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Ferromagnetism at the edges of the stacked graphitic fragments: an ab initio study

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Abstract

We carry out first-principles density functional calculations to investigate electronic and magnetic structures of the stacked graphitic fragments. Ferromagnetically ordered ground states are found to be stable in the zigzag edges of an isolated graphene, regardless of whether or not the edges are passivated with hydrogen atoms. However, the localized moments in the hydrogen-terminated edge vanish upon stacking the graphite fragments. Interlayer and inter-edge interactions are investigated in detail, and it is found that dangling bonds are indispensable to the formation of the ferromagnetism at the edges of the stacked graphitic fragments.

The observations of magnetic signals in the doped fullerenes [1] and in the highly oriented pyrolytic graphite (HOPG) [2], have prompted numerous research works toward understanding as well as synthesizing the carbon-based magnetic systems [1,3]. Diverse experimental results include spin-glass-like state [4], paramagnetic state [5], and ferromagnetic (FM) state [2,6,7]. Among them, the observation of the stable ferromagnetism in the glassy carbon [7] as well as in the polymerized C_{60}'s [8] have revived the long-pending questions about the intrinsic ferromagnetism in the carbon systems. Meanwhile, researchers have investigated the ferromagnetism of graphite nodule in meteorite [6] and cautioned that some of the carbon ferromagnetism claimed so far might have extrinsic origins. The recent report of ferromagnetism in the proton-irradiated graphites [9] is thought to be another piece of evidence for the possible magnetic ordering in a graphitic sample without magnetic impurities.

In parallel with experimental findings, there have been a series of theoretical studies on the magnetism in carbon systems, especially in the graphitic fragments. An earlier work based on the π-orbital tight-binding model [10] revealed the localized states at the zigzag edge, which leads to flat bands at the Fermi level. Subsequent first-principles calculations [11–13] demonstrated that the Fermi instability, arising solely from the localized π-orbital states, could result in the magnetically ordered edge states. It was shown that the ferromagnetically ordered spins along one edge have the opposite direction to the direction of spins at the other edge [12]. However, it remains as an open question whether these edge-localized spins could make a measurable contribution to the bulk magnetism.

In this Letter, we carry out ab initio calculations to study the stacking effect on the magnetism localized at the graphitic edges. We show that the presence of dangling bonds is a crucial factor in the formation of a magnetic moment in pure carbon systems. While the

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magnetic ground states are found to be most stable in the hydrogen-terminated edges of the isolated graphene sheet, it is shown that the localized spin moment in these edges disappears upon stacking of the graphitic fragments. Nevertheless, the interlayer interactions between the edges with dangling bonds are found to favor ferromagnetic ordering of the edge magnetic moments.

We perform ab initio calculations based on the density-functional theory (DFT) [14,15] by using the plane-wave basis set with PWSCF package [16]. The ultrasoft pseudopotentials [17] are employed for the ionic potential and the local spin density approximation (LSDA), parameterized by Perdew and Wang [18], is used for the exchange-correlation potential. The kinetic energy cutoff for the plane-wave basis is set to 30 Ry throughout the calculations. For the graphitic fragment, we choose a one-dimensional strip as a model geometry as illustrated in Fig. 1. The graphitic strip is chosen to have the zigzag shape at both sides of the edges [19] and a periodically repeated unit-cell, which is so-called a supercell method commonly used in the electronic structure calculations. In order to allow for an antiferromagnetic ordering along the edge of the strip, we choose the unitcell along the x-direction as twice the minimal unit-cell of the strip, as indicated by the dashed lines in Fig. 1. Along the directions perpendicular to the strip direction (i.e., y- and z-directions in Fig. 1) the unit-cell dimensions are set to be large enough that the smallest distance between atoms in the neighboring cells, i.e., the length of the vacuum region is larger than 10 Å. In the later part, we perform the calculation for the stacked fragments by fixing the interlayer distance (along z) to 3.335 Å, which corresponds to the inter-layer separation of bulk graphite. For the finite number of stacked layers, we also include a vacuum region (larger than 10 Å) between the stacked fragments along the z-direction. The width of a strip is denoted by the number of zigzag chains parallel to the strip direction (i.e., the x-direction). In Fig. 1, we have the strip of width $W = N$ where the zigzag chains are numbered from left to right. The integration over the Broulline zone (BZ) is performed with the uniformly sampled 30 k-points along the strip direction.

We first calculate the electronic structure of the isolated graphitic strips with hydrogen passivation at both edges. The computational results are found to be consistent with the previous first-principle works. [11,12]. The flat bands arise from the localized π-orbital state at the edge, as discussed by Fujita et al. [10], and extend over a range of BZ, $2\pi/3 \leqslant |k| \leqslant \pi$. The π-orbital flat bands split into the spin-up (occupied) and spin-down (unoccupied) levels, thereby leading to the magnetic ground state with the exchange splitting $\Delta_\pi \approx 0.2$ eV for the strip of width $W = 6$.

Considering the magnetic structure of graphitic strip without hydrogen-passivation, i.e., with dangling bonds remaining at the edge atoms, there exist several self-consistent solutions with different spin configurations: (i) ferromagnetically ordered spins at both edges in the same direction, to be denoted by FM-F, (ii) another ferromagnetically ordered spins at the opposite edge but with opposite direction to the spin ordered in the other edge, to be denoted by FM-A. (iii) anti-ferromagnetically ordered spins in each edge, respectively, to be denoted by AF-E. We also perform the spin-unpolarized calculation and denote the corresponding electronic structure by PM. Fig. 2 shows the band structure of the FM-F case with $W = 8$. The flat bands marked by triangles in Fig. 2a,b originate from the edge-localized π state as described in the above. We recall that the unit-cell here is twice that of the simple graphene ribbon, and the flat π bands at the zone boundary are now folded into the Γ point. These is another set of flat bands derived from the dangling-bond states, which are marked by circles in Fig. 2a,b. The number of dangling-bond orbitals in the unit-cell is four, and so is the number of the circled bands. The circled bands in Fig. 2a are doubly degenerate, whereas all four bands in Fig. 2b are nearly degenerate. It is remarkable to

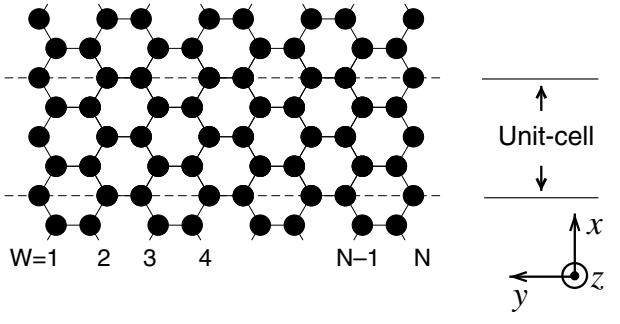

Fig. 1. The graphitic strip of width $W = N$. The region between two dashed lines indicates the unitcell along the strip. The indices $W = 1,2,\ldots,N$ count the columns of the zigzag chains parallel to the strip direction, i.e., x-direction.

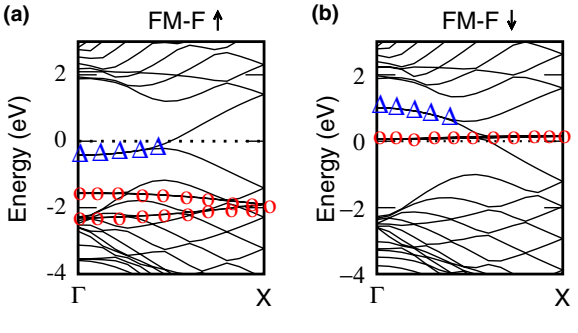

Fig. 2. The band structure of the graphitic strip with dangling bonds at the edges. (a) and (b) are for the majority and minority spin of the FM-F case with $W = 8$, respectively. The Fermi level is set to zero. The circled bands in (a) have twofold degeneracy and the circled band in (b) has fourfold degeneracy.

observe that the exchange splitting of the dangling-bond states, Δ_σ, and the localized π-orbital states, Δ_π, are $\Delta_\sigma \approx 2.0$ and $\Delta_\pi \approx 1.2$ respectively, where the exchange interaction for the π-orbital is vastly enhanced over the case with H-passivations, e.g., $\Delta_\pi \approx 0.2$.

In Table 1, we compare the total energies of the strips of $W = 8$ in various spin configurations. It is found that the ferromagnetic ordering along the edge (FM-F, FM-A) is strongly favored. By increasing the width of the strip ($W = 4$, 6, 8, 12), the energy difference between the FM-A and FM-F cases gradually decreases as the width increases. These calculated results are consistent with the previous work [12] which shows FM-A is the ground state. The subtle differences in the total energy and magnetic moments of FM-F and FM-A can be understood in terms of the sub-lattice magnetic polarization due to the edge-localized π-orbital states [12]. The exchange energy gain in the magnetic sub-lattice structure of FM-A are attributed to the lower total energy and the larger magnetic moment of the FM-A in comparison with those of the FM-F. Magnetic moment of the system is obtained by calculating the difference between the numbers of spin-up and spin-down electrons.

