Octagonal defect lines in graphene nanoribbons and carbon nanotubes

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Experimental techniques allow nowadays to pattern graphene into nanometer size ribbons with well controlled size and shape of the edges [1]. Graphene ribbons can be connected by introducing topological defects at their interfaces and it concerns also junctions between carbon nanotubes. Junctions between such systems are interesting because they can reveal localized states of magnetic nature at Fermi energy. Junctions between carbon nanotubes are usually realized by pentagon/heptagon (5/7) topological defects. Pentagon and heptagon defects strongly mix the graphene sublattices. Therefore, they cannot yield localized states at Fermi energy, since they break the condition of localization at only one sublattice, necessary to the appearance of zero-energy states. Interfaces between graphene nanoribbons form one-dimensional grain boundaries, where octagons may also happen. It has been recently shown [2] that such grain boundaries can act as quasi-one-dimensional metallic wires.

Here, we study several graphene systems containing octagonal defect lines. All the calculations are performed within the π-electron tight binding (TB) approximation. The electron interaction effects are taken into account by means of the Hubbard model. We show that contrary to pentagon/heptagon defects, octagonal defects give rise to localized states at Fermi energy even if the graphene sublattices are mixed. We also prove that the localization along chains of octagons is a consequence of the zigzag nature of graphene edges forming the defect lines.

First, we study zigzag graphene ribbons (ZGNR) containing defect lines made of octagons only as shown in Fig.1(a). Such ZGNR can be considered as two joined zigzag sub-ribbons, one of them having the so-called Klein edge at one side (the Klein node is the node having only one nearest neighbor). Although this system is not a pure graphene structure, there is no sublattice mixing in this case.

The TB energy bands are shown in Fig.2(a). The four TB wave functions at k=0, corresponding to 4-times degenerate band at Fermi energy, are presented in panel (b). The wave functions of a couple of flat bands extending in the entire Brillouin zone are localized at the octagonal defects, but in opposite sublattices. One of them is a resonance state between two edge states of zigzag sub-ribbons joined to form the octagonal defect line, while the other resembles the state localized at the Klein edge.

The results of calculations performed within the Hubbard model, i.e., after inclusion of on-site electron-electron interaction effects, are presented in Fig.2(c). The solid lines correspond to spin-down bands and the dotted lines represent spin-up solutions. At $k < 2/3\ \pi$ there are three almost degenerate spin-down bands and one spin-up band below the Fermi level. As the result, the spin polarization is equal 2 and the system reveals spontaneous magnetization of 2 Bohr magnetons, which is consistent with Lieb's theorem (there are two atoms imbalance between graphene sublattices in the unit cell).

Next, we consider a system in which every second octagon in the defect line is reconstructed into a pair of pentagons, as shown in Fig.1(b). Such system has been very recently studied experimentally [2]. The presence of pentagons mixes locally both sublattices. Consequently, one flat band drops down and disappears from the Fermi level. It is that band, the wave function of which was localized at the Klein nodes (they are now mixed and connected by bonds). However, the state of resonant character, that was previously localized at the octagons, survives with energy at the Fermi level. Spontaneous magnetization also survives, but drops down to 0.6 Bohr magnetons.

We have studied also rolled-up systems, i.e., carbon nanotubes with octagonal defect lines along the tube axis or at junctions between tubes. We have shown that localization at octagons with energies at the Fermi level is robust and present in all the system considered, independently whether the graphene sublattices are mixed or not. It suggests that octagonal defects can indicate reactivity sites in graphene. Finally, we show that the appearance of localized flat bands at the Fermi energy may be explained using the hybridization rules introduced in Ref. [3] for graphene ribbons with arbitrary edges.

References

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Figures

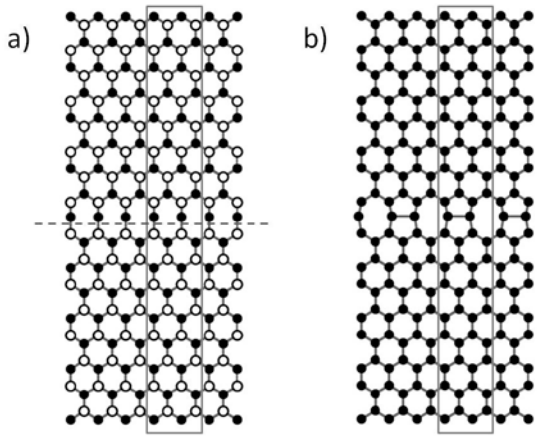

Fig. 1. ZGNRs with defect lines composed of (a) consecutive octagons and (b) octagons with an adjacent pair of pentagons. The ZGNRs extend horizontally. Rectangles mark the unit cells of ribbons. The dashed horizontal line in (a) marks a cutting line which separates the structure into two sub-ribbons, one of them having a Klein-like edge at one side (the central line of nodes).

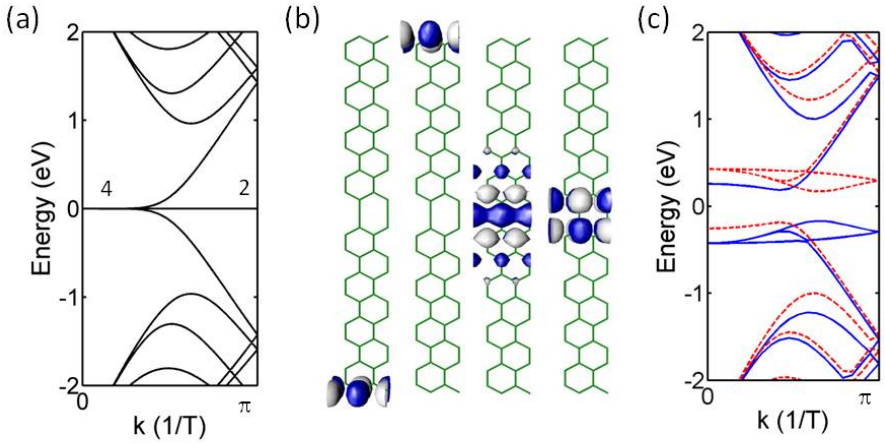

Fig. 2. (a) Energy bands of a ZGNR with a defect line composed of octagons as depicted in Fig.1(a), calculated within the TB approximation. The wave vector *k* is given in units of 1/T, where T is the length ofthe unit cell. The degeneracies (without counting the spin) of E=0 bands at *k*=0 and k=π are indicated. (b) TB wave functions corresponding to four zero-energy bands at *k*=0. (c) Energy spectrum calculated in a Hubbard model. Blue lines denote spin up bands; red-dashed lines show the spin down bands. The Fermi energy is at 0 eV in both cases.