Divacancy-induced Ferromagnetism in Graphene Nanoribbons

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Zigzag graphene nanoribbons have spin-polarized edges, anti-ferromagnetically coupled in the ground state with total spin zero. Customarily, these ribbons are made ferromagnetic by producing an imbalance between the two sublattices. Here we show that zigzag ribbons can be ferromagnetic due to the presence of reconstructed divacancies near one edge. This effect takes place despite the divacancies are produced by removing two atoms from opposite sublattices, being balanced before reconstruction to 5-8-5 defects. We demonstrate that there is a strong interaction between the defect-localized and edge bands which mix and split away from the Fermi level. This splitting is asymmetric, yielding a net edge spin-polarization. Therefore, the formation of reconstructed divacancies close to the edges of the nanoribbons can be a practical way to make them partially ferromagnetic.

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I. INTRODUCTION

Magnetism in zigzag graphene nanoribbons (ZGNR) is related to edge-localized states, which appear as two flat bands at the Fermi energy \( E_F \) in a simple noninteracting model. In fact, the electron interaction splits these bands, so the edges are antiferromagnetically coupled with total spin zero \([1,2]\). This magnetic behavior is rather general, because similar localized bands are also present in any non-armchair graphene ribbon \([3,5]\). When the edges of the nanoribbon are identical, all the bands remain spin-degenerate. For dissimilar edges with sublattice balance, the spin splitting may be different for each edge \([6]\), but the ribbons have total spin zero. In order to exploit spin effects in ZGNRs for applications, spin degeneracy should be lifted, so uncompensated spin channels are obtained. Such splitting can be achieved under a strong external electric field \([1,7]\) or by chemical attack \([8]\).

In general, one way to attain ferromagnetic graphene nanostructures is to impose sublattice imbalance. According to Lieb’s theorem, a bipartite lattice has a total spin moment proportional to the difference of the number of atoms belonging to the two sublattices \([9]\). For instance, ZGNRs with one decorated edge of Klein-type atoms \([10,11]\), triangular graphene nanoislands \([12]\), and graphene systems with vacancies that remove a different number of nodes from each sublattice \([13,16]\) have a non-zero spin due to the imbalance. In this work we show another way of producing a net magnetic moment in zigzag graphene nanoribbons by including reconstructed divacancies.

We consider divacancies produced by the removal of two neighbor carbon atoms, so that the two sublattices are balanced. They rebuild into the so-called 5-8-5 defects, composed of an octagon and a pair of pentagons which mix the two sublattices. Divacancies may naturally appear as stable defects during growth or can be created on purpose by electron or ion irradiation \([17,22]\). They are the source of defect-localized states with energies close to \( E_F \), as it was recently shown for the case of semiconducting armchair ribbons \([23]\). Since divacancies do not introduce sublattice imbalance, they have not been regarded to this date as possible sources of magnetization in graphene. However, we show here that when these defects are present in zigzag nanoribbons, they give rise to localized states which may interact with those originated from the zigzag edges, so they can lead to spin effects and ribbon magnetization.

Two previous calculations for 5-8-5 defects in ZGNRs presented results in apparent contradiction, showing either zero spin polarization \([24]\), or spin-polarized transport in ribbons with narrow widths \([25]\). The issue of whether these defective nanoribbons are ferromagnetic or not was not addressed in those works. In principle, one could interpret that spin polarization arose in narrow ribbons because of size effects.
In order to clarify this point, in this work we perform a systematic study of the magnetic behavior of ZGNRs with reconstructed divacancies. We have found that, although these divacancies arise from lattice-balanced defects, can nevertheless produce a net magnetic moment in zigzag nanoribbons. This happens when they are located close to the zigzag ribbon edge. We attribute the appearance of a nonzero spin to the strong interaction between edge and divacancy states.

![FIG. 1. (Color online) (a) Divacancies in ZGNRs. The position of the defect in the ribbon is given by the integer \( N \). (b) Schematic drawing of the periodically placed defects along the ribbon forming a superlattice. The translation period \( T \) spans the length of the unit cell.](image)

We have examined systematically how the magnetic properties of ZGNR depend on the position of 5-8-5 defects. We show that when defects are centrally located in wide ZGNRs, the ribbons have zero net magnetic moment. However, when they are placed close to one of the zigzag edges, the defect-localized and the nearby edge bands interact, so they mix and split in energy. The zero energy band corresponding to the other edge situated farther from the defect remains unmixed. The inclusion of electron-electron interaction results in the spin splitting of all these bands. The aforementioned unmixed band is symmetrically split around \( E_F \), while the hybridized defect-edge bands are asymmetrically split, yielding a non-zero net magnetization. We propose that the production of reconstructed divacancies by techniques such as ion bombardment may produce magnetic ribbons. As the one of the most abundant defects in ZGNRs are divacancies [26], which are preferentially found at the edges [25], this defect engineering could be a feasible way to produce spin-polarized ZGNRs.

II. MODEL AND SYSTEMS STUDIED

We study reconstructed divacancies in wide zigzag graphene nanoribbons. The ribbon width \( W \) is defined [27] as the number of carbon dimers across the ZGNR. The divacancies are located at different positions \( N \), measured in units of two carbon dimers from the edge of the ribbon, as shown in Fig. 1 (a). The 5-8-5 defects are periodically situated in an infinite ZGNR, as schematically depicted in Fig. 1 (b). The translation period \( T \) of the ribbon is defined as the number of zigzag edge nodes in the unit cell. The electronic properties are calculated with a one \( \pi \)-orbital tight-binding (TB) model. The electron-electron interaction is considered within a Hubbard model solved in the mean-field approximation. We choose this approach in order to calculate large unit cells, which are not feasible with first-principles methods. We assume all hoppings \( t \) to be equal throughout the ribbon. We previously tested this approach for the study of the magnetic properties in graphene with topological defects using the hopping parameter \( t = -2.7 \) eV and the Coulomb interaction term \( U = 3 \) eV [6, 28].

III. RESULTS

We first consider centrally located 5-8-5 defects, periodically placed along a wide ribbon with \( W = 19 \) and \( T = 3 \). It is the smallest periodicity of a ZGNR with horizontally placed defects separated by at least one hexagon. Note that for \( T = 2 \) the consecutive octagon-pentagon pair defects form a defect line, which was studied elsewhere [28–32]. The energy spectra calculated within the TB approximation and the Hubbard model are presented in Figs. 2 (a) and (b), respectively. The spectra are not symmetric with respect to \( E = 0 \) because of the electron-hole symmetry breaking induced by the pentagons. The insets show the band structure of a ZGNR with \( T = 3 \), i.e., the three times folded spectrum of the pure (1,0) ZGNR with the Dirac point at \( k = 0 \). It has a pair of zero-energy bands extending in the entire zone in the TB approximation (Fig. 2 (a)), which are split when the electron-electron interaction is included (Fig. 2 (b)) [2]. The 5-8-5 defects introduce divacancy-localized states, which in the TB approximation form a flat band exactly at \( E = 0 \), as shown in Fig. 2 (a) [23]. When the Coulomb interaction is considered, as in Fig. 2 (b), the two edge localized bands are spin-split in the same way as in the pristine ZGNR. The unoccupied defect-localized band re-
mains spin-degenerate. As the defect is symmetric about the center of the ribbon, the ground state remains antiferromagnetic.

![FIG. 2. (Color online) Bands of a ZGNR with \( W = 19 \) and \( T = 3 \) with 5-8-5 defects located at the center of the ribbon, calculated in (a) the TB approximation and (b) the Hubbard model. For comparison, the corresponding spectra of pure ZGNR folded three times \((T = 3)\) are included as insets. The Fermi level lies at \( E = 0 \). Notice that in (b) the zero energy edge bands are spin-split, but they remain spin degenerate with no spin polarization; the defect band is spin-degenerate.](image)

More interesting is when we move the 5-8-5 defect close \((N = 1)\) to one of the edges of the ribbon, e.g., the upper one. The energy spectra calculated in the TB and Hubbard models are shown in Figs. 3 (a) and (b), respectively. In the TB approximation the flat band at \( E = 0 \) is localized at the lower edge, and it remains unaffected by divacancies. However, the states localized at the upper edge strongly interact with the defect-localized states; they hybridize and split. The bonding combination of these states is the band below \( E = 0 \), while the anti-bonding combination is unoccupied. All the bands are spin-degenerate. The inclusion of electron-electron interaction lifts the spin degeneracy and significantly modifies the spectrum, as it can be seen in Fig. 3 (b). The bands localized at the lower edge are marked in Fig. 3 (b) by arrows. The spin-down polarized states are almost fully occupied. The bonding and anti-bonding combinations between the upper-edge and defect-localized bands also spin-split. However, their splitting is weaker because of the defect-edge mixing. The spin-split pairs are marked with ellipses. In the TB approximation the bonding combination is situated closer to \( E_F \) than its anti-bonding counterpart. Now, when the Hubbard term is included, spin-up and spin-down bands cross the Fermi level at different \( k \)-values. This produces a non-zero final spin polarization, about 0.2 \( \mu_B \). Note that this result does not contradict Lieb’s theorem: although the lattice was balanced before reconstruction, the mixing of sublattices produced by the topological defects makes the theorem inapplicable to this case. Significantly, ZGNRs on one hand and 5-8-5 defects on the other hand have a total spin zero. However, when the defect is placed close to one of the edges, a net spin appears due to the asymmetrical band splitting produced by the defect-edge interaction.

Figure 4 (a) shows how the spin polarization depends on the position of the defect with respect to the edge of the ribbon. We consider a ribbon with \( T = 6 \) and \( W = 39 \), which is wide enough to have the defect in several sites between the center of the ribbon and its edge. When the defect is situated close to the edge, i.e. \( N = 1 \), the spin polarization is 1.3 \( \mu_B \). Moving the defect towards the center makes the polarization decrease rapidly to zero. This may explain why no magnetization was reported in the study presented in Ref. 24 for ZGNR with slightly off-center divacancies. Another work 25 gives an example of a very narrow ribbon, not large enough to distinguish the magnetic polarization effect induced by such defects from that caused by the edges themselves. We have systematically studied how the spin polarization depends on the translation period \( T \) for the ribbon of width \( W = 39 \), as shown in Fig. 4 (b). When \( T \) increases, the ribbon polarization also increases (albeit non monotonically), and saturates for large \( T \) at 2 \( \mu_B \).

![FIG. 3. (Color online) Bands of a ZGNR with \( W = 19 \) and 5-8-5 defects placed close to the upper edge \((N = 1)\) and separated by the translation vector \( T = 3 \), calculated in the TB (a) and Hubbard (b) models. Spin-down bands are denoted by dotted lines, spin-up by solid lines. Arrows mark the up and down spin bands localized at the lower edge. Ellipses mark the spin-split bands of the bonding and anti-bonding combinations between the upper edge and the defect-localized states.](image)

![FIG. 4. Dependence of spin polarization on (a) the position \( N \) of defects with respect to the edge of the ribbon, and (b) the translation period \( T \), for a wide ribbon of \( W = 39 \).](image)

In order to understand the values of spin polarization presented above, we have also studied in more detail the energy spectra of ZGNR with larger \( T \). When the defects are situated at the center of the ribbon, no spin polarization is observed for any \( T \). In order to compare the results with those with \( T = 3 \) presented above, in which the Dirac point is at \( k = 0 \), we choose \( T \) to be a multiple
of three. The smallest translation period for which the polarization converges to $2 \mu_B$ is $T = 9$. The TB energy spectrum of a pure ZGNR (9,0) has 6 flat bands at $E = 0$. Three of them are localized at the lower edge, and another trio is at the upper edge.

When the 5-8-5 defects are close to the upper edge, defect and upper-edge bands interact, so they mix and split. Fig. 6 shows the TB energy bands for the $W = 19$ and $T = 9$ ZGNRs with a 5-8-5 defect close to the edge. There are four flat bands near to the Fermi level. Three bands are localized at the lower edge (LE) and one at the upper edge (UE). These states are mostly localized at the edge nodes and have a negligible overlap with the defect atoms. The two remaining upper edge bands hybridize with the defect band, yielding three bands (UE+D) of mixed upper edge-defect character, with only one occupied and all away from $E_F$.

A diagram showing how these bands spin-split when the Coulomb interaction is taken into account is presented in Fig. 7 (b). The LE bands (blue) are strongly split so they are fully spin-polarized; we take the occupied spin as the down projection. The unperturbed $E = 0$ UE band (green) is split with a spin opposite to the LE bands, as expected. The UE+D bands are spin-split more weakly because of the sublattice mixing at the defect. Consequently, we have four spin-down and two spin-up occupied states, summing up to $2 \mu_B$. Calculations employing the Hubbard model confirm this picture, as displayed by the energy bands in Fig. 3 (c). We have checked that our results are robust, i.e., independent on the Coulomb term for a wide range of $U$ values.

