Structural Stability and Electronic and Magnetic Properties of Fluorinated Bilayer Graphene

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ABSTRACT: As a first step toward gaining a microscopic understanding of the fluorination of bilayer graphene (BLG) as the electrode material for lithium-ion batteries, the structural stability and electronic and magnetic properties of fluorinated BLG have been investigated using density functional theory. For the fully fluorinated BLG (CₓFₙ), the chair configuration is found to be energetically more stable than the boat one, while both CₓFₓ's exhibit semiconducting behavior due to the sp²-hybridized C atoms. For the half-fluorinated BLG (CₓFₓ), two configurations, namely, CₓF₁ and CₓF₃, are energetically favored. The electronic characteristics of the half-fluorinated BLG depend sensitively on its atomic configurations. The CₓF₁ exhibits a semiconducting nature, while CₓF₃ is metallic. In addition, the presence of a fluorine vacancy defect in fluorinated BLG is also studied. It is manifested that the nonfluorinated C atoms (sp²-hybridized) in the fluorinated BLGs are of remarkable significance in improving their electrical conductivity.

I. INTRODUCTION

Recently, the fluorides have become more and more important in energy storage and conversion because of their great performance. They have already been introduced in many applications of energy conversion, such as electrolytes for fuel cells and transparent electrodes for solar cells. The carbon fluorides (such as fluorinated graphite, carbon fiber, and coke, CₓFₐ or CₓFₙ), have also manifested themselves to a great extent in the applications in high energy primary lithium batteries. The carbon fluorides as electrode material of lithium batteries were first demonstrated by Watanabe et al. in 1972 and then commercialized by Matsushita Electric Co. in Japan a few years later. The commercialized Li/CₓFₓ (where C represents coke) batteries were able to exhibit many outstanding electrochemical properties such as high energy density (up to 360 W/kg), high average operating voltage (about 2.4 V vs Li⁺/Li), long shelf life (>10 years at room temperature), stable operation ability, and wide operating temperatures (from −40 to 170 °C). Recently, Yazami et al. reported that the energy and power densities are intimately dependent on the F:C molar ratio, and a Li/CₓFₓ (where C represents carbon fiber) battery with x = 0.76 shows the maximum power density of 8057 W/kg, which is about 14 times higher than the one of commercial graphite fluoride. These findings have caused renewed interests in the electrochemical properties of fluorinated ultrathin layers of graphite such as single layer graphene (SLG) and bilayer graphene (BLG). Representatively, Nair et al. reported their experimental findings on the fully fluorinated SLG (named fluorographene). They showed that the fluorographene could inherit the mechanical strength of SLG, exhibit a large Young’s modulus of 100 N/m, and sustain strains of 15%. These prominent properties of fluorographene, together with its chemical inertness and thermal stability (remain stable up to 400 °C even in air), have promised it to be a good counterpart of Teflon.

Recent progress in synthesizing or isolating multilayer graphene films has provided access to understand their physical properties and interesting transport phenomena, including the anomalous quantum Hall effect, the ballistic electron transport at room temperature and the novel many-body couplings. These effects resulted from the effectively massless Dirac fermion, the carriers derived from graphene’s valence bands which exhibit a linear dispersion degenerate near the so-called Dirac point. In addition, their outstanding structural characteristics, such as the high surface area, high chemical stability, and mechanical strength, have also led to their important applications in energy storage devices. The physics of fluorinated BLG are rich and also important; however, to our best knowledge, few studies have been done on the fluorinated BLG. Available studies have been mostly...
dedicated to the BLG’s electronic structures, such as its unique tunable band gap $^{20-22}$ and compressible electron gas. $^{23}$

In this work, besides the BLG’s electronic structures, the structural stability and magnetic properties of the distinctive structural characteristic of fluorinated BLGs are systematically investigated. Due to the fact that the composition of carbon fluorides (e.g., the fluorinated graphite and carbon fiber) experimentally obtained is always a mixture of C$_1$F (fully fluorinated) and C$_2$F (half-fluorinated BLGs), $^{7,24}$ we have therefore focused our investigations on the structural stability and electronic and magnetic properties of only the fully and half-fluorinated BLGs. The importance of the present work can be further emphasized. First, fluorinated graphene is indeed of great importance in materials sciences, and so is the fluorinated BLG. The present work focuses mainly on the structural stability and the electronic and magnetic properties of the fluorinated BLGs. Second, conclusions obtained in this work can be very helpful in the microscopic understanding of the fluorinated carbon and its extent.

II. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were performed by using the projector augmented wave method (PAW) $^{25,26}$ with the plane wave basis set, as implemented in the Vienna Ab initio Simulation Package (VASP). $^{27,28}$ The exchange-correlation energy functional is treated within the local density approximation (LDA). $^{27,28}$ The wave functions are expanded by the plane waves with a kinetic energy cutoff of 450 eV. The Brillouin zone integrations are approximated by using a special $k$-point sampling of the Monkhorst–Pack scheme. $^{29}$ A series of $\Gamma$-centered $k$-point meshes of $15 \times 15 \times 1$, $13 \times 13 \times 1$, and $7 \times 7 \times 1$ are employed for the pristine BLG, C$_1$F, and C$_2$F, respectively. A supercell model is used to simulate an isolated single BLG, where BLGs are supposed to be placed in the $x$–$y$ plane. A vacuum layer of 20 Å in the $z$-direction is chosen so that the interactions between the adjacent BLG are expected to be negligible. All of the atomic configurations are fully relaxed until the Hellmann–Feynman forces on all atoms are smaller than 0.01 eV/Å. Moreover, aiming at understanding the sensitivity of C$_1$F and C$_2$F to the spin-polarized effect, the spin-polarized calculations were first performed. It is shown that both the pristine C$_1$F and C$_2$F are insensitive to the spin-polarization effect; therefore, all of the results presented here are based on the non-spin-polarized scheme except for the cases of C$_1$F and C$_2$F with fluorine vacancy defects where DFT calculations are based on the spin-polarized schemes.

III. RESULTS AND DISCUSSION

Since BLG consists of two single atomic layers of graphene, two configurations (i.e., Hexagonal and Bernal BLGs) for BLG are considered and shown in Figure 1(a) and 1(b), respectively. The calculated lattice parameters, C–C bond lengths, equilibrium interlayer distances, and binding energies of both the BLGs are listed in Table 1, where the binding energy is defined as the total energy per atom of BLG with respect to the atomic energy of carbon. It is shown that the Bernal binding (see Figure 1(b)) is marginally more stable than the hexagonal one by about 5 meV/C (see Figure 1(a)), and the equilibrium interlayer spacing of the Bernal BLG (3.35 Å) is a bit smaller than that of the hexagonal one (3.55 Å). Actually, interactions between two graphene layers in both the Hexagonal and Bernal BLGs are weak van der Waals forces, resulting in their very small binding energy difference. These calculated results of BLGs are in excellent agreement with available studies. $^{22,30}$ On the other hand, both the Bernal and Hexagonal BLGs are semimetal, i.e., gapless semiconductor, and the difference between their band structures can be told from the corresponding two Dirac cones (see Figure 1(c) and 1(d)). The bands are nested for the Bernal BLG but interpenetrated for the Hexagonal one. In this study, because of the higher energetic stability and experimental accessibility $^{20,31}$ of the Bernal BLG than the Hexagonal one, we will mainly focus our attention on the fluorination of BLG in the Bernal configuration.

For the fully fluorinated BLG (C$_1$F), two configurations, i.e., the chair- and boat-C$_1$F, are considered and illustrated in Figure 2. The calculated structural and energetic properties are summarized in Table 2. The chair-C$_1$F is calculated to be more stable than the boat-C$_1$F by about 157 meV/C, and the two graphene layers in both C$_1$F’s are separated by about 5.6 Å. This is well consistent with the case of graphite monofluoride, for which it is believed so far that the chair structure is more favorable. $^{32-36}$ Moreover, in the chair-C$_1$F, the C–F bond lengths are marginally larger, while the C–C bond lengths are distinctly smaller, than the corresponding ones in the boat-C$_1$F (see Table 2), respectively.

