Nanotube-based molecular magnets with spin-polarized edge states

2004 J. Phys.: Condens. Matter 16 S5689

(http://iopscience.iop.org/0953-8984/16/48/028)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S5689–S5692 PII: S0953-8984(04)79311-X

Nanotube-based molecular magnets with spin-polarized edge states

Yusuke Higuchi[1], Koichi Kusakabe[2], Naoshi Suzuki[2], Shinji Tsuneyuki[3], Jun Yamauchi[4], Kazuto Akagi[3] and Yoshihide Yoshimoto[5]

[1] Graduate School of Science and Technology, Niigata University, Niigata, Niigata 950-2181, Japan
[2] Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[3] Graduate School of Science, University of Tokyo, Bunkyo, Tokyo 113-0033, Japan
[4] Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223-8522, Japan
[5] Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

Received 15 April 2004, in final form 10 September 2004
Published 19 November 2004
Online at stacks.iop.org/JPhysCM/16/S5689
doi:10.1088/0953-8984/16/48/028

Abstract

Edge effects on possible magnetism appearing in finite hydrogenated zigzag nanotubes are investigated using the DFT–LSDA calculations. Our result shows that two types of edges, i.e. a mono-hydrogenated zigzag edge (MHZE) and a di-hydrogenated zigzag edge (DHZE), can give magnetic moments in finite nanotubes. Due to curvature of the tube, however, the total magnetic moment S_{tot} is smaller than an expected value given by a counting rule of S_{tot}, which holds for magnetic nanographite ribbons. In addition to magnetic nanotubes found by Okada and Oshiyama, we show that a $(7, 0)$ tube and an $(8, 0)$ tube with both MHZE and DHZE are magnetic. The reactions to create hydrogenated $(7, 0)$ and $(8, 0)$ tubes are exothermic.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotubes are known to show almost every interesting physical property found in condensed matter physics [1, 2]; their application is thus widespread. Magnetism, however, is a remaining phenomenon which is not listed in intrinsic physical properties of nanotubes. Recently, several theoretical groups have concluded magnetic solutions for carbon nanotubes without magnetic elements [3–6]. Mechanisms of magnetism discussed in these investigations are classified into two categories. The first one is the edge effect [3–5] and the other is the effect of defects in the π network [6].

As a typical edge effect, one of the present authors (KK) and Maruyama showed that the di-hydrogenated zigzag edge (DHZE) is a key to creating magnetic nanographite [3, 7]. Creating a structure with the DHZE at one end and the mono-hydrogenated zigzag edge (MHZE) at the

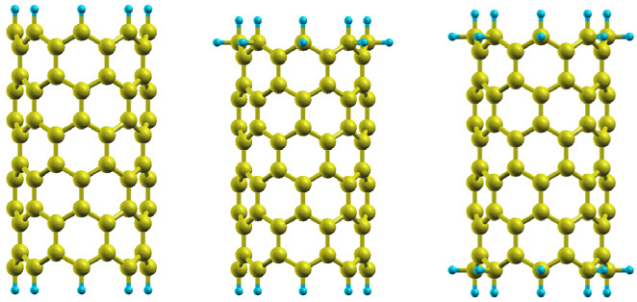

Figure 1. Possible structures of nanotubes with the mono-hydrogenated zigzag edge and/or the di-hydrogenated zigzag edge (MHZE, DHZE). Combining these edges in a structure, we obtain three possible tubes. Structures are (a) an MM tube, (b) an MD tube and (c) a DD tube.

other end, we can make finite graphitic structures, e.g. graphene ribbons and tubes, magnetic. This is because two hydrogen atoms at an edge carbon behave like a π site, where two 1s orbitals form a π orbital. Then, addition of extra π sites occurs and balance between numbers of sublattice sites is broken. This imbalance causes magnetism, as expected for alternant hydrocarbons. Otherwise, magnetism is not expected, if we consider a tube as an alternant hydrocarbon with a network of π orbitals.

Interestingly, this simple mechanism seems not always to be true for the nanotubes. There could be magnetism for a tube with only the MHZE, where the diameter of the tube was asserted to be a decisive factor [4]. The mechanism here is a spin polarization of nearly degenerate edge states appearing on these finite tubes. Bare edges with dangling bonds are another magnetic edge; however, the spin moment is localized at edge atoms [5].

In this paper, we reinvestigate finite zigzag nanotubes which can be magnetic. We will compare atomic structures of tubes studied so far using the same calculational conditions. For tubes with fairly small diameter, the spin polarization is dominated by spin polarization of edge states and a finite moment appears, depending on both the diameter of the tubes and the type of edge.

2. Structures and methods

If we look at existing DFT–LSDA calculations on magnetic hydrocarbon nanotubes, three types of edges, i.e. the bare zigzag edge (BZE), MHZE and DHZE, are known to have magnetic moments. However, we should stress that combination of these edges formed in a structure is an important factor. We performed structural optimization calculations for three structures shown in figure 1. We investigated a $(7, 0)$ tube and a $(8, 0)$ tube. The length of the tubes is $N = 6$. Here the length N denotes the number of carbon zigzag lines perpendicular to the tube axis. Since the BZE is energetically more unstable than the others, we focus on the MHZE and DHZE in this work. Each structure is referred to by the type of edge as MM, MD and DD. Here, M and D represent MHZE and DHZE, respectively. MM tubes are identical to those investigated by Okada and Oshiyama.