The energy and spatial schemes presented in Fig. 9 describe these edge-defect interactions in detail. The edge bands of the pure ZGNR (1,0), which extend from $k = 2\pi/3$ to $k = \pi$, contribute in average with one electron for every three edge nodes. For $T = 9$ this band folds into three edge bands. For the divacancy close to the upper edge, the defect band hybridizes with two edge bands, giving three bands away from $E_F$, as shown in Fig. 6 (a). The defect does not mix with the remaining upper edge band (green), because it stems from the states close to $k = \pi$ of the unfolded edge band of the ZGNR (1,0): as it is mostly localized at the edge atoms, it has a small overlap with the defect. Likewise, the lower edge discrete states (blue) are also unaffected by the divacancy due to the spatial separation. These unchanged states are spin-split as for a pure ZGNR. However, the spin splitting of the hybridized states (red) is much weaker, with a state below $E_F$ occupied for both spin polarizations. For even larger $T$, the spins of the extra occupied upper edge states far from the defect cancel with the spins of the occupied lower edge states. Thus, an isolated straight divacancy in an infinite ZGNR has a total spin polarization equal to $2 \mu_B$. We have also checked that tilted vacancies have a similar behavior, although the total magnetic moments tend to be reduced.

This divacancy-induced magnetism at the edge of zigzag ribbons is now brought into contact with experiments. We propose that ion irradiation of zigzag ribbons could be employed to create divacancies. This technique is used nowadays to produce vacancies in graphene \[21\]. In fact, vacancies are mobile and cluster in the form of divacancies \[22\]. Note that for nanoribbons, it is more energetically favorable for these vacancies to move close to the edge because of its lower coordination, where they can coalesce in the more stable and abundant divacancies \[20\].

IV. CONCLUSIONS

In summary, we have studied the electronic and magnetic properties of ZGNRs with reconstructed divacancies, which can be viewed as the removal of two neighbor carbon atoms from different sublattices before reconstruction to 5-8-5 defects. Although 5-8-5 defects stem from lattice-balanced vacancies, they can give rise to a net spin magnetic moment. We have shown that a nonzero magnetization arises when the defect is located close to the edges of the zigzag ribbon. The 5-8-5 defects introduce localized states with energies close to $E_F$. When they are located at the center of the ribbon, the total spin polarization is zero, keeping the magnetic edge configuration of pristine ribbons. However, when the defects are placed closer to one of the edges of the ribbon, the defect band interacts with the edge-localized band, so they hybridize and split asymmetrically from $E_F$. States localized at the other edge remain strongly spin-split, leading to a net spin polarization and spontaneous magnetization of the ribbon, despite they are derived from systems with balanced sublattices before reconstruction. The total magnetic moment saturates for large periods to a value of $2 \mu_B$. Finally, we have also clarified the apparent contradiction between previous works, namely, the absence of spin polarization shown for some defective ribbons, in contrast with the observation of spin-polarized currents in similar systems \[24, 25\]. In narrow ribbons, divacancies are naturally close to edges, so a spin-polarized current may arise. In wider ribbons, divacancies situated at the central region of the ribbon do not produce such spin polarization.

Our findings indicate that it is possible to design spin-transport devices based on graphene nanoribbons by introducing divacancies close to its edges by means of electron or ion irradiation.

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FIG. 5. (Color online) (a) Bands of a ZGNR of $W = 19$, $T = 9$ and a 5-8-5 defect placed close to the edge ($N = 1$), calculated with the TB model; all the bands are spin-degenerate. Bands localized almost exclusively at the upper and lower edge nodes for $k = \pi$ are denoted by UE (green) and LE (blue), respectively. Bands localized both at the upper edge and at the defect are marked as UE+D (red). (b) Schematic diagram showing how the bands are spin-split when the Coulomb interaction is considered. (c) Band structure calculated with the Hubbard model. Spin-up (full symbols) and spin-down (empty symbols) bands at the nodes of the upper edge (up triangles, green), the lower edge (down triangles, blue) and the defect atoms (circles, red). The symbol sizes are proportional to the probability density at the defect atoms, upper edge atoms and lower edge atoms. Inset: Hubbard bands of the pure ZGNR (9,0).

FIG. 6. (Color online) (a) Schematic energy diagram showing how the defect-localized state mixes with two upper-edge localized states. The TB levels are shown in black; filled and half-filled dots indicate that the state is fully or half-occupied, respectively. Electron interaction splits these levels; colors indicate their localization as in Fig. 5 (b). Occupied states are represented with an arrow indicating the spin direction. (b) Diagram illustrating the final distribution of occupied spin states due to divacancy placed close to the edge.

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