present the results from DFT-D calculations (i.e., UB3LYP-D2) for the MLG, BLG, BLG-1V, BLG-2V, BLG-3V, BLG-1Nb, and BLG-1Ta layered materials. The present DFT calculation shows that the Dirac cone exists at

the K-point in the band structure of MLG, which is consistent with previous results.^{9–12} The valence and conduction bands of MLG arise from the $2p_z$ sub-shells in C atoms, which form the Dirac cone [see Fig. 1(a)]. Our present computation shows that AB-stacked BLG (which has $P-3m1$ symmetry) is thermodynamically more stable than the AA-stacked BLG (which have $P6/mmm$ symmetry). The valence and conduction bands overlap at the K-point for both the AA- and AB-stacked BLG. However, both bands do not align perfectly with the E_F , thus, the AA- and AB-stacked BLG have no Dirac cone [Fig. S1 of the [supplementary material](#) and Fig. 1(b), respectively], which agrees with previous experimental results,^{52,53} i.e., the AA-/AB-stacked BLG materials are ordinary non-zero/zero band gap semiconductors. The bond distances, lattice constants (a and b), and intercalation distance (d) are reported in Table I. The distance between the two monolayers in the pristine AB-stacked BLG material is about 3.390 Å which agrees with the previous experimental and theoretical results.⁵² We have also calculated the binding energy (ΔE_f) of all the systems studied here as shown in Table II. The binding energy, ΔE_f , to form the AB-stacked BLG from two MLG, is about -0.86 eV, which is in agreement with the previous experimental and theoretical results.^{54–57} It is well known that a twist in bilayer graphene breaks the local symmetry, introducing a number of intriguing physical properties, such as opening new band gaps, and AB-stacked BLG including a rotation forming Moire bands when examined by scanning probes.^{58–60} Although experimentally relevant and computationally interesting, we do not consider the possibility of Moire band structures in the present article as the imposed symmetry of our unit cell would be broken in order to shift the graphene layer. Moreover, we studied the transition metal atom (here V, Nb, and Ta) intercalation in the AA-stacked BLG and not in the AB-stacked BLG materials.

We have also performed an optimization calculation of the BLG-1V material without symmetry (high hexagonal $P6/mmm$ symmetry) constraint, i.e., with P1 symmetry. The present DFT-D calculations found that lattice parameters (a and b) were almost equal with a very small difference about 0.00034 Å which is well below the DFT error bar. The intercalation distance d was increased by an amount 0.001 Å and the C–V bond distance remained constant when there was no symmetry constraints. Therefore, it did not affect the electronic properties of BLG-1V. Metal adsorption on graphene shows that transition metals, in general, prefer the hollow

TABLE I. Bond distances and lattice constants for MLG, BLG, and BLG-TM materials (where TM is the transition metal). d is defined as the interlayer distance between the monolayers.

Component	C–C (Å)	C–V (Å)	a (Å)	b (Å)	d (Å)
MLG	1.416	N/A	2.451	2.451	N/A
AA-stacked BLG	1.414	N/A	2.449	2.449	3.201
AB-stacked BLG	1.421	N/A	2.449	2.449	3.390
BLG-1V	1.439	2.243	4.942	4.942	3.441
BLG-2V	1.442	2.335	8.575	5.022	3.645
BLG-3V	1.464	2.413	5.032	5.032	3.658
BLG-1Nb	1.439	2.313	4.950	4.950	3.600
BLG-1Ta	1.445	2.284	4.952	4.952	3.522

TABLE II. Relevant properties of the MLG, BLG, and BLG-TM; the binding energy, ΔE_f , is with respect to their individual components: MLG and TM atoms.

Component	State	ΔE_f (eV)	Dirac cone
MLG	Semimetal	N/A	Yes
AA-stacked BLG	Semiconductor	-0.78	No
AB-stacked BLG	Semiconductor	-0.86	No
BLG-1V	Metal	-5.97	Yes
BLG-2V	Metal	-5.67	No
BLG-3V	Metal	-5.36	No
BLG-1Nb	Metal	-11.18	No
BLG-1Ta	Metal	-16.35	No

sites of the hexagonal centers, likely for favorable orbital interactions between the d -orbitals of the metals with the p -orbitals of graphene. A natural extension to preserve this behavior would be to intercalate the metals between AA-stacked bilayer graphene which results in the $P6/mmm$ symmetry. The buckling is likely due to the favorability of the orbital interactions between the metal and the graphene layers. We believe that the imposed $P6/mmm$ symmetry produces the ideal structure; however, experimental results could yield a shift in one graphene layer which depending on the shifting angle may or may not preserve the periodic nature of our symmetry.

The optimized structure between vanadium and graphene follows an AA-stacking arrangement with the vanadium atom placed at the center of the honeycomb to form BLG-1V. After intercalating one vanadium atom in the AA-stacked BLG, the BLG-1V has the same hexagonal which has $P6/mmm$ symmetry like MLG and AA-stacked BLG. In this conformation, the vanadium d -orbitals are well situated to favorably interact with the p_z orbital orthogonal to the graphene layer. The BLG-1V structure is highly favorable by -5.97 eV relative to BLG and one free V atom. Intercalating additional vanadium atoms is also viable as two metal atoms decrease the energy by 5.67 eV relative to the single metal structure, and triple metal addition decreases the energy further by 5.36 eV relative to the two metal atom structure as shown in Table II. The present DFT calculations show that the intercalation distances gradually increased when more V atoms are added from BLG-1V to BLG-3V, but not equally as shown in Table I. Our computation also shows that the C–C bond distance has been increased by a cumulative average of 0.014 Å in BLG-1V, BLG-2V, and BLG-3V due to the presence of V atoms between the graphene layers compared to BLG. We also calculated the stability of BLG intercalated with four V atoms (BLG-4V), but the frequency calculations show that the structure is unstable thermodynamically as it has many imaginary frequencies, and hence this result is excluded from this article.

The addition of vanadium atoms was found to substantially alter the electronic properties of graphene bilayer. The addition of a single vanadium atom intercalated in AA-stacked BLG (i.e. BLG-1V) yields a Dirac cone along the K-direction as shown in Fig. 1(c). The individual components of the p -orbital electron density for C atoms and the d -orbital electron density for V atoms have been explicitly shown along with

the total DOSs in Fig. 1(c). The DOS calculations for BLG-1V show electron density around the E_F indicating metallic behavior and is coming from the p_z sub-shells of C atoms in graphene and the d_{yz} sub-shell of the V atom. In other words, the p_z sub-shell of carbon and d_{yz} sub-shells of vanadium are mostly responsible for the emergence of the Dirac cone in BLG-1V.

In MLG, the Dirac cone comes from the p_z sub-shells of p -orbitals of the C atoms alone. However, for BLG-1V, the nature of the Dirac cone might be different because it might come from the p -orbitals alone in C, d -orbitals alone of the V atom, or $p-d$ hybridized orbitals of C and V atoms. To resolve this, we used the coordinates of the optimized geometry of BLG-1V and then (i) removed the BLG and, in another calculation, (ii) removed the V atoms. We then calculated the electronic properties of these structures (Fig. S2 of the [supplementary material](#)). The band structure shows that the Dirac cone disappears when only the V atoms are used and also when only BLG is used. In the BLG case, the Dirac point was still present but it shifted above E_F , just like in the ideal AA-stacked BLG. This suggests that $p-d$ hybridized orbitals are the source of the Dirac cone in BLG-1V. As an excellent conductor and Dirac material, BLG-1V can be used in various modern electronic devices.

