

## INCORPORATION OF Ni NANOFILAMENT INSIDE CARBON NANOTUBES: DFT CALCULATIONS

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First principles calculations have been performed to investigate ground state properties of monoperoiodic carbon nanotubes (CNTs) containing nanochain of Ni atoms inside. Using PBE exchange-correlation functional ( $E_{xc}$ ) within the framework of density functional theory (DFT), we predict the fragmentation of Ni nanofilament inside  $(n,0)$  CNTs for  $n > 10$ , while in  $(n,n)$  NTs the nanochain composed from Ni atoms is stable irrespectively on the nanotube diameter. The variations in formation energies obtained for equilibrium defective nanostructures allow us to predict the most stable compositions, irrespectively on the growth conditions. The changes in the electronic structure are analyzed in order to show an extent of localization for the ferromagnetic ground state.

### 1. Introduction

Carbon nanotubes (CNTs) and nanochains from metal atoms are important one-dimensional (1D) nanostructures fabricated and studied in recent years due to their remarkable physical, chemical and mechanical properties as well as perspective applications in nanodevices [1]. CNTs filled with magnetic elements, like Ni or other transition metals (Ni@CNT), make them potentially applicable for magnetic data storage and drug delivery. In addition, carbon walls can provide an effective barrier against oxidation and, thus, ensure long-term stability of encapsulated metal nanochains. Nevertheless, the Me@CNT complexes do not display always designed properties since both amount and location of magnetic particles inside the nanotubes are difficult to be controlled. For reproducible fabrication of these complexes, it is important to understand the formation mechanism of metal nanowires or nanoparticles in the tubes.

In this paper, we consider monoatomic chains of nickel atoms encapsulated into single-walled CNTs of zigzag-type (zz)  $(n,0)$  and armchair-type (ac)  $(n,n)$  chiralities with varied  $n$  indices. We determine the optimal nanotube size for both

zz- and ac-chiralities, to encapsulate there a single-atomic nanowire, as well as the most stable atomic arrangement adopted by this nanowire.

## 2. Computational details

Using a model of structural transformation ( $3D \rightarrow 2D \rightarrow 1D$ ) [2,3] we have constructed a monoprotic unit cell (UC) of ideal carbon nanotubes of ac- and zz-chiralities (Fig. 1).

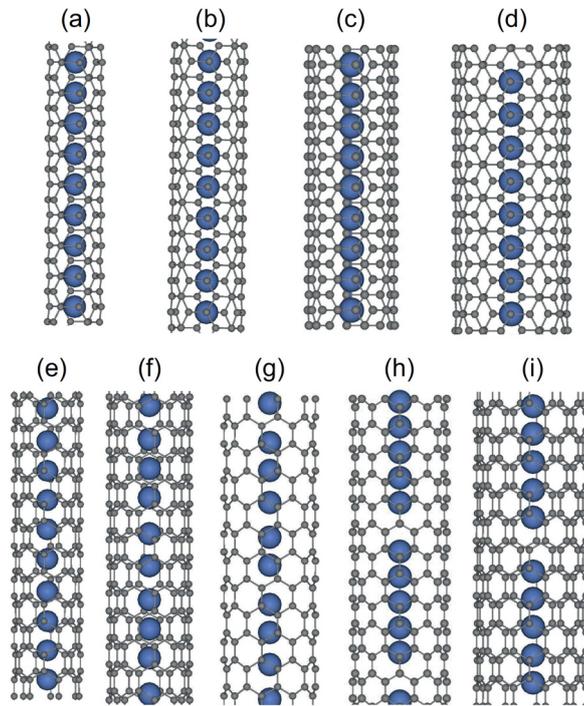


Figure 1. Equilibrium structures for Ni nanofilament inside (a) CNT (3,3), (b) CNT (4,4), (c) CNT (5,5), (d) CNT (6,6), (e) CNT (7,0), (f) CNT (8,0), (g) CNT (9,0), (h) CNT (10,0) and (i) CNT (11,0) as calculated by the DFT method using PBE functional.

The coordinates of all atoms for each nanostructure containing Ni nanofilament have been optimized using PBE-LCAO method as implemented in the total energy computer code CRYSTAL [4] based on the formalism of the localized Gaussian-type functions (GTFs), which form the basis set (BS), and exploiting the periodic rototranslation symmetry for efficient ground-state calculations. In the current study, the all-electron Ni BS has been employed:  $8s64111sp41d$  [4] with the exponents of core and valence shells unchanged. In

addition, two virtual Ni *sp*-functions with the exponents of 0.63 and 0.13, respectively, and *d*-function with the exponent 0.38 have been used as optimized in bulk calculations. The all-electron BS for carbon has been adopted in the form of *6s-311sp-11d* [4].

