Energetics and stability of vacancies in carbon nanotubes

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ABSTRACT

In this work we present *ab initio* calculations of the formation energies and stability of different types of multi-vacancies in carbon nanotubes. We demonstrate that, as in the case of graphene, the reconstruction of the defects has drastic effects on the energetics of the tubes. In particular, the formation of pentagons eliminates the dangling bonds thus lowering the formation energy. This competition leads to vacancies having an even number of carbon atoms removed to be more stable. Finally the appearance of magic numbers indicating more stable defects can be represented by a model for the formation energies that is based on the number of dangling bonds of the unreconstructed system, the pentagons and the relaxation of the final form of the defect formed after the relaxation.

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1. Introduction

Nanoscopic systems have attracted significant attention from the scientific community due to the possibility of designing ever-smaller electronic devices. Amongst candidates with greatest potential for application one can find carbon-based materials such as carbon nanotubes (CNT) [1,2], and more recently graphene [3].

Intrinsic defects are often seen as the source of deleterious effects in semiconductor materials [4]. For instance, vacancies and clusters of vacancies have important well known effects on the properties of many semiconductors of technological importance such as Si [5], GaAs [6], SiGe [7,8] and Ge [9]. The same, however, cannot be clearly stated about carbon based materials. In fact, defects in carbon nanotubes can be used as binding sites for different types of gaseous species in CNT-based sensors [10,11], as well as in a new family of disordered graphene spintronics devices [12]. One point is clear: defects can lead to drastic changes in the electronic structure of carbon-based systems. Thus if these materials are to be the building blocks of tomorrow's electronics, characterizing these defects is of utmost importance.

In carbon nanotubes one can find many different types of defects ranging from Stone–Wales [13], to adatoms [14–16] and vacancies [17–27]. Recently, Saito et al. [28] have reported on the existence of point defects in graphene, ranging from a single vacancy to an octovacancy [29]. The authors also show that the divacancy, the tetravacancy, and the hexavacancy, are the most stable defects in a graphene sheet.

In order to highlight the stability of specific vacancies one introduces the concept of magic numbers [28]. These magic numbers indicate the size – the number of atoms removed – of a defect that lead to the most stable multivacancies. Previous studies using positron annihilation in graphite suggest that the hexavacancy, V_6, was the most stable defect [24]. This stability was explained by the dangling bond counting model (DBCM), where the number of dangling bonds (DB) of the system, N_{DB}, decreased as the vacancy became more stable. This model was also successful in explaining the stability of multivacancies in silicon [5] and GaAs [6].

In graphene, however, Saito et al. [28], noted that the stability of the defect also depends on pentagons formed upon reconstruction of the system. Subsequently extending the dangling bond counting model – adding to that the effect of the pentagons – the authors proposed the pentagon and dangling bond counting model (PDBCM). The PDBCM is based on the average energy per DB and per pentagon in all defects considered. The model was then used in explaining the stability of vacancies (and consequently the existence of magic numbers) in graphene.

The aim of the present study is twofold. The first one is to determine what are the most stable vacancies in carbon nanotubes and whether the PDBCM is applicable in the presence of hybridization between π orbitals due to curvature effects.

Secondly and most importantly we propose a modified model based on the PDBCM that uses only two defects for the construction of the model. In other words, one does not need to perform calculations for all vacancies to determine the parameters for the model; all the parameters – as we will show – can be obtained

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by two preliminary calculations. Most importantly, as it will be demonstrated, it contains all the physical ingredients to predict the existence of magic numbers in carbon nanotubes, even in the case of large curvature effects.

2. Method

Ab initio total energy calculations based on the density functional theory [30,31] were performed for different types of vacancies on (5, 5), (7, 7), (9, 9) and (10, 10) carbon nanotubes. These smaller-radius nanotubes were chosen in order to give rise to large curvature effects, as opposed to the planar graphene sheet. We used the generalized gradient approximation (GGA) [32] for the exchange and correlation potential within the Perdew–Burke–Ernzerhof approach [33]. Our simulations were performed using a plane-wave DFT method within the VASP code [34,35] and with ultrasoft pseudopotentials. [36] In all our calculations a plane wave energy cutoff of 290 eV and 8 k-points along the reciprocal axis of the CNT were used.

Initially the defects are created by simply removing n ($n = 1, \ldots, 8$) carbon atoms from a pristine structure containing 8 irreducible unit cells for each nanotube [37]. The (5, 5) nanotubes with different numbers of carbon atoms removed prior to relaxation are shown in Fig. 1(a1)–(h1) – left hand-side panel (the defects on the other nanotubes are equal). Hereafter we label V_n the respective vacancy where n carbon atoms have been removed. We note that the creation of vacancies leads to the formation of dangling bonds – carbon atoms with two-fold coordination instead of the expected three-fold one – which are energetically unfavorable. The systems are allowed to atomically rearrange using a conjugate gradient method (CG) until the forces on all the atoms are lower than 0.02 eV/Å. The final relaxed structures are shown in Fig. 1(a2)–(h2) – right hand-side panel. One can notice that the defects undergo a reconstruction that leads to the formation of pentagons and subsequent saturation of the dangling bonds. We note that in the case of n even, the number of DBs goes to zero (except for V_8).