BLG-2V and BLG-3V can be formed with the addition of one V atom and two V atoms to the BLG-1V material, respectively. The original high hexagonal $P6/mmm$ symmetry was lost in the BLG-2V material when one V atom was intercalated in BLG-1V, and the $P6/mmm$ symmetry again was appeared in the structure of BLG-3V when one more V atom was added in BLG-2V. Different spin states of BLG-2V and BLG-3V have been considered, but only the most stable configurations are discussed here, while the other less stable spin states are discussed in Table S1 of the [supplementary material](#). First, we will discuss the ferromagnetic (FM) state for both materials, which results in the Dirac cone disappearing, and the band shifting, which shows a metallic behavior when the spins of vanadium atoms align. Interestingly, in general for all these materials in the FM state, the $3d$ orbitals of V receive more electron donation from the graphene $2p_z$ sub-shells when the total spin is increased. The band structure reveals that along the M to K directions, the valence band crosses the Fermi level in both BLG-2V and BLG-3V, resulting in large electron distribution around the Fermi level as shown in Figs. 1(d)

and 1(e), respectively. Thus, both BLG-2V and BLG-3V show metallic behavior as depicted in their total DOSs. In both materials, the total DOSs show that the electron density around the Fermi level is due to the p_z sub-shell electrons from the C atoms in graphene and the d_{yz} sub-shell electrons from the V atoms as depicted in the sub-shell DOS calculations [see Figs. 1(d) and 1(e)].

The other relevant arrangement for both BLG-2V and BLG-3V is the anti-ferromagnetic (AFM) state, which is now briefly discussed. By considering the AFM arrangement of spins, we can drastically modify the properties of BLG-2V. The spin conformations of all the BLG-intercalated materials are reported in Table S1 of the [supplementary material](#). Figure 2 shows the band structure and DOSs of the AFM state for BLG-2V. To further analyze the wave function, we calculated a Mulliken spin population analysis. In the case of BLG-2V, the AFM conformation yielded higher spin of individual V atoms, 2.22 and -2.22 compared to the FM conformation, which had a value of 1.86 for each vanadium. Relative to its FM counterpart, the AFM BLG-2V structure is more stable by $\Delta E_f = 0.410$ eV. Examining the electronic properties, we noticed considerable differences in BLG-2V between its AFM and FM states. Once in the AFM state, BLG-2V has a degenerate pair of band structures (for alpha and beta electrons) with a band opening between the valence and conduction bands. The band gaps are 0.101 eV for the indirect transition and 0.681 eV for the direct transition. The most important finding is that by altering the spin to generate the AFM state in BLG-2V, this material becomes a semiconductor, which may be useful for modern electronic devices. Thus, this calculation reveals that a band gap can be introduced in BLG-2V by altering the spin alignment of the intercalated V atoms. The AFM state for BLG-3V was also found, but it was not as interesting as the AFM state of BLG-2V (Fig. S3 of the [supplementary material](#)).

We further extended our studies on the equilibrium structures and electronic properties of niobium (Nb) and tantalum (Ta) intercalated BLG materials (BLG-1Nb and BLG-1Ta) to investigate if the Dirac cone exists in these two materials; see Fig. 3. The structural parameters of both materials are reported in Table I. The DFT calculations found that the intercalation distance d was increased in both materials compared to BLG-1V by at least 0.1 Å, which is consistent with Nb and Ta being larger than V. However, the interaction between the Nb or Ta

