Bistability, softening, and quenching of magnetic moments in Ni-filled carbon nanotubes

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The authors apply first-principles calculations to investigate the interplay between structural, electronic, and magnetic properties of nanostructures composed of narrow nanotubes filled with metallic nanowires. The focus is on the structural and magnetic responses of Ni-filled nanotubes upon radial compression. Interestingly, metastable flattened structures are identified in which radially deformed nanotubes are stabilized by the interactions with the encapsulated wire. Moreover, our results indicate a quenching of the magnetic moment of the wire upon compression, as a result of the transfer of charge from *s* to *d* orbitals of the atoms in the wire.

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The possibility of metal encapsulation in carbon nanotubes has attracted the attention of the physics community since the very beginning of the research in this field. In the early years, following Iijima's paper on the synthesis of nanotubes,[1] several groups reported capillarity effects and filling of large diameter multiwall nanotubes with a variety of elements.[2–4] However, the synthesis of subnanometer structures of this type remained a challenge until recently, when a protocol to fill very narrow nanotubes (~8.0 Å in diameter) with metallic wires was reported.[5,6] Encapsulation protects the wire against oxidation, opening up the possibility of the experimental confirmation of theoretical predictions, such as the enhancement of magnetic moment of transition-metal nanowires relative to bulk values.[7–10] In parallel to these reports, important advances in manipulation processes have been achieved. For instance, electric force microscopy measurements have been employed to probe effects of deformation on the electronic and structural properties of nanotubes, confirming theoretical predictions[11,12] of a semiconductor-metal transition upon flattening of the nanotube cross sections.[13,14]

In the present work, we apply first-principles calculations to investigate the behavior upon radial compression of narrow nanotubes filled with metallic wires. The interplay between structural, electronic, and magnetic properties is the main focus of our study. We address the following questions: (i) how does the total energy behave as the nanotube is flattened, when a metallic chain is encapsulated within the nanotube, and how does this elastic response compares with that of empty nanotubes?[14] (ii) If the encapsulated metal is magnetic, how does the magnetic moment vary, if it does at all, upon compression?

To address these and related questions, we perform first-principles electronic-structure calculations based on the density-functional theory[15] within the generalized gradient approximation.[16,17] We employ the SIESTA implementation,[18,19] which makes use of norm-conserving pseudopotentials[20,21] and a basis set composed of pseudoatomic orbitals of finite range. The geometries in the unconstrained calculations are relaxed until the total energy of the unit cell changes by at most 0.03 eV.[22]

As a model for the metallic filling of the nanotube, we consider a Ni nanowire (see Ref. 23) along the z direction with four base atoms at (x,y,z) coordinates given by $(\pm b,0,0)$ and $(0,\pm b,a/2)$, where $b=1.52$ Å, and $a=2.36$ Å is the lattice parameter along the z direction. This choice is justified because, in this geometry, the nanowire is nearly commensurate with a nanotube with a diameter in the range of those observed in the above-mentioned experiments.[5,6] From the initial geometry, the whole nanowire-nanotube structure relaxes, and the nanowire undergoes a small transformation (akin to a slight dimerization) into an eight-atom unit that is commensurate with the nanotube period.

In Figs. 1(a) and 1(b), we show the cross sections of two metastable energy-minima geometries (on-center and off-center, respectively) for the encapsulation of the Ni wire in a (11,0) carbon nanotube. The off-center configuration is found to be energetically favorable by 0.52 eV/unit (i.e., 65 meV/Ni atom), when compared to the on-center one. Such stability enhancement is followed by an increase in the charge transfer from the wire to the nanotube (0.484e in the off-center as compared with 0.440e for the on-center geometry), indicating stronger interaction and hybridization. Concurrently, the magnetic moments are $5.83\mu_B$ and $4.28\mu_B$ for the on-center and off-center configurations, respectively. This suggests that there is a reduction in μ caused by the enhanced C-Ni interaction, which is in agreement with the findings of Jo *et al.*,[10] who found a decrease in the magnetic moments of encapsulated Ni wires when going from the

