Physica B: Condensed Matter 534 (2018) 184–188

Contents lists available at ScienceDirect

Physica B: Condensed Matter

journal homepage: www.elsevier.com/locate/physb

Magnetism of a relaxed single atom vacancy in graphene

Yunyi Wu [a,b,1], Yonghong Hu [a,*,1], Li Xue [a], Tieyu Sun [c], Yu Wang [d]

[a] School of Nuclear Technology and Chemistry & Biology, Hubei University of Science and Technology, Xianning 437100, China
[b] Department of Energy Materials and Technology, General Research Institute for Nonferrous Metals, Beijing, China
[c] Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong SAR, China
[d] School of Materials Science and Engineering, Nanchang University, Nanchang, Jiangxi 330031, China

ARTICLE INFO

Keywords:
Graphene
Magnetism
Vacancy
Spin polarization
Boundary conditions
Density functional calculations

ABSTRACT

It has been suggested in literature that defects in graphene (e.g. absorbed atoms and vacancies) may induce magnetizations due to unpaired electrons. The nature of magnetism, i.e. ferromagnetic or anti-ferromagnetic, is dependent on a number of structural factors including locations of magnetic moments and lattice symmetry. In the present work we investigated the influence of a relaxed single atom vacancy in garphnene on magnetization which were obtained under different pinning boundary conditions, aiming to achieve a better understanding of the magnetic behaviors of graphene. Through first principles calculations, we found that major spin polarizations occur on atoms that deviate slightly from their original lattice positions, and pinning boundaries could also affect the relaxed positions of atoms and determine which atom(s) would become the main source(s) of total spin polarizations and magnetic moments. When the pinning boundary condition is free, a special non-magnetic and semi-conductive structure may be obtained, suggesting that magnetization should more readily occur under pinning boundary conditions.

1. Introduction

Over the past decade, extensive studies have been carried out on graphene, a chemically stable two-dimensional (2D) material that exhibits excellent mechanical, thermal, electrical and optical properties [1]. Owing to its 2D structure, the behaviors of electrons in graphene are unique when compared with other conventional materials that leads to many unique properties of graphene. For example, the effective masses of electrons and holes in graphene are both zero at Dirac point [2–4], and there are six equivalent Dirac points lying on the corners of the first Brillouin zone [5].

Although spin polarizations and magnetism cannot exist in perfect graphene due to the absence of unpaired electrons, defects such as absorbed atoms or vacancies, which are common due to thermodynamic laws, will make certain electrons unpaired and induce spin polarizations and magnetic moments. Usually, the directions of induced magnetic moments on sublattices A and sublattices B (Please see Fig. 1(a) for the difference between sublattices A and sublattice B) are opposite, and obey Lieb's theorem [6,7].

Absorbed atoms induce spin polarizations and magnetic moments because they may introduce unpaired electrons [8,9]. The RKKY (Ruderman-Kittel-Kasuya-Yoshida) interaction energy [10–13] can be calculated by perturbation method with a special assumption of energy band of graphene [14–17]. When absorptions occur on the same sublattices (i.e., all are on A or all are on B), the RKKY interaction energy will be negative and the magnetism will be ferromagnetic. However, when absorptions occur on different sublattices, the RKKY interaction energy will become positive and cause the absorbed graphene to become anti-ferromagnetic [18,19]. When absorptions occur neither on A sublattices nor B sublattices but between them, the RKKY interaction energy could be greatly reduced as the magnitudes fall from $1/R^2$ to $1/R^3$ where R is the distance between two magnetic moments [15].

Besides, vacancies may also induce dangling chemical bonds with unpaired electrons, which could result in spin polarization and lead to magnetism in graphene. Recent studies show that magnetization may be induced at locations of isolated vacancies [7,20–23] or continuous vacancies [20,24,25], or edges as well [26–28]. However, compared with absorbed atoms, the phenomena of vacancies induced magnetization would be more complicated since spin polarization could be induced by dangling bonds of sp^2 orbiting on remaining atoms near the vacancy. Additionally, one vacancy will induce not only dangling bonds but also magnetic moments, so some approximation methods for long distance

* Corresponding author.
E-mail address: hchyh2001@tom.com (Y. Hu).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.physb.2018.01.040
Received 6 October 2017; Received in revised form 16 January 2018; Accepted 17 January 2018
Available online 31 January 2018

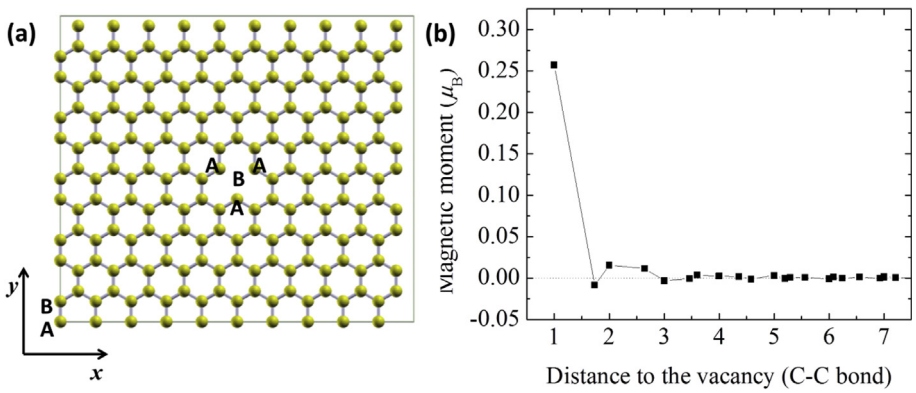

Fig. 1. (a) The initial rectangle unit cell. The vacancy is located on B-site. (b) The relationship between the magnetic moment on each atom and the distance to the vacancy. The unit of *x*-axis is the length of C—C bond in graphene, 1.42 Å.

are not suitable to estimate the RKKY interaction energy. Also vacancies could cause atoms around them to rearrange in new 5-, 7- or other numbered rings [29–32], which will break the symmetry of sublattices and complicate the problem.