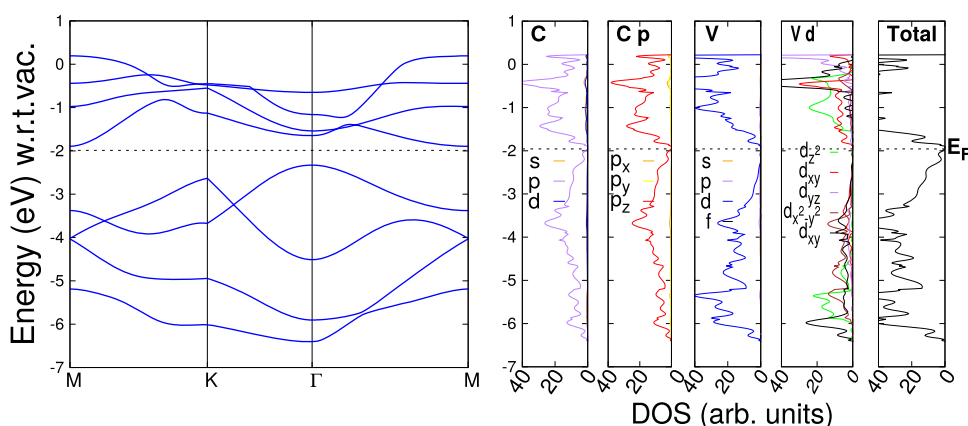


FIG. 2. Band structure and DOSs of the alpha electron in the AFM state for BLG-2V are presented. The beta electrons exhibit identical information. The individual and total components of DOSs of the C and V atoms are also shown. Compared to the FM state, in the AFM state, a band gap appears.

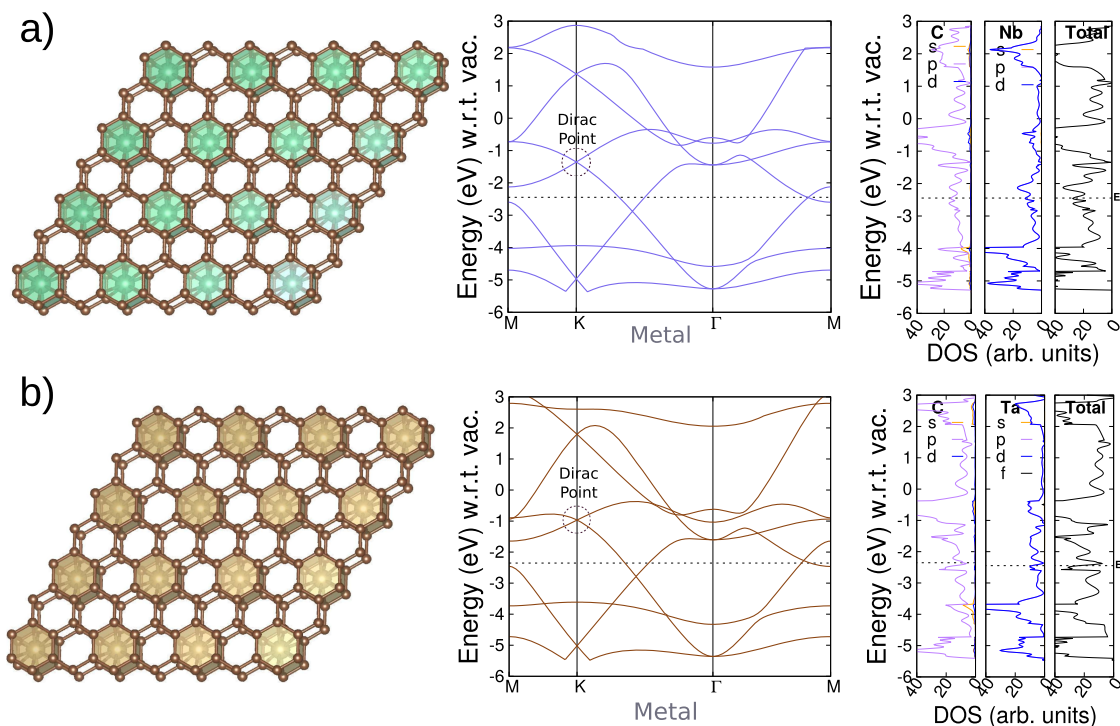


FIG. 3. The optimized structures, band structures, and density of states (DOSs) are shown for (a) BLG-1Nb and (b) BLG-1Ta. The individual components of the DOSs of the C, Nb, and Ta atoms and total DOSs (depicted by “Total”) are also presented in here.

and graphene layers is stronger than that in BLG-1V, as suggested by the ΔE_F shown in Table II. The electronic properties of both materials are shown in Fig. 3. The band structure calculations showed that they have no Dirac cone; instead, the Dirac point moved above the E_F . The total DOSs calculation found that the electron densities were large around the E_F , which arises from the p -subshells of C atoms and d -subshell of Nb and Ta atoms as depicted in Fig. 3. These calculations also showed that they have metallic behavior. In the present study, we considered only one Nb and Ta atom intercalated in BLG because we showed that if the concentration of TM is increased, the Dirac cone disappears [see BLG-2V and BLG-3V band structures in Figs. 1(d) and 1(e)]. Therefore, we excluded the investigation on BLG-2Nb, BLG-3Nb, BLG-2Ta, and BLG-3Ta from this article.

We have investigated why the Dirac cone does not exist in BLG-1Nb and BLG-1Ta, but the Dirac point still does. The BLG-1V, BLG-1Nb, and BLG-1Ta materials have the $p6/mmm$ layer symmetry, which is the same as monolayer graphene. The Mulliken spin population analysis found that the total spin of BLG-1V is 2.082, with vanadium having a spin of 2.245, whereas, the total spins of BLG-1Nb and BLG-1Ta are 1.399 and 1.294, with niobium and tantalum having spins of 1.245 and 1.068, respectively. These calculations suggest that the number of unpaired electrons decreased when we intercalated heavier atoms such as Nb and Ta in bilayer graphene. As a consequence, the Dirac cone moved away from the Fermi level, as shown in Fig. 4. The present DFT calculations found that the band crossing points in the band structures of BLG-1Nb and BLG-1Ta were shifted by 1.003 eV and 1.384 eV, respectively, as depicted in Fig. 4. Thus, the individual unpaired electrons

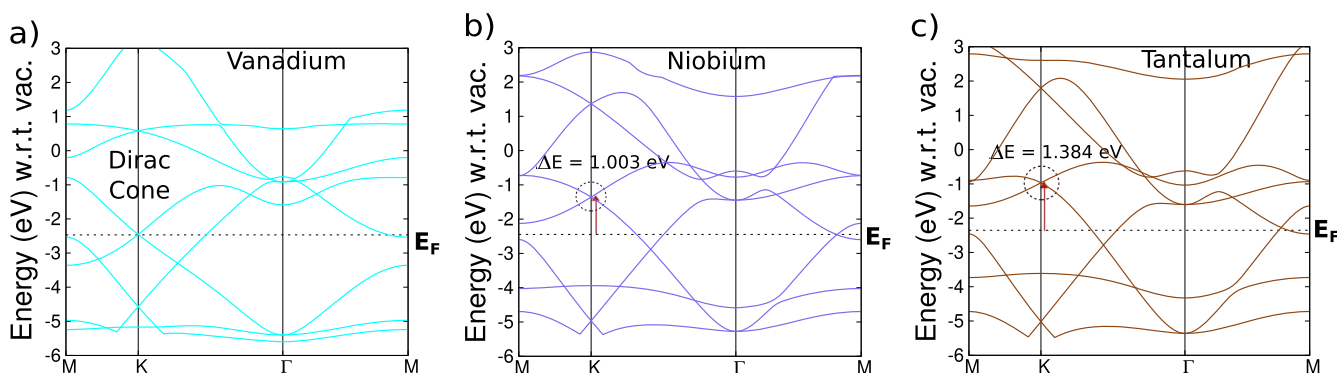


FIG. 4. Comparison of band structures of (a) BLG-1V, (b) BLG-1Nb, and (c) BLG-1Ta showing how the Dirac point remains but is shifted up with respect to the E_F .

of V, Nb, and Ta play an important role the existence of a Dirac cone in the band structures of the BLG intercalated materials. The BLG-2V material lost the $p6/mmm$ layer symmetry; therefore, the Dirac point cannot be present. Additionally, since the concentration of V atoms is increased, the metal features dominate [Fig. 1(d)]. Apart from the spin and symmetry, the concentration of the metal atoms in the BLG system is another important factor. BLG-3V has the same symmetry ($p6/mmm$), but the concentration of V atoms increased; thus, the symmetry allowed it to have graphene features. These features do not show up around the E_F because mostly the TM properties dominate. In other words, it loses the Dirac cone because of the dominance of the TM concentration, as displayed in Fig. 1(e).

The purpose of this article is to suggest the synthesis and predict the properties of these BLG-TM (TM = V, Nb, and Ta) materials and while none of the materials (BLG-1V, BLG-2V, BLG-3V, BLG-1Nb, and BLG-1Ta) studied here have been synthesized experimentally. However, the calculated vibrational frequencies and binding energies predict that these materials are energetically and thermodynamically stable. The frequency analysis and binding energy have been shown enough to demonstrate a material stability like alkali metal atom intercalation graphene and graphite.^{23–27,30,31} Thus, we expect these BLG-TM materials to be readily fabricated experimentally by TM atom intercalation between weakly bound pristine graphene layers. The emerging 2D materials exhibit a wide range of electronic properties, ranging from insulating hexagonal boron nitride (hBN), semiconducting transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), to semi-metallic graphene.⁴⁵ Many experiments provide solid evidence that 2D spaces under the 2D material overlayers can act as stable nanoreactors for molecule adsorption and chemical reactions, which provide intriguing confined spaces for catalysis.^{61–63} Therefore, this study indicates a possible application in nano-confinement technology. Our present study may have future application of highly reliable transition metal atom intercalation in BLG intercalation and it paves the way for graphene as a next-generation interconnect material for a variety of semiconductor technologies and applications.

IV. CONCLUSIONS

We have studied the electronic structure and properties of the 2D-materials: MLG, BLG, and BLG intercalated with transition metals (TM), where the TM = V, Nb, and Ta. The individual components of the p -subshell of the C atoms and the d -subshell of the V, Nb, Ta atoms are reported along with the total DOSs. These materials have favorable binding energy; thus, they might be feasible to synthesize experimentally. Among all the systems, MLG and BLG-1V materials have a Dirac cone at the K-point. Once the concentration of vanadium is increased, the Dirac cone disappears. We have also found that the $2p_z$ sub-shell of C atoms and the $3d_{yz}$ sub-shell of the V atoms in the BLG-1V, BLG-2V, and BLG-3V materials are the main components around the E_F . This plays the main role in the presence of the Dirac cone and the conducting properties. Thus, we have shown that the control of the Dirac cone on the intercalated BLG is a delicate balance between

the amount of unpaired electrons, concentration of the TMs, and symmetry. This means that the layer symmetry ($p6/mmm$) is necessary for the Dirac point to appear in graphene-like materials (BLG-1V, BLG-1Nb, and BLG-1Ta); however, the E_F is controlled by the number of unpaired electrons. In other words, if the concentration of TMs is too high, even having the same symmetry ($p6/mmm$) will not be sufficient to keep the Dirac point at the E_F because the band features will be dominated by the TM. This is clearly shown in how the material properties have been changed in BLG-1V and BLG-3V due to the presence of vanadium atoms with the same symmetry. The nature of the Dirac cone in MLG and BLG-1V is different with the former having p -orbital character, while the latter having p - and d -orbital characters. These materials show how to control a Dirac point and tune it to become a Dirac cone. Thus, this work presents a promising approach to create more Dirac 2D-materials, which may be useful for a carbon-based interconnect technology as well as nano-confinement technology in near future.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for detailed (a) optimized geometry, band structure, and density of states of AA-stacked bilayer graphene; (b) nature of the Dirac cone in BLG-1V; (c) effect of spin alignment on the BLG-3V material; and (d) optimized structures (.cif format).

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