3. Results

The formation energy, $E_f[n]$ for the V_n vacancy is calculated using,

$$E_f[n] = E_r[n] - E_p[n] - n\mu_C, \tag{1}$$

where E_p is the total energy of the pristine nanotube, $E_r[n]$ is the total energy of the reconstructed nanotube with a V_n defect, n is the number of carbon atoms removed from the system and μ_C is the chemical potential of 1 carbon atom, which is the total energy of the pristine nanotube divided by the number of atoms on the system.

The total formation energy as a function of vacancy size is shown in Fig. 2(a). From the figure, one might be tempted to say that the V_2 is the most stable vacancy. However, a more reasonable approach is to compare each vacancy normalizing the number of atoms that have been removed from the system [38]. In that case we observe from Fig. 2(b) that the hexavacancy has the lowest formation energy per C atom removed. We also note that $E_f[n]$ is nonmonotonic. Instead, it has local minima for even n. This result is in line with previous results for graphene indicating the existence of the so-called magic numbers, namely 2, 4 and 6 for carbon nanotubes as well as graphene.

That, however, is not the full picture. One step further into fully understanding the stability of vacancies in CNTs is to determine how they are correlated with closely sized vacancies, for instance, whether a V_6 will break into a single vacancy, V_1, and a pentavacany, V_5, and so on.
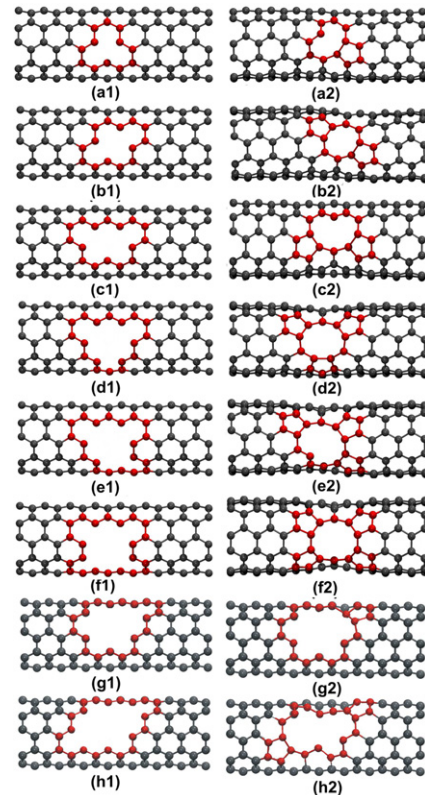

Fig. 1. Unrelaxed (left hand-side panel) and relaxed (right hand-side panel) multivacancies: (a) single vacancy, V_1; (b) divacancy V_2; (c) trivacancy V_3 (d) tetravacancy V_4; (e) pentavacacy, V_5; (f) hexavacancy, V_6; (g) heptavacancy, V_7; (h) octavacancy, V_8.
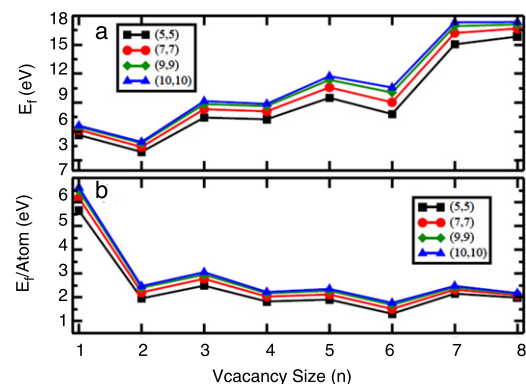

Fig. 2. (a) Total formation energy, and (b) formation energy per carbon atom removed for a (5, 5), (7, 7), (9, 9) and (10, 10) carbon nanotubes obtained via DFT calculations.

Hence, in order to address defect stability Saito et al. [28] proposed two quantities associated with distinct dissociation processes. The first one assumes that a V_n-*type* defect breaks up into a single vacancy, V_1, and a V_{n-1}-*type* vacancy,

$$V_n \rightarrow V_{n-1} + V_1. \tag{2}$$

In that manner the first dissociation energy is defined as the energy change between initial and final states,

$$D_1[n] = E_f[n-1] + E_f[1] - E_f[n]. \tag{3}$$

For the second case, one would have two V_n-*type* defects that reconstruct into a V_{n-1}-*type* and a V_{n+1}-*type* vacancy. In other words, a single vacancy breaks away from one of the defects and migrates to another one close by

$$2V_n \rightarrow V_{n-1} + V_{n+1}. \tag{4}$$