Native defects in hybrid C/BN nanostructures by density functional theory calculations

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First-principles calculations of substitutional defects and vacancies are performed for zigzag-edged hybrid C/BN nanosheets and nanotubes which recently have been proposed to exhibit half-metallic properties. The formation energies show that defects form preferentially at the interfaces between graphene and BN domains rather than in the middle of these domains, and that substitutional defects dominate over vacancies. Chemical control can be used to favor localization of defects at C-B interfaces (nitrogen-rich environment) or C-N interfaces (nitrogen-poor environment). Although large defect concentrations have been considered here ($10^6$ cm$^{-1}$), half-metallic properties can subsist when defects are localized at the C-B interface and for negatively charged defects localized at the C-N interface; hence the promising magnetic properties theoretically predicted for these zigzag-edged nanointerfaces might not be destroyed by point defects if these are conveniently engineered during synthesis.

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I. INTRODUCTION

Hybrid C and BN nanostructures have been studied since the first attempts to dope carbon nanotubes with boron or nitrogen.\(^1\) Nanotubes (NTs) with C, B, and N were theoretically predicted\(^2\) and experimentally synthesized in the mid-1990s,\(^1,3–5\) but the recent advent of graphene has revitalized the field. Hybrid C and BN nanosheets are becoming accessible,\(^6,7\) offering a new route to enhance graphene’s promise, enabling the fine-tuning of the electronic and optical properties (for example, modulation of the electronic band gap, chemical reactivity, etc.).

Following the advances in experimental growth of hybrid C-BN nanostructures,\(^7,9\) the stability of domain-separated C and BN nanosheets and nanotubes has been studied by first-principles simulations in the last few years.\(^10–14\) There is general agreement that segregation is energetically advantageous, because B-N and C-C bonds are more stable than C-N and C-B bonds and the former are favored by the formation of C and BN domains. Furthermore, according to molecular dynamics simulations, hybrid C-BN armchair nanotubes can be spontaneously formed via the connection of zigzag-edged BN and graphene nanoribbons (BNNRs and GNRs) at room temperature,\(^11\) and their stability can be competitive with that of the corresponding pristine BN and C nanotubes (BNNTs andCNTs).\(^14\) These zigzag-edged heterostructures are particularly appealing for spintronic applications, as the polarity of the BNNR gives an interfacial dipole and hence an effective electric field acting on the graphene ribbon.\(^15\) It has been predicted that half metallicity can be induced in zigzag GNRs by application of a sufficiently large in-plane electric field perpendicular to the edges of the ribbon.\(^16\)

Magnetism in zigzag-edged graphene-based nanostructures is related to the presence of electronic states that are mainly localized at the edges.\(^17\) These states seem to be ubiquitous in hexagonal structures with zigzag borders\(^18\) and are not present in armchair edges. Roughness and defects have been shown to strongly affect the electronic properties of zigzag GNRs, inducing a continuous decrease of the magnetic moments with increasing concentration of defects until the system becomes nonmagnetic for concentrations of one defect per ~10 Å, which might be a typical concentration for real samples.\(^19\) Nevertheless half metallicity induced by external electric fields seems to survive at similar defect concentrations with the same critical field strength.\(^16\) At zigzag interfaces between C and BN domains, however, defects can change the electronic screening of the edge polarity, hence affecting the effective electric potential on graphene’s ribbon and destroying its intrinsic half metallicity. It is then important to address the role played by point defects at the boundary between graphene and BN domains. In this work, first-principles simulations are performed to determine the formation energies and electronic properties of intrinsic point defects (vacancies and substitutional defects) at zigzag interfaces between C and BN nanodomains that could exhibit magnetism. It is shown that these defects are energetically favored when localized close to domain interfaces, and their electronic properties are determined by the presence of a defect-induced electronic state localized at the C-N interface which could be occupied or empty depending on the donor or acceptor nature of the defect.

The paper is organized as follows. After describing the technicalities in Sec. II, we present and discuss the findings in Sec. III. Results of the energetics of neutral defects at the interfaces are examined and compared to similar defects placed at a graphenelike or BN-like monodomain. Magnetism at the interfaces and other electronic properties are then analyzed and the effect of defect concentration and charge state discussed. Finally, Sec. IV summarizes the conclusions.