Table 1
Total energies and magnetic moments of the graphitic strip of width $W = 8$

Configuration	Total energy (meV/edge atom)	Magnetic moment (μ_B/edge atom)
FM-F	2.3	1.19
FM-A	0.0	1.28
AF-E	81.4	0.82
PM	239.9	0.00

Total energies are measured with respect to that of the FM-A case.

As the whole band of the dangling-bond states is splitted below and above the Fermi level as shown by red circles in Fig. 2a,b, each atoms at the edge acquires the magnetic moment of 1 μ_B. In addition, the contribution to the magnetization by the edge-localized π states is also substantial so that the FM-F and FM-A cases can have larger magnetization than 1 μ_B per edge atom, as shown by blue triagles in Fig. 2.

Now we investigate the effect of stacking on the magnetic structure at the edge of the graphitic fragment. Here we consider two different stacking sequences, AA and AB. The interlayer distance is fixed to that of graphite, 3.335 Å. In the AA stacking, all the atoms in upper layers is directly above the atoms in the lower layers, whereas in the AB stacking, B layers are shifted by a length of C–C bond along the C–C bond direction and only the half of atoms in upper layers is above the atoms in the lower layers. This means that all the atoms in the AA stacking interact with other layers but in AB stacking, half of the atoms interacts with other layers directly. Although we consider only the ferromagnetic ordering within each edge, several different spin configurations can arise depending on the relative magnetic orientation between stacked edges. The parallel spin direction between the neighboring layers is to be denoted by FM, and the anti-parallel spin direction between the neighboring layers is to be denoted by AF. In Fig. 3, we show the band structure of the FM and AF states of the AA- and AB-stacked graphitic fragments with dangling bonds at the edges. The circles and triangles in Fig. 3 represent the contributions of the dangling bond states and the localized π states, respectively.

In Table 2, we list total energies and magnetic moments of each configuration. The AB-stacking

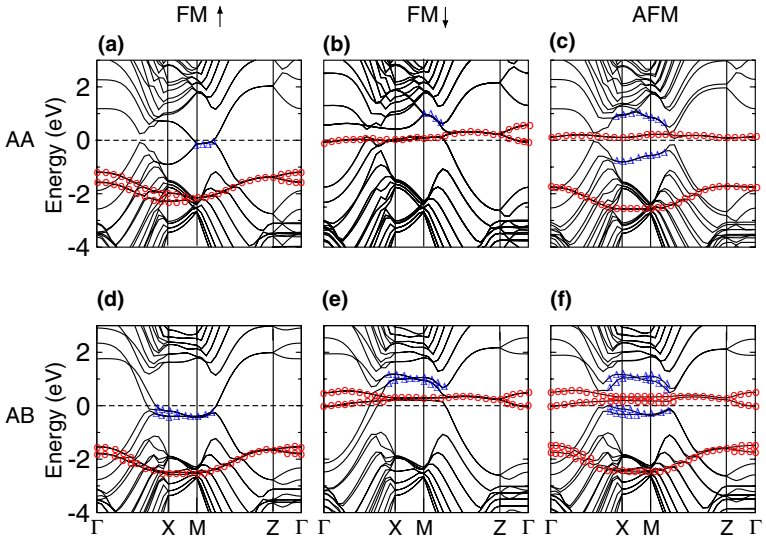

Fig. 3. Band structures of stacked graphite fragments with dangling bonds at the edges. (a) and (b) are for the band structure of majority spin and minority spin of the AA–FM state, respectively. (c) is for the AA–AF state. (d) and (e) represent the band structure of majority spin and minority spin of the AB–FM state, respectively. (f) For the AB–AF state.

Table 2
Total energy and magnetic moment of the stacked graphitic strips without hydrogen passivation

Configuration	Total energy (meV/edge atom)	Magnetic moment (μ_B/edge atom)
AB–FM	0	1.26
AB–AF	2.0	1.26
AA–FM	72.5	1.03
AA–AF	40.5	1.00

Total energies are measured with respect to that of the AB–FM configuration.

configuration is found to be more stable than that of AA stacking as in the case of the bulk graphite. It is interesting to see that the AB-stacking favors the FM configuration while the AA stacking prefers the AF configuration. It can be argued that the interlayer interactions favor the opposite spin direction between the local magnetic moments of the nearest atoms in the adjacent layers. It appears that the interlayer interaction is mainly mediated by the small overlap between p_z orbitals of the nearest atoms in the adjacent layers, leading to the AF configuration in the AA stacking and the FM configuration in the AB stacking. Consequently, the macroscopic contribution by the edge-localized π states in the AA stacking will be negligible because of the alternating spin direction along the stacking direction (the z-direction in Fig. 1). Indeed the AA stacking cases (AA–FM, AA–AF) results in only 1 μ_B per edge atom that is solely from the dangling-bond states as seen in Table 2.