To understand the interatomic bonding characters of the fully fluorinated BLGs in both the chair and boat configurations (i.e., chair- and boat-C$_1$F), the deformation charge densities of the specified planes of both the C$_1$F’s are shown in Figure 3, where the range and interval value of deformation charge densities plotted are all the same. The deformation charge

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**Table 1. Calculated Lattice Parameters, C–C Bond Lengths ($d_{C-C}$), Interlayer Distances ($d_{layer}$), and Binding Energies ($E_b$) of the Hexagonal and Bernal BLG**

<table>
<thead>
<tr>
<th>BLG</th>
<th>(a) (Å)</th>
<th>(d_{C-C}) (Å)</th>
<th>(d_{layer}) (Å)</th>
<th>(E_b) (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal</td>
<td>2.449</td>
<td>1.414</td>
<td>3.550</td>
<td>8.973</td>
</tr>
<tr>
<td>Bernal</td>
<td>2.449</td>
<td>1.414</td>
<td>3.350</td>
<td>8.978</td>
</tr>
</tbody>
</table>

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**Figure 1.** Atomic configurations and band structures of: (a), (c) Hexagonal BLG and (b), (d) Bernal BLG, respectively. In panel (b), C atoms in the upper and lower layers are shown in green and gray, respectively.
Table 2. Structural and Energetic Properties of the Fully and Half-Fluorinated BLGs, Including the Lattice Parameters, Inplane C–C Bond Lengths (\(d_{\text{c-c}}\)), C–F Bond Lengths (\(d_{\text{c-f}}\)), Interlayer Distances (\(d_{\text{dy}}\)), Buckled Heights (\(\Delta_z\)), Band Gaps (\(E_{\text{gap}}\)), and Binding Energies (\(E_b\))

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(a/\text{Å})</th>
<th>(b/\text{Å})</th>
<th>(d_{\text{c-c}}/\text{Å})</th>
<th>(d_{\text{c-f}}/\text{Å})</th>
<th>(d_{\text{dy}}/\text{Å})</th>
<th>(\Delta_z/\text{Å})</th>
<th>(E_{\text{gap}}/\text{eV})</th>
<th>(E_b/\text{eV/C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_1)F &amp; (C_2)F</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
<td>[\text{chair-}C_1\text{-F, boat-}C_2\text{-F}]</td>
</tr>
<tr>
<td>(C_1)F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chair-(C_1\text{-F})</td>
<td>2.530</td>
<td>2.530</td>
<td>1.540</td>
<td>1.365</td>
<td>5.592</td>
<td>0.489</td>
<td>2.787</td>
<td>12.588</td>
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<tr>
<td>boat-(C_2\text{-F})</td>
<td>2.570</td>
<td>4.451</td>
<td>1.557 (a), 1.607 (b)</td>
<td>1.362</td>
<td>5.604</td>
<td>0.624</td>
<td>2.705</td>
<td>12.431</td>
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<tr>
<td>(C_2)F</td>
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<tr>
<td>(C_2)F-1</td>
<td>2.552</td>
<td>2.552</td>
<td>1.538 (a), 1.556 (d)</td>
<td>1.361</td>
<td>2.052</td>
<td>0.499</td>
<td>4.037</td>
<td>10.773</td>
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<tr>
<td>(C_2)F-2</td>
<td>2.511</td>
<td>2.511</td>
<td>1.507</td>
<td>1.400</td>
<td>2.727</td>
<td>—</td>
<td>—</td>
<td>10.001</td>
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<tr>
<td>(C_2)F-3</td>
<td>4.955</td>
<td>4.955</td>
<td>1.404–1.518</td>
<td>1.389 (e), 1.386 (f)</td>
<td>4.575</td>
<td>0.568</td>
<td>metal</td>
<td>10.657</td>
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<tr>
<td>(C_2)F-5</td>
<td>4.963</td>
<td>4.963</td>
<td>1.425–1.509</td>
<td>1.391</td>
<td>4.491</td>
<td>—</td>
<td>—</td>
<td>10.344</td>
</tr>
</tbody>
</table>

