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Magnetism of Co_{13}-Filled Carbon Nanotubes of Diverse Chiral Symmetry

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ABSTRACT

The attempt to study magnetism in (n,m) chiral space of single-walled carbon nanotubes (SWNTs) with embedded metal cluster is presented. Co_{13} metallic cluster inside zigzag and chiral single-walled nanotubes was investigated using density functional theory (DFT). Magnetic properties of the endohedral nanotubes with the various chiral index (n,m) were characterized by calculation of the total spin magnetic moment (S). The dependence of S on the chiral symmetry of nanotubes, as well as the orientation of Co_{13} cluster within nanotubes was found. Longitudinal orientation of icosahedral Co_{13} cluster was preferable for magnetization in general. However, it was shown that the magnetic landscape $M = f(n,m)$ of endohedral nanotubes is very complex and sharp.

Keywords: Magic Co_{13} Cluster; Endohedral Nanotubes; Chirality; Total Spin Magnetic Moment

1. Introduction

Thorough investigation of nanoobjects, such as metal [1] and carbon [2] clusters, is essential because their characteristics are unlike bulk materials [3,4]. Carbon fullerenes and nanotubes have been paid immense attention to since they were discovered in 1985 and 1991 [5,6]. Tiny space inside a fullerene or a carbon nanotube (CNT) may be considered as a unique place for atomic clusters. The endohedral fullerenes and CNTs show many remarkable physical and chemical features [7-12].

I reported recently on computational results on magnetic properties of putative $Co_n@C_m$ (n = 5, 13; m = 60, 70 and 80) endohedral metallofullerenes [13,14]. Instead of fullerenes, single-walled nanotubes (SWNTs) may be preferable, because ends of nanotube are open allowing entering the tube [15-17]. In this paper, I use the same computational approach as done in [13,14] to study the magnetism of SWNTs with various chirality which were filled by the icosahedral magnetic Co_{13} cluster in alternative orientations to the nanotube's channel.

2. Method

CoNTub 1.0 program [18,19] was used to determine atomic coordinates of SWNTs with chiral vector (n,m). The diameter of nanotubes was calculated from (n,m) indices as follows:

$$d = \frac{a}{\pi}\sqrt{\left(n^2 + nm + m^2\right)},$$

where a = 0.246 nm. Obtained nanotubes were filled by Co_{13} cluster using SPDB viewer 4.1 [20]. Magnetic moments of the endohedral nanotubes were calculated on the basis of density functional theory (DFT) [21] within OpenMX 3.5 software [22-25]. Two density functionals, such as the local spin density approximation of Ceperley-Alder (LSDA-CA) [26] or the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) [27], both with the active spin polarization, were used to compare outputs. Energy convergence was performed by the generalized divide-conquer optimization technique using parameters fitted to d-orbitals of Co-atoms. The self consisted field (SCF) criterion corresponded to 6×10^{-6} Hartree. The atomic species were defined as C4.0-s1p1 and Co5.5-s2p2d2f1. Electronic temperature was 300.0 K and the energy cutoff was 200.0 Ry. Total spin S was accepted as a value of magnetic moment.

3. Data Processing and Results

The computation parameters for pure Co clusters were chosen and checked as described previously in [13,14]. The idea was to calculate metal-carbon complexes using the OpenMX's basis set, which was originally developed to simulate large systems [22]. I also used the relative

assessment and internal reference. The values of magnetic moments for Co_5 and Co_{13} clusters were obtained, such as 2.60 and 2.39 μ_B/atom respectively, which is in agreement with [28]. It is higher than for the bulk Co material, 1.62 μ_B [29]. The computational procedure was tested on Co_5- and Co_{13}-carbides giving reliable results. LDA and GGA approximations demonstrated similar outputs $\left(R_{LDA/GGA} = 0.99\right)$. However, the standard deviation of magnetic moments for $Co_{13}C_{12}$ carbides was bigger than for Co_5C_5 carbides after five independent runs for each system, such that 0.0521 versus 0.0004 μ_B [13]. That allowed me to use this computational approach to investigate the endohedral fullerenes $Co_n@C_m$ (n = 5, 13; m = 60, 70, 80), then to attack the endohedral nanotubes filled with Co_{13} cluster. The length of SWNTs was 10 Å; the number of carbon atoms varied around 60. For example, the zig-zag (7,0) tube consisted of 56 C-atoms, as well as the chiral (5,3) or (6,2) tube included 64 C-atoms. As the gradient and sub-space optimization methods did not allow always reaching a ground state for complex systems, the SCF criterion was decreased to 10^{-6} Hartree.

In experiments, I varied the chiral index (n,m) of SWNTs to investigate the (n,m) parametric space. The smallest stable endohedral structures were zigzag (7,0) and chiral (5,3) tubes having the diameter 5.48 Å with an internal space still available for doping Co_{13} cluster 4.67 Å in size in different orientations.

When local spin density approximation (LDA functional) was applied, the zigzag (7,0) nanotube with an across oriented Co_{13} cluster showed the magnetic moment 1.54 μ_B that is 4.8 times less than for along oriented Co_{13} cluster with the corresponding magnetic rate 7.34 μ_B. In the case of generalized gradient approximation (GGA functional), the values were 2.99 and 8.14 μ_B in across and along orientations, respectively (**Figure 1**).

The similar pattern of magnetic activities depending on orientation of the Co_{13} cluster was found for the chiral (5,3) tube with the same diameter 5.48 Å as the zigzag (7,0) tube. In the frame of LDA approach, when the Co_{13} cluster took a cross orientation to the channel, the magnetic rate was 3.42 μ_B, and when an along orientation of Co_{13} cluster was considered, then the magnetic moment of the complex was 6.24 μ_B that is 1.8 times higher. When I used GGA method, the magnetism was estimated as 3.24 and 5.27 μ_B, respectively. It is interesting that the difference in magnetic moments depending on Co_{13} cluster orientation was smaller for a chiral tube than for a zigzag tube with the same diameter.

An unexpected result was obtained from experiments on the chiral (6,2) tube with a bigger diameter 5.65 Å. The magnetic moments of this filled nanotube for various orientations of Co_{13} cluster were smaller than in the case of the chiral (5,3) tube, such as 1.15 μ_B for across orientation and 3.65 μ_B for longitudinal orientation with LDA calculations, as well as 0.86 and 3.37 μ_B, respectively for GGA technique.

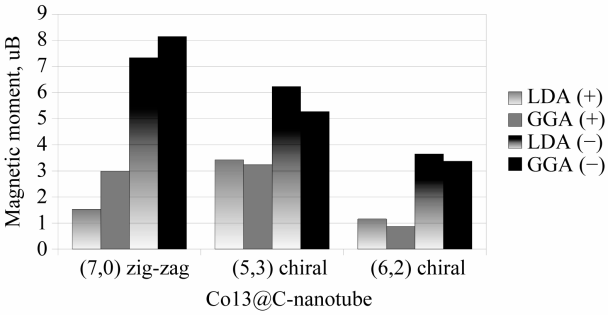

Figure 1. Total spin magnetic moments $S(\mu_B)$ of endohedral carbon nanotubes depending on the chiral symmetry and position of Co_{13} impurity, where (+) is across orientation, and (−) is longitudinal orientation of the Co_{13} cluster to the nanotube's channel.

In general, the correlation between LDA-CA and GGA-PBE methods on the given experimental set was significant $\left(R = 0.937\right)$.

4. Analysis and Discussion

As follows from the outcome above, the Co_{13} cluster emits more magnetism in an along orientation than in a cross orientation to the channel of a nanotube (**Figure 1**). This data is in good agreement with the result on doped by Co_5 elongated fullerene C_{70}-D_{5h} and confirms the earlier conclusion: the closer carbon and cobalt atoms, the less magnetic moment of the Co-C complex [13,14]. Nevertheless, this simple rule does not work in the matter of chiral nanotubes. As such, the Co_{13} cluster emits less magnetism in the (6,2) tube with the diameter 5.65 Å than in the (5,3) tube with the diameter 5.48 Å, which demonstrates a nontrivial role of the carbon structure in magnetisation of Co-C complex. This finding is very interesting because the transmission electron microscopy, electron diffraction, and X-ray spectroscopy showed a structural transition of Co particles inside CNTs from hexagonal-close-packed (hcp) arrangement to face-centered-cubic (fcc) organization as a result of interaction between Co nanoparticles with CNTs [30].

Although the magnetic features of Co_{13} cluster in nanotubes were noticeable in our calculations, the hidden mechanisms of magnetism and peculiarity of electron actions in filled nanotubes are out of DFT approach [31, 32]. The chemical structure of nanotubes is composed of sp^2 bonds, similar to those of graphite. Like in graphite, electrons can move along a tube, parallel to the graphene sheet. However, some tubes have a band gap like semiconductors that depends on chirality. For instance, (n,n) armchair tubes are metals, chiral (n,m) tubes with n-m divisible by 3 are small band gap semiconductors, all

other tubes are large-band gap semiconductors [33]. Hence, experimental nanotubes with chiral indexes (7,0), (5,3), (6,2) are large-band gap semiconductors. Nonetheless, they demonstrated different properties of magnetism with introduced Co_{13} cluster, depending on the chiral symmetry that was not observed early on regarding endohedral fullerenes with chirality types (1,1) and (2,0) [14].

5. Conclusion

The total spin magnetic moment S of Co_{13} cluster with icosahedral symmetry decreased in the SWNT environment more significantly in the case of across orientation of the cluster than in the longitudinal orientation to a channel of nanotube. The magnetism did not monotonically descent with the decreasing diameter of filled carbon tube like endohedral fullerenes. Thus, open ends of carbon nanotubes are an important factor in the magnetic behavior of SWNTs doped with metallic cluster.

The parametric space in which the chiral vector (n,m) presented the symmetry of a nanotube was partly investigated. The magnetic moment of Co_{13} cluster embedded into carbon nanotubes of different chirality (n,m) varied in a wide range. The landscape of $M = f(n,m)$ was very ruffle and unpredictable. Most structures were hard to calculate with LDA and GGA functionals. However, I hope a protonation of nanotube's ends and new approaches will possibly allow to investigate extensive (n,m) space.

In summary, the magnetic states of endohedral carbon nanotubes were strongly dependent on the orientation of Me-cluster within nanotube and on the fine atomic structure of carbon shell, *i.e.* on the specific arrangements between the metal and carbon atoms.

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