II. METHODOLOGY

\textit{Ab initio} pseudopotential density functional calculations are performed for both planar \textit{(two-dimensional (2D)) superlattices}\(^15\) and \textit{(n, n)} armchair nanotubes \textit{(5 ≤ n ≤ 14)} with zigzag-edged C-BN domains along the tube axis following the geometries discussed in the literature.\(^11,12,14,20\) Troullier-Martín-type pseudopotentials\(^21\) and numerical atomic orbitals with double-\(\zeta\)-plus polarization are used to describe the electronic valence states within the spin-polarized generalized-gradient approximation\(^22\) as implemented in the \textsc{fiesta} code.\(^23\) The atomic positions
In terms of the chemical potentials of the species involved in the defect and the Fermi level $\mu_e$ measured relative to the top of the valence band $E_v$:

$$E_f(X) = E_{\text{tot}}(X) - \sum_i n_i \mu_i + q(\mu_e + E_i),$$  \hspace{1cm} (1)

where $E_{\text{tot}}$ is the energy of the defective supercell containing $n_i$ atoms of species $i$ (C, B, and N) with chemical potential $\mu_i$, at $T = 0$ (entropic contributions are neglected). These chemical potentials are specified by a reference system that acts as the reservoir of atoms. Typically, reference values used in the literature are taken from graphene, molecular nitrogen, and bulk boron. These, however, will give formation energies only in the limits of high concentrations of C, N, or B. Formally, one can use the formation energies of these reference systems as thermodynamic limits to the chemical potentials, which must satisfy the following conditions:

1. stability of the C-BN complex:
   $$\mu_C + \mu_B + \mu_N = \Delta E_f(CBN);$$  \hspace{1cm} (2)
2. the values that cause precipitation into its constituents,
   $$\mu_C \leq 0, \mu_B \leq 0, \mu_N \leq 0;$$
3. the values that cause formation of each domain,
   $$\mu_B + \mu_N \leq \Delta E_f(BN),$$
   $$\mu_C \leq \Delta E_f(C),$$

where $\Delta E_f$ denotes the generalized formation free energy of the corresponding system relative to a pure C or BN nanotube. Relation (2) can be used to write one of the atomic chemical potentials in terms of the other two. Considering that C doping in BNNTs has proved elusive, whereas BNNTs can be synthesized by substitutional reaction from CNTs, in the following the chemical potential of C will be set to the value that corresponds to a clean CNT, meaning that the defect formation energies will be given in the C-rich limit. Equation (2) is then used to express $\mu_B$ in terms of $\mu_N$, which will be used as a free parameter, with values ranging between precipitation into molecular nitrogen (N rich, or condition 2 above) and the poorest nitrogen atmosphere that, nevertheless, allows for h-BN growth (condition 3).

### III. RESULTS AND DISCUSSION

Substitutional carbons on the boron and nitrogen sublattices (C$_B$ and C$_N$), boron or nitrogen atoms in carbon sites (B$_C$ and N$_C$), and vacancies of each species (V$_C$, V$_B$, and V$_N$) were considered, as shown in Fig. 2. Ghost orbitals are used to improve the localized atomic orbital description at the (unreconstructed) vacancy sites. The labels $N$ and $B$ will be used to denote the edge at which the defect is placed, where $N$ designates the interface with C-N bonds, whereas $B$ is the edge with C-B bonds. Accordingly defects are classified into set $N(C_N, B_C, V_N^N, V_B^N, or V_C^N)$, and set $B(C_B, N_C, V_N^B, V_B^B, or V_C^B)$.

The formation energies for the interfacial (neutral) defects in a (5,5) C-BN nanotube are shown in Fig. 2 and compared to the energetics of the same defects in a pristine pure CNT and pure BNNT of the same chirality. The energies of pure C and BN nanotubes are in agreement with values...
FIG. 2. (a) Atomic positions considered for the different defects. Circles, filled squares, and empty squares denote C, B, and N atoms. Periodic boundary conditions require that both C-N and C-B edges are included in the simulation box. The arrow indicates the axis of the unit cell and 2D nanosheets (dashed lines) with seven repetitions of the unit cell and 2D nanosheets (dashed lines) with seven repetitions of the unit cell, and (d) BN nanotubes with (5,5) chirality.

FIG. 3. Density of states (DOS) around the Fermi level (at 0 eV) for defects localized at the C-N (top) and C-B (bottom) interfaces. Dark shaded regions correspond to the projected DOS (PDOS) on C orbitals localized at the N interface. Gray regions for $V_C^N$ and $V_B^N$ are the PDOSs on C or N orbitals close to the C or B vacancy, respectively.

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published in the literature, considering that the formation energy depends on the chirality and increases with tube’s diameter. The cost of removing atoms (vacancy formation) is generally larger than the energy of atom substitution (disorder), which is indicative of the high stability of the honeycomb structure. First-principles calculations have shown that vacancy formation is energetically more favorable near the edge of zigzag BNNRs than in the center of the ribbon. A similar effect is observed now, with defects at the edge being at least 1 eV less energetic. Interestingly, recent experiments have shown that carbon substitution (doping) in BN nanostuctures is favored at the edges.