For the electronic structure calculation, we used an LSDA functional given by Perdew and Wang [8]. The ultrasoft pseudopotential was adopted to describe electron–ion interactions [9]. The valence wavefunctions of the Kohn–Sham orbitals were expanded in a plane-wave basis set. We adopted an energy cut-off $E_c = 25$ Ryd. Since we utilize the super-cell technique

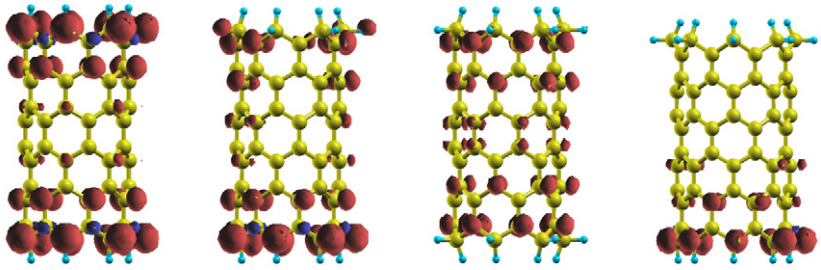

Figure 2. Optimized structure of (7, 0) tubes with various combinations of edge structures: (a) a (7, 0) MM tube ($S = 2$); (b) a (7, 0) MD tube ($S = 3/2$); (c) a (7, 0) DD tube ($S = 1$). (d) An (8, 0) tube with MHZE and DHZE ($S = 1$) is also shown. The spin density is shown by isosurfaces.

Table 1. The total spin of various tubes. Symbols MM, MD, and DD denote a tube with only MHZE, that with MHZE and DHZE, and that with only DHZE. (n, m) represents the index of the tube. For a (7, 0) MD tube, a state with $S = 3/2$ is energetically close to a state with $S = 1/2$. Thus, we cannot determine the total spin of the ground state for this structure.

	MM	MD	DD
(7, 0)	2	3/2 or 1/2	1
(8, 0)	0	1	0

Table 2. The creation energy in hydrogen addition to MM or MD tubes. Symbols ΔE and $\Delta E'$ denote the creation energy of an MD tube from an MM tube and that of a DD tube from an MD tube, respectively. The reaction is endothermic if the value (eV) is positive, and it is exothermic if the value is negative.

	ΔE	$\Delta E'$
(7, 0)	−1.64	−1.75
(8, 0)	−1.37	−1.71

for isolated molecules, sampling on the k points was done with only the Γ point. Structural optimization was performed until each component of the interatomic force became less than 1×10^{-4} H au^{-1}.

3. Magnetic hydrocarbon nanotubes

For MM, MD and DD tubes, we obtained stable structures. The length of the tubes is $N = 6$ for (7, 0) and (8, 0) tubes. We summarize the ground-state total spin for these tubes in table 1. A (7, 0) tube has total spin in all structures which consist of a combination of MHZE and DHZE. The total spin of an MM tube [4] is the largest of the three stable structures. But only the MD tube has total spin $S = 1$ in an (8, 0) tube. The magnetic profile is shown in figure 2 for (7, 0) MM and MD tubes as well as that for an (8, 0) MD tube. The spin density is localized at both ends in the former two tubes. For an MD tube, the spin density around the DHZE is lower than that around the MHZE. For an (8, 0) MD tube, the spin density around the DHZE is almost invisible and it is nearly localized around the MHZE. This result is different from the previous result on a graphene ribbon with both MHZE and DHZE [3, 7], where the DHZE has a clear magnetic moment and the total moment per carbon atom is much larger. For a (7, 0)

DD tube, the spin density is distributed on the whole structure. This tendency is similar to the case of the MM tube.

The creation energy of an MD tube from an MM tube and H_2 molecules, and that of a DD tube from an MD tube and H_2 molecules, are shown in table 2. All reaction are exothothermic. Thus hydrogen addition makes nanotubes energetically stable. This result is also different from the case of graphene ribbons, where hydrogenation is endothermic. Curvature in a graphene structure, thus, makes reactivity and magnetism different from the planar structures.

4. Summary

In summary, we have performed *ab initio* calculations on (7, 0) and (8, 0) tubes with several types of edges. We have reinvestigated the effect of hydrogen addition at edges. A (7, 0) tube which has both ends terminated by hydrogen has the total spin in the ground state. Only an (8, 0) tube which has MHZE and DHZE shows a finite spin moment in the ground state. The hydrogenation of (7, 0) or (8, 0) MM tubes is exothermic.

Acknowledgments

The theoretical calculation was performed with TAPP (Tokyo *Ab initio* Program Package) [10, 11]. This work was partly supported by a Grant-in-Aid for Scientific Research (No 15310086) from JSPS and a Grant-in-Aid from the MEXT of Japan (No 15GS0213), the MEXT Special Coordination Funds for Promoting Science and Technology (Nanospintronics Design and Realization), NEDO under the Materials and Nanotechnology Programme and the Research and Development Applying Advanced Computational Science and Technology Programme of ACT–JST.

References

[1] Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)
[2] Dresselhaus M S, Dresselhaus G and Avouris Ph 2001 *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* (Berlin: Springer)
[3] Kusakabe K and Maruyama M 2003 *Phys. Rev.* B **67** 092406
[4] Okada S and Oshiyama A 2003 *J. Phys. Soc. Japan* **72** 1510
[5] Kim Y H *et al* 2003 *Phys. Rev.* B **68** 125420
[6] Park N *et al* 2003 *Phys. Rev. Lett.* **91** 237204
[7] Maruyama M and Kusakabe K 2004 *J. Phys. Soc. Japan* **73** 656
[8] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244
[9] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892
[10] Tsukada M *et al* 1983–2000 *Computer Program Package TAPP* University of Tokyo, Tokyo, Japan
[11] Yamauchi J *et al* 1996 *Phys. Rev.* B **54** 5586