\(a\) C–C bonds parallel to the \(x-y\) plane. \(b\) C–C bonds parallel to the \(x-y\) plane. \(c\) Interlayer C–C bonds. \(d\) C–F bonds in the interlayer spacing. \(e\) C–F bonds outside the interlayer spacing.

Table 3. Averaged Valence Electrons of Each F and C Atom Obtained by Bader Analysis, for the Chair-\(C_1\)F, Boat-\(C_2\)F, \(C_2\)F-1, and \(C_2\)F-3

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(F_1/\text{(lel)})</th>
<th>(F_2/\text{(lel)})</th>
<th>(C_1/\text{(lel)})</th>
<th>(C_2/\text{(lel)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_1)F</td>
<td>chair-(C_1\text{-F})</td>
<td>7.617</td>
<td>7.613</td>
<td>3.384</td>
</tr>
<tr>
<td></td>
<td>boat-(C_2\text{-F})</td>
<td>7.589</td>
<td>7.588</td>
<td>3.411</td>
</tr>
<tr>
<td>(C_2)F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_2)F-1</td>
<td>7.592</td>
<td>7.592</td>
<td>4.003 (c)</td>
<td>3.405</td>
</tr>
<tr>
<td>(C_2)F-3</td>
<td>7.597</td>
<td>7.601</td>
<td>3.403, 3.994 (d)</td>
<td>3.398, 4.003 (d)</td>
</tr>
</tbody>
</table>

\(c\) \(F_1\) and \(F_2\) are fluorine atoms bonded with \(C_1\) and \(C_2\), respectively. \(d\) Valence electrons of the nonfluorinated C atoms.

Figure 2. Top and side views of \((2 \times 2)\) optimized configurations of the fully fluorinated BLGs in (a) chair and (b) boat configurations, respectively.

Figure 3. Deformation charge densities of the \((11\overline{2}0)\) and \((100)\) planes for the (a) chair-\(C_1\)F and (b) boat-\(C_1\)F, respectively.

Length in chair-\(C_1\)F is smaller than that of boat-\(C_1\)F (see \(d_{\text{c-c}}\) in Table 2).

On the other hand, the electronic total density of states (TDOS) and partial DOS (PDOS) of the chair- and boat-\(C_1\)F are presented in Figure 4. The DOS below the valence band maximum (VBM) is divided into two explicit regions. A distinctive C–F (\(s_p, s_p\)) bonding is exhibited at around \(-25.0\) eV for both \(C_1\)F’s, corresponding to the strong ionic component of the C–F bond. The DOS from about \(-17.0\) eV to VBM is dominated by the C–C sp \(^3\) bond, the C–F (\(p_z, p_z\)) \(\sigma\) and C–F (\(p_y p_y, p_y p_y\)) \(\pi\) bonds, corresponding to the covalent component of the C–F bond.

For the half-fluorinated BLGs, five candidate configurations (i.e., \(C_2\)F-1, \(C_2\)F-2, \(C_2\)F-3, \(C_2\)F-4, \(C_2\)F-5) are considered and illustrated in Figure 5(a) and (b). The first two candidates (i.e., \(C_2\)F-1 and \(C_2\)F-2) represent the case where no F atoms are intercalated into the interlayer spacing of BLG, while the other three candidates (i.e., \(C_2\)F-3, \(C_2\)F-4, \(C_2\)F-5) see Figure 5(c) the case where F atoms are intercalated into the two graphene layers of BLG. Their structural and energetic
properties are summarized in Table 2, where the interlayer distance \( (d_{\text{layer}}) \) is the one between the averaged \( Z \)-coordinates of C atoms of each layer, and the buckled height \( (\Delta z) \) of each layer is the difference between the maximum and minimum \( Z \)-coordinates of C atoms in the layer.