Note that $V_C$ and $V_B$ (defects of set $N$) are energetically favorable in a nitrogen-poor environment (B rich), and the same is true for $N_C$ and $N_B$ (set $B$) in a N-rich situation, so that the localization of defects at each edge of the heterojunction could be chemically controlled. Furthermore, when neutral $N_C$ and $B_C$ defects are formed, one hole is added to the system, so that these defects can act as electron traps. On the other hand, $N_C$ and $B_B$ add one extra electron to the system and could possibly become positively charged under appropriate conditions (low electron chemical potential $\mu_e$). In pure BN nanosheets and nanotubes, $V_B$ is also an acceptor that can trap charges to form $V_B^-$, whereas $V_N$ has two one-electron states in the gap, one occupied and the other empty, enabling the formation of either $V_N^+$ or $V_N^-$, depending on the value of $\mu_e$. Figure 3 shows the electronic density of states (DOS) for set $N$ (top) and set $B$ defects. Let us first discuss the latter type of defect (set $B$). Notice that, even for the high defect concentration considered in these simulations ($5 \times 10^9$ cm$^{-1}$), the system remains half metallic, with a sharp peak in the DOS at the Fermi level. This peak corresponds to a defect-induced electronic state that is localized at the $N$ edge rather than at the defect itself (placed at the $B$ edge). Hence, electrons coming from these donor defects are transferred through the C domain to the region with lower electronic potential, as described in Ref. 15. This can be seen from the DOS projected on the carbon orbitals localized at the C-N interface (shaded regions in the figure). This localized band has some dispersion along the edge axis (there is slightly more contribution to the PDOS from the left than from the right). The exchange splitting for this band is $\sim 0.3$ eV for all the set $B$ defects, and the calculations give a total magnetic moment of $\sim 1 \mu_B$ for $V_B$, $N_B$, and $V_B^N$, $2 \mu_B$ for $V_B^B$, and $\sim 3 \mu_B$ for $V_B^-$. Notice, however, that the supercell approach used here might not be appropriate to describe the long-range magnetic interactions between these defect-induced localized magnetic moments.

On the other hand, the missing electron (extra hole) for set $N$ defects has a dramatic effect on the corresponding DOS, which does not show half-metallic properties. There is a similar defect-induced electronic state localized at the C-N interface for $N_C$, $B_C$, and $V_C^N$, but now it is unoccupied ($\sim 0.1$ eV above the Fermi level) and not spin polarized ($C_N$ and $B_C$ have total magnetic moments of $\sim 0.5 \mu_B$). $V_N^C$ and $V_B^N$ are slightly different, with an empty C-N interfacial state at $\sim 0.4$ eV above the Fermi level and a rather localized electronic state on the atoms surrounding the vacancy site (shaded light regions in the figure), which is spin polarized (total magnetizations of $\sim 1.8 \mu_B$ and $1 \mu_B$, respectively. The
FIG. 4. Density of states for substitutional defects as a function of defect concentration for planar C/BN superlattices (similar results are obtained for nanotube geometries). From left to right, supercells with three, four, and seven units of repetition along the interfacial axis, corresponding to concentrations of $13 \times 10^6$, $10 \times 10^6$, and $6 \times 10^6$ cm$^{-1}$. Dark and light shaded regions correspond to projected DOSs over C orbitals at the N/B interface.

lowering of the Fermi level means a partial depopulation of the $\pi_B$ state and a weakening of the magnetic instability induced by electron-electron interactions. The reduction of the electronic occupation of the $\pi_B$ state lowers the electronic potential at the B edge and significant decrease of the induced electric field in the graphene ribbon, so that half metallicity cannot survive.

Let us focus in the following on those defects that have the lower formation energies, i.e., substitutionals. The effect of increasing the defect concentration even further is shown in Fig. 4, where the DOSs of different supercells of planar bidimensional superlattices are shown. Small differences arise between this planar geometry and the previous tubular case, mainly because of the different C:BN ratio, but the general results are equivalent. For $p$-type set $N$ defects (BC and CN), the reduced number of electrons shifts the Fermi level toward lower values as we move toward higher defect concentrations (smaller supercells, from right to left), depopulating the initially fully occupied majority spin band, localized at the C-B interface (light shaded region), until the full spin polarization at the Fermi level is destroyed. On the other hand, for $n$-type set B defects (NC and CB), the extra electrons added to the system shift the Fermi level to higher values as we move toward higher concentrations, increasing the occupation of the C-N electronic states, and eventually destroying half metallicity. Notice again that defects localized at the C-B interface add extra electrons that are transferred to the C-N interface, while defects localized at the C-N interface, which are electron deficient, tend to remove charge from the C-B interface.

For the limit of low concentration of defects, the semimetallic graphene domain could be considered as the electron reservoir so that $\mu_e$ is fixed by the position of the GNR’s Fermi level, and hence only neutral defect calculations were considered up to now. However the donor or acceptor character of the defects became relevant when discussing their electronic properties, revealing the need to address charged defects. When charge states for defects in semiconductors and insulators are addressed, the value of $\mu_e$ in Eq. (1) ranges between zero (the top of the valence band) and the energy band gap, and a careful alignment of the reference energy has to be considered to compare energetics of neutral and charged defects. Here, however, the system is semimetallic regardless of the charge state, so that the position of the Fermi level can be used to align the energetics, and $\mu_e = 0$ can be used to compare formation energies.

As shown in Fig. 5, when an extra electron is added to the system ($q = -1$), it localizes at the N-edge state (dark peaks) close to the Fermi level, recovering half metallicity for the set $N$ defects (the states become fully occupied for set $B$ defects which remain half metallic). The formation energies for these charged defects are reduced by $\sim 2.3$ eV (at $\mu_e = 0$ eV).
There is a decrease in the system’s total magnetization for set $N = -0.1 \mu_B$ and an increase to $2 \mu_B$ for set $B$. On the other hand, removal of an electron (giving defects with charge state $q = +1$) has negative effects on the electronic properties of substitutionals: the lowering of the Fermi level depopulates the $N$-edge state for set $B$ defects (although the total DOS remains half metallic), and destroys magnetization for all defects (set $N$ remains metallic). In this case, the formation energies are increased by $\sim 3.6$ eV, clearly destabilizing these positively charged defects.

Following the above results, a N-rich environment together with a high $\mu_e$ (providing electrons to the system) would increase the possibilities for subsistence of half metallicity in these hybrid C-BN structures. $B$-edge localized defects are favored by an N-rich atmosphere, and even at large defect concentrations ($10^6$ cm$^{-1}$) conducting electrons remain fully spin polarized. On the other hand, under these chemical conditions, there will be a lower concentration of defects localized at the $N$ edge (higher formation energies), which although they hinder half metallicity when neutral do not in their negative charge state. It is interesting that similar conditions have been suggested to be best for manufacturing hybrid compounds through electron-beam-induced doping of BN nanostructures with C.

IV. CONCLUSIONS

First-principles density functional theory calculations have shown that intrinsic defects in hybrid C-BN nanostructures are more stable at the boundaries between C and BN domains. Both bidimensional superlattices of alternating graphene and BN nanoribbons and armchair nanotubes with axial domains of C and BN that have zigzag edges have been analyzed, giving similar results. In these systems, the electronic band structure close to the Fermi level is determined by characteristic zigzag-edge states localized at the boundary of the hexagonal lattice, as already discussed in the literature.

The stability of the honeycomb structure results in a higher formation energy for vacancies ($V_C$, $V_B$, or $V_N$) than for substitutionals. While a nitrogen-poor environment favors the formation of defects at C-N interfaces (mainly $C_N$ and $B_C$), nitrogen-rich atmospheres favor defects localized at the C-B boundary ($C_B$ and $N_C$), which can be classified as electron acceptors and donors, respectively. Extra electrons provided by the latter are transferred to a defect-induced partially occupied electronic state localized at the opposite edge (C-N) and the system remains half metallic, even for the large defect concentrations considered here. If extra electrons are added to the system, they are transferred to this electronic state, and the defects are further stabilized (in their negatively charged state), whereas electron deficiency drains the electronic level and increases the defect formation energy. On the other hand, substitutional defects localized at the C-N interface add one hole to the system, hence lowering the Fermi level and weakening the magnetic instability (through depopulation of the $\pi_{C_B}$ orbital), resulting in the cancellation of half metallicity. The defect-induced electronic state localized at the C-N interface is still there, but unoccupied. Extra electrons added to the system will populate this level, recovering half metallicity and lowering the defect formation by a few eV.

Finally, the analysis of the magnetic properties reveals that half metallicity (i) could survive defect concentrations at the interfacial line of up to $10^7$ cm$^{-1}$, and (ii) could be tuned through appropriate electronic doping that avoids an excessive charge depletion from the C-B interface for high concentrations of $p$-type substitutionals or excessive charge increase at the C-N interface for $n$-type substitutionals. Experimental investigation of magnetism in these hybrid nanostructures is encouraged.

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C doping can be achieved in BN nanosheets and nanotubes through in situ electron-beam irradiation as a postsynthesis process (Ref. 9).

Single vacancies in graphene undergo a Jahn-Teller distortion leading to the formation of five-membered and nine-membered rings. Neither these (5-9) defects nor other reconstructions such as Stone-Wales defects were considered here.