In this paper, we attempt to use some simple cases to examine spin polarizations induced by a single vacancy in graphene. To understand how atom positions might affect spin polarizations, we first selected several unstable states and calculated the spin polarizations on a few special atoms near the vacancy location. We then applied different pinning boundary conditions to obtain the relaxed positions of the atoms around the single vacancy, which may correspond to the stable states, and calculated the spin polarizations of the special atoms. Our findings show that pinning boundary conditions could affect which atom(s) could become the main source(s) of magnetism, and relaxation under a special boundary condition might even out all spin polarizations. Here we assume that the spin polarizations should be proportional to the magnetic moments with a constant.

2. Computational details

First principle calculations were conducted in this work using open source code Quantum-ESPRESSO [33] based on density-functional theory, plane waves, and pseudopotentials. The exchange-correlation LDA function [34–37] dependent on pseudopotentials was used in our calculations. The initial unit cell is a rectangle as shown in Fig. 1(a), containing 199 carbon atoms and one vacancy. And the length of C—C bond length is 1.42 Å. As marked by A and B in Fig. 1(a), there are two types of sublattices in graphene and the vacancy is located on sublattices B. During the calculations of self-consistency field with spin polarizations, the cutoff kinetic energy for wave functions was 25.0 Rydberg. The cutoff kinetic energy for charge density and potential was 100.0 Rydberg. The k-point grid was $8 \times 8 \times 1$, and the convergence threshold was 1.0×10^{-6} a.u. As graphene is a 2D material, to simplify the problem, localized spin density approximation (LSDA) method was used in this work. During the calculations of relaxation, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm method was applied with the first-order Methfessel-Paxton spreading smearing method [38]. The k-point grid was $4 \times 4 \times 1$ and the convergence threshold on total energy was 1.0×10^{-6} a.u, and the convergence threshold on forces was 1.0×10^{-3} a.u.

3. Results and discussion

We first calculated the spin polarizations of the initial structure without any relaxation. Similar to previous results, sublattices A and sublattices B show opposite polarization directions. The relationship between the magnitudes of spin polarizations and the distance from the atoms to the vacancy is shown in Fig. 1(b). It is obvious that the total spin polarization is mostly contributed by the nearest neighbor atoms (which contain three atoms), and the magnitude of spin polarizations drops rapidly as distance increases.

This initial structure should be unstable because of the imbalanced forces on the atoms around the vacancy. The three nearest neighboring atoms will become closer to each other and reach their new positions. To understand how displacement could affect the spin polarization, we did an imaginary "experiment". We assumed a group of imaginary unstable states and calculated the spin polarization of each atom in these states. As shown in Fig. 2(a), we assumed an atom on sublattices An underneath the vacancy moves from its original position towards the vacancy on B site, and investigated the change of spin polarizations of certain chosen atoms (the moving atom A_1, and some neighboring atoms A_2 and B_2 as marked in Fig. 2(a)). The findings are presented in Fig. 2(b). It can be seen that the spin polarization of the moving atom A_1 drops to negative rapidly, and then slowly increase to a negative and minor value. For the other neighboring atoms, the maximum value of the spin polarizations on A_2 has the same position as the minimum value of the spin polarizations on A_1, while the spin polarization on B_2 always increases. We only move the atom A_1 for a distance of half of the length of C—C bond towards B_1 as the situations in the other half should be symmetrical. These results suggest that spin polarization of an atom near the vacancy falls rapidly when the atom departs from its original lattice position, and thus we believe major magnetic moments could be found on atoms remain close to their original lattice positions. The geometric symmetry and charge distribution of two-dimensional materials is closely in connected with their distribution of magnetic moment [39]. In case of slightly deviation from their original positions, the changes to the geometric symmetry and charge distribution are mostly significant, therefore the major spin polarization occur on the atoms.

Since the spin polarizations are mainly contributed by the nearest neighbor atoms which often undergo the largest displacements in relaxation, it would be interesting to study which atom(s) will become the main source(s) of spin polarization after relaxation. Therefore this work has also examined some relaxed structures that may correspond to the real cases. Different relaxed structures can be obtained with different boundary conditions. In our work, three different boundaries were used: (1) pinning along *x*-axis, i.e. the lattice parameter along *x*-axis of the unit cell in Fig. 1 (a) is fixed in the relaxation, and the lattice parameter along *y*-axis is allowed to change (referred as *x*-pinning); (2) pinning along *y*-axis, it is similar to *x*-pinning with switching *x*- and *y*-axes (referred as *y*-pinning); and (3) free of pinning, i.e. the two lattice parameters are both allowed to change.

The relaxed positions of the atoms near the vacancy are shown in Fig. 3(a), (b) and (c), with their backgrounds showing the relative original lattice positions. It is clear that the lattice parameters along *x*-axis become shorter and that along *y*-axis become longer under *x*-pinning, oppositely under *y*-pinning (note: to emphasize the displacements of the atoms, their backgrounds have also been stretched). The figures show that atoms with major displacement under *x*- or *y*-pinning are not the