The above results suggest that the spin polarization in the π states could be disturbed upon the stacking. To confirm the role of the π-orbitals in the stacking cases, we perform the calculations for the stacked graphite layers with the edges passivated by hydrogen atoms. As results, we obtain the spin-unpolarized ground states, which show that the ordered spin in the edge-localized π-states does not survive upon the stacking. In order to arrive at a more comprehensible picture, we calculate on the isolated one layer, two and three layers of the graphitic fragment with and without the hydrogen passivation at the edges. Regardless of the stacking sequences, either AB or AA, the magnetic moment of the hydrogen-passivated strip is found to disappear immediately by adding up an extra layer. In Fig. 4, we show the exchange-splitting of the dangling-bond states (Δ_σ), the localized π-states (Δ_π) of the bare-edged graphitic fragment, and the localized π-states (Δ_π(H)) of the hydrogen-passivated graphitic fragment, together with their contributions to the magnetic moments. Here the two- and three-layer cases correspond to the AB stacking geometry. It is clear that the ordering in the edge-localized π states of the hydrogen passivated edge is readily diminished upon the stacking while in the strip with bare edges, the magnetic orderings in the π states as well as in the dangling-bond states are found to be insensitive to the stacking.

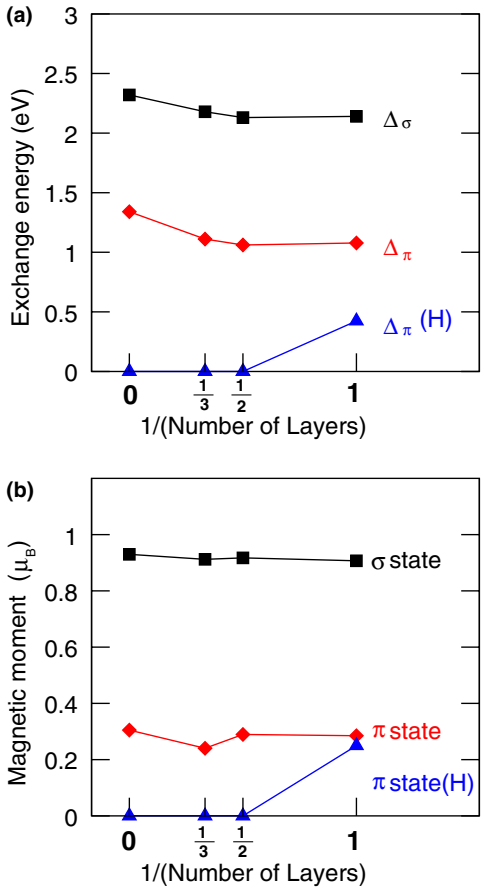

Fig. 4. The exchange splitting and magnetic moment of the edge atoms of the isolated one, stacked two and three layers of the graphitic fragments. Squares and diamonds represent the contributions from the dangling bond states and from the edge-localized π states of the bare edges, respectively. Those from the edge-localized π states in the hydrogen-passivated edges are presented with triangles. Lines here are for a visual convenience.

A theoretical work has investigated a possible magnetic ordering in the graphitic system with various shape of hydrogen terminations [20]. Assuming such kinds of di-hydrogenated edges or asymmetrical edges could exist in realistic samples, we investigated those geometry in detail. However, as the strip width increases, we found that spins in those geometry are still localized at the hydrogen-passivated edges, and those spins would disappear upon the stackings of the graphites [21].

In summary, we performed ab initio calculations to show that a pure carbon ferromagnetism can originate from the surface of the stacked graphitic edges with dangling bonds. Several experimental works have cited localized spin in the hydrogen-passivated zigzag edges as a plausible model of pure carbon ferromagnetism [2,6,8]. We demonstrated that the localized spin at the hydrogen-passivated graphitic edges disappears in the presence of the interlayer interactions. Therefore, some other types of hydrogen passivation may explain a large magnetic moment of proton-irradiated graphite. When

dangling bonds are exposed, the ferromagnetically ordered moments survive after stacking layers. We note that reported ferromagnetic carbon structures generated by the α-particle irradiation [22] might contain hollow spaces developed inside the graphite, retaining a number of ferromagnetically interacting dangling bonds. We believe that our results provide an important clue for understanding the magnetism in pure carbon-based system.

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