To provide the balanced summation over the direct and reciprocal lattices, the reciprocal space integration has been performed by sampling the Brillouin zone (BZ) with the  $10 \times 1 \times 1$  Monkhorst-Pack *k*-mesh that results in 6 eventually distributed *k*-points at the segment of irreducible BZ. Calculations are considered as converged when the total energy obtained in the self-consistent field (SCF) procedure differs by less than  $10^{-7}$  a.u. in the two successive SCF cycles. Effective charges on atoms as well as bond populations have been calculated according to the Mulliken population analysis [4].

### 3. Results and discussion

In Table 1 we present calculated parameters of Ni@CNTs. The formation energies of Ni nanofilament inside relaxed CNTs (Table 1) have been found increasing along with the diameter of the nanotube. It can be explained by a weakening bond between Ni and C atoms. On the other hand, this results in a stronger Ni-Ni bonding in Ni nanochain (Table 1 shows that the  $P_{\text{Ni-Ni}}$  is increasing with CNT diameter growth). In the case of *zz*-CNTs starting from  $n = 10$ , our calculations predict formation of 1D Ni nanoclusters inside the nanotube. Note, that the formation energy is negative for all Ni@CNT complexes under study that means the exothermic formation of nanostructures.

Table 1. Equilibrium diameter of Ni@CNTs ( $D$  in Å), energy of nanostructure formation ( $E^{\text{form}}$  in eV/atom), the distance between the closest neighbored Ni atoms in the Ni nanofilament encapsulated into CNT ( $d_{\text{Ni-Ni}}$  in Å), the difference in Ni-Ni distance in the encapsulated nanochain with respect to the nanofilament exposed in the vacuum ( $S_{\text{Ni-Ni}}$  in %), Ni-Ni bond populations ( $P_{\text{Ni-Ni}}$  in milli  $e$ ), and the magnetic moment on Ni atoms ( $M_{\text{Ni}}$  in Bohr magnetons) as calculated using the PBE-DFT method.

	$D$	$E^{\text{form}}$	$d_{\text{Ni-Ni}}$	$S_{\text{Ni-Ni}}$	$P_{\text{Ni-Ni}}$	$M_{\text{Ni}}$
Ni/CNT (3,3)	4.32	-0.21	2.49	10.8	142	0.32
Ni/CNT (4,4)	5.56	-0.17	2.46	9.5	414	1.09
Ni/CNT (5,5)	6.88	-0.13	2.46	9.3	472	1.12
Ni/CNT (6,6)	8.22	-0.10	2.46	9.2	512	1.27
Ni/CNT (7,0)	5.62	-0.16	2.49	10.4	400	1.13
Ni/CNT (8,0)	6.38	-0.14	2.56	13.5	544	1.32
Ni/CNT (9,0)	7.15	-0.12	2.37	5.4	607	1.27
Ni/CNT (10,0)	7.92	-0.10	2.13	-5.2	676	1.26
Ni/CNT (11,0)	8.70	-0.09	2.13	-5.5	684	1.21
Ni nanochain			2.25	0	600	1.21
Ni (bulk)			2.50	11.1	174	0.62

Magnetic moments calculated on Ni atoms are twice larger than in Ni bulk, that reflects an enhancement of magnetic properties in Ni@CNT nanostructures.

The projected density of states calculated for the Ni filament encapsulated inside (5,5) and (10,0) CNTs reveals the Fermi level  $\varepsilon_F$  positioned at spin-down sub-band of Ni *d*-states while the spin-up sub-band of Ni *d*-state is shifted by 1.5 eV below  $\varepsilon_F$ . The ferromagnetic metallic ground state has been predicted for all Ni/CNTs under study even if pristine CNTs were semiconducting.

#### 4. Conclusion

We have performed large-scale first-principles calculations on CNTs with encapsulated Ni nanochains. Armchair-type CNTs with incorporated Ni are found to be the more stable structures, with the stronger interatomic Ni-C bonding than in zz-CNTs due to the smaller energy of formation. CNT(5,5) and CNT(10,0) have been found the most preferable for Ni filament insertion. In all the cases, Ni nanofilament preserves the ferromagnetic ground state. The calculated magnetic moment of Ni filament is twice as larger than in the Ni bulk ( $0.62 \mu_B$ ). Ni filament tends to be clustered if placed inside the CNT (*n*,0) with *n* > 10. The main reason for this effect is the mismatch between the nanotube and the nanofilament. Our calculations show that CNTs with Ni filament exhibit metallic behavior, even if pristine CNTs are semiconducting (*i.e.*, zz-type).

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