According to the binding energies listed in Table 2, the C\(_2\)F-1 is the energetically most favored configuration for the five models considered. The C\(_2\)F-3 is the most stable structure for the case when F atoms are intercalated into graphene layers of BLG. In the C\(_2\)F-1, the interlayer C–C bond lengths are just a little bit shorter than those in the graphene layer (see Table 2), while the energy required to break the interlayer C–C bonds (which is calculated to be about 4.1 eV) is so large that the C1F might be hardly obtained through further fluorination of C\(_2\)F-1. This is consistent with the experimental results which show that graphite fluoride C\(_2\)F can be formed by a direct fluorination of graphite between 340 and 360 °C\(^3\)\(^7\)–\(^3\)\(^9\) while C\(_1\)F formed between 500 and 550 °C\(^3\)\(^7\). Temperatures above 500 °C could greatly prevent the formation of the interlayer C–C bond of C\(_2\)F-1; therefore, fully fluorinated BLG (C\(_1\)F) could then be achieved by further fluorination of the half-fluorinated BLG (C\(_2\)F-3). Consequently, C\(_2\)F-3, which could only exist at high temperatures (>500 °C), can be considered as an intermediate phase in the formation of C\(_1\)F. Thus, in the general case, all phases with F/C ratio between 0 and 1 have a similar structure, with fluorinated carbons and unfluorinated carbons. The influence of temperature on the structural stability could be significant; however, the present calculations are performed by first-principles technique based on the density-functional theory without considering the temperature factor. Moreover, the C–F bond lengths (1.361 Å) in the C\(_2\)F-1 are almost equivalent to those in the C\(_1\)F, matching also well with the case of graphite fluoride\(^3\)\(^7\),\(^4\)\(^0\). On the other hand, for the C\(_2\)F-3, the intralayer C–C bond lengths are not unique but range from 1.404 to 1.518 Å, where the bond lengths between the non-fluorinated C atoms (1.404 Å) are almost equivalent to those of the pristine BLG (see Table 1). While the C–F bond lengths in C\(_2\)F-3 are found to be a bit larger than those in C\(_2\)F-1. In addition, it is noticeable that the non-fluorinated C armchair chains are presented in C\(_2\)F-3, which plays a critical role in its electrical conductivity as discussed below. Experimentally, the F/C ratio for graphite fluoride of the structure called C\(_1\)F is often greater than one (1.1–1.3) and for the structure called C\(_2\)F is greater than 0.5 (≈0.6). This fluorine excess is normally due to the fluorination of the graphene layer edge\(^3\)\(^7\),\(^4\)\(^1\)–\(^4\)\(^3\). However, the influence of the fluorine excess on the stability of the configurations of both systems C\(_1\)F and C\(_2\)F BLG is still unknown theoretically (before doing a detailed computation).

To see the bonding characters in C\(_2\)F-1 and C\(_2\)F-3, the corresponding deformation charge densities of the (11̅00)
planes are shown in Figure 6. The strong covalent bonds between C–C atoms in the C2F-1 are vividly illustrated by the charge accumulation between the interlayer sp$^3$ C–C atoms as well as the fluorinated and nonfluorinated C–C atoms (see Figure 6(a)). The valence electron obtained by the Bader analysis for the C1 atom (C1 and C2 represent carbon atoms of the two sublattices of graphene, respectively) is almost equal to 4.0 $\text{e}^{-}$ (see Table 3). The bonding characters between C and F atoms are clearly ionic mixed with covalent, which is quite similar to the C–F bonds in the fully fluorinated BLG, C1F. On the other hand, from the total and partial density of states plots for the C2F-1 configurations as shown in Figure 7, the C(s, p$\alpha$)–F(s, p$\alpha$) bond in the C2F-1 contributes to the DOS peaks around the energy of about $-25.0$ eV, while the bands (or DOS) from about $-19.0$ eV to the VBM are dominated by the sp$^3$ C–C and C(p$\sigma$, p$\sigma$, p$\pi$)–F(p$\sigma$, p$\sigma$, p$\pi$) hybridization. Such a bonding character in the C2F-1 is again very similar to the case in the C1F. The C atoms in the C2F-1 are all in the sp$^3$ hybridizations, together with the strong ionic and covalent characters of sp$^3$ C–F bonds, and such a bonding picture consequently leads to the large electronic band gap (>4 eV) of the C2F-1.

For the C2F-3, the fluorinated C atoms are four-coordinated (with three C and one F atoms), while the nonfluorinated C atoms are three-coordinated (with three C atoms), leading to the coexistence of sp$^3$ and sp$^2$ C–C bonds in the C2F-3, as can be seen from Figure 6(b). Besides, there are two types of C–F bonds in the C2F-3, which are characterized by whether they are in the interlayer spacing or not. These C–F bonds are also mainly ionic but mixed with covalent, and the C–F bonds inside the graphene interlayer spacing are somewhat stronger than the other C–F bonds (see Figure 6(b)). The bonding characters of C–F bonds have been further verified by the Bader analysis (see Table 3). On the other hand, from the total and partial DOS plots for the C2F-3 shown in Figure 7(b), it suggests that the bands at around $-25.0$ eV are mainly contributed by the C(s, p$\pi$)–F(s, p$\pi$) bonding, while the bands from about $-18.0$ eV to the Fermi level are contributed by the C–C sp$^3$, C–C sp$^3$, and C(p$\sigma$, p$\sigma$, p$\pi$–F(p$\sigma$, p$\sigma$, p$\pi$) bonding. Therefore, in the C2F-3, all the electrons are well bonded, and their states are below the Fermi level, except for the p$\pi$ electron orbitals of the nonfluorinated C atoms. The DOS at the Fermi level is shown to be mostly contributed by the C$p\pi$–C$p\pi$ $\pi$ bonding between the nonfluorinated C atoms, which is also responsible for the metallic behavior of the C2F-3.

Experimental results suggest that the fluorine atoms in the carbon fluoride, even in a small amount, is shown to favor higher electron flow. Therefore, the sp$^3$-hybridized nonfluorinated C atoms, but not the sp$^3$-hybridized fluorinated C atoms (they are well bonded), are shown to be propitious for the conductivity of C2F. Whether or not the nonfluorinated C atoms are beneficial to the electrical conductivity of fluorinated BLG is closely dependent on their hybridizations.

It is well-known that the defect states play significant roles in the semiconductor physics. What is more, defects (or impurity) are always there in the samples synthesized in many experiments, and we therefore further studied the fluorinated BLG with fluorine vacancy defects ($F_{\text{vac}}$). For the cases of chair-C1F, boat-C1F, C1F-1, and C1F-3 systems, (3 $\times$ 3), (2 $\times$ 2), (3 $\times$ 3), and (2 $\times$ 2) supercells are employed to calculate the corresponding systems with $F_{\text{vac}}$, respectively. In these configurations, the smallest distances between the nearest neighboring $F_{\text{vac}}$ are all larger than 5.1 Å. One $F_{\text{vac}}$ corresponds to one more nonfluorinated C atom which is denoted as C$^{\text{vac}}$ hereafter. The calculated spin-polarized total DOSs of the chair-C1F, boat-C1F, C1F-1, and C1F-3 with $F_{\text{vac}}$ are presented in Figure 8(a)–8(d), respectively. For the chair-C1F and boat-C1F with $F_{\text{vac}}$, the systems again exhibit semiconducting behavior; however, defect states are introduced in the band gaps. Moreover, both the chair- and boat-C1F’s are magnetic with the same magnetic moment of about 1.0 $\mu_B$. The spin-polarized charges in both the chair- and boat-C1F’s with $F_{\text{vac}}$ are mostly contributed by the p$\sigma$ electrons of the C$^{\text{vac}}$ atoms. The induced magnetic moments in the two systems can be reasonably understood from the perspective of their structural and electronic characteristics. Since the p$\sigma$ electrons of C$^{\text{vac}}$ atoms

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**Figure 7.** Total and partial density of states for (a) C2F-1 and (b) C2F-3 configurations, respectively.

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in both the C₁F’s with F vac are “unpaired” (i.e., being the dangling bond states), it is expected that the pₓ states of C atoms will fall in the energy gaps, and the local characteristics of such pₓ electrons could induce magnetic moments easily in both the chair- and boat-C₁F’s.

For the half-fluorinated BLGs, in which half of the C atoms are nonfluorinated, it is noticeable that the C₂F-1 with F vacancies introduces defect states at the Fermi level, as can be seen from Figure 8(c). Moreover, for the C₂F-3 with F vacancies, more states are introduced in the band gap (around and above the Fermi level), as shown in Figure 8(d). From Figure 8, the C₂F-1 and C₂F-3 with F vac are both magnetic while in different magnetic configurations. For C₂F-1, all of the nonfluorinated C atoms are four-coordinated except for the C_F atoms (created due to the presence of F vacancy) which are three-coordinated, and the spin-polarized charges around the Fermi level are then mostly contributed from the pₓ states of C_F atoms, which could also lead to the induced ferromagnetic moment of about 1.0 \(\mu_B\) (see also the inset of Figure 8(c)). However, for the C₂F-3, in which all the nonfluorinated C atoms are three-coordinated, the spin-polarized charges of C₂F-3 with F vac are contributed by the pₓ states of both the originally nonfluorinated C and the C_F atoms (when F atoms are extracted, Figure 8(d)). Then, these spin-polarizations in the C₂F-3 with F vac are arranged in an antiferromagnetic way along the armchair C chains; namely, the majority and minority spin states are alternately arrayed in the two sublattices of the nonfluorinated C chains. Such a magnetic pattern can be understood from the distributed defect states over the sites of the sublattice along the nonfluorinated C chains and the exchange interactions in such systems. For Figure 8(d), not only could the nonfluorinated C atoms (those when F atoms are extracted) lead to magnetic moment but also these C atoms could induce magnetism on the C atoms which are originally nonfluorinated. Furthermore, the bands (DOS) around/across the Fermi level in both the C₁F’s and C₂F’s with F vac suggest that the existence of fluorine vacancies should be helpful for improving the electrical conductivities of the fluorinated BLG.

IV. CONCLUSIONS

We have performed the first-principles calculations on the structural stabilities and the electronic and magnetic properties of the fluorinated bilayer graphenes. For the fully fluorinated BLGs, two configurations, i.e., the chair- and boat-C₁F, are studied. It is shown that both C₁F’s are semiconducting, with the chair-C₁F energetically a bit more stable than the boat one by about 157 meV/C. All of the C atoms in both C₁F’s are in sp³ hybridizations, resulting in their semiconducting properties. For the half-fluorinated BLGs, five candidate configurations are considered. Two energetically favorable configurations, i.e., C₂F-1 and C₂F-3, are found according to the calculated binding energies. The electronic characteristics of the half-fluorinated BLGs are shown to depend sensitively on their atomic configurations. The C₁F-1 is presented to be semiconducting with a very large band gap of about 4.037 eV, which results from the coexistence of sp³ C–C and C–F bonds. However, the C₂F-3 exhibits a metallic behavior with the electronic states at the Fermi level mainly contributed by the nonfluorinated C atoms (sp²-hybridized). Furthermore, the property of existence of fluorine vacancy defect in fluorinated BLG is also studied. It is manifested that the electrical conductivities of both the C₁F’s and C₂F’s could be improved when the fluorine vacancies are involved, due to the existence of nonfluorinated C atoms (sp²-hybridized).
This is a scientific paper discussing various topics related to lithium batteries, fluorinated carbon nanofibers, and other related materials. The references are cited in the text, and the authors declare no competing financial interest.

**REFERENCES**