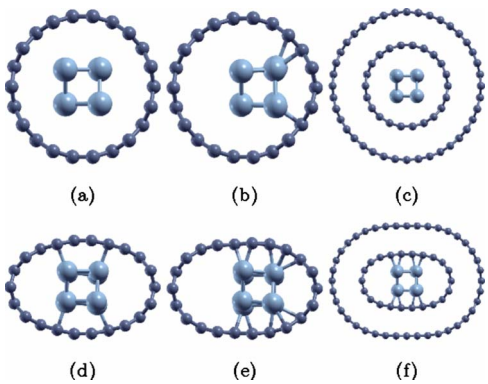

FIG. 1. (Color online) In (a), (b), and (c) are shown circular cross sections for on-center $Ni_8@(11,0)$, off-center $Ni_8@(11,0)$, and on-center $Ni_8@(11,0)@(20,0)$ configurations, respectively. In (d), (e), and (f), we show unconstrained optimized flattened versions of (a), (b), and (c), respectively.

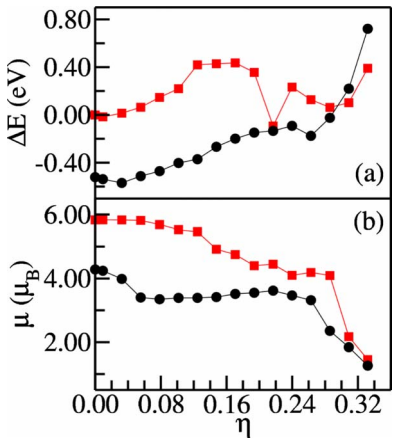

FIG. 2. (Color online) (a) Energy and (b) total magnetic moment for an eight-atom Ni wire inside a (11,0) carbon nanotube as a function of flattening (η is defined in the text). Red squares and black circles correspond to the on-center and off-center configurations, respectively.

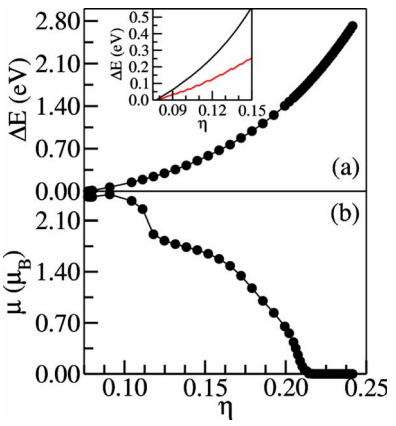

FIG. 3. (Color online) (a) Energy and (b) total magnetic moment for an eight-atom Ni wire inside a (9,0) carbon nanotube as a function of flattening (η is defined in the text). In (a), the inset shows a comparison between filled-nanotube (black line) and empty-nanotube (red line) responses to flattening.

(7,7) nanotube to narrower (5,5) one. In the following, we show that this is indeed the case, and ascribe this behavior to an increase in the charge transfer from s to d orbitals of the Ni atoms, upon confinement.

Taken together, the above results for the wire energetics and magnetic moments suggest that radially compressed structures might be relevant. To enforce radial compression, we use a methodology similar to the one employed in the investigation of the elastic and electronic properties of flattened carbon nanotubes:[11,13] deformed configurations are produced by building initial geometries for the nanotubes with cross sections composed of semicircles joined together by straight lines. We define the compressive strain $\eta=1-d/D$, where D is the diameter of the undeformed nanotube and d is the distance between the straight lines, kept fixed during the relaxation by constraining the positions of the atoms belonging to the planar regions.

The results of our calculations for the radially compressed Ni-filled nanotubes are displayed in Figs. 2(a) and 2(b), respectively, for the total energy (ΔE) and magnetic moment (μ) as a function of η, for both the on-center (red squares) and off-center (black circles) configurations. Figure 2(a) shows metastable (local minima) configurations around $\eta=0.22$ and $\eta=0.29$ for the on-center structure, and around $\eta=0.26$ for the off-center case. At these minima, the magnetic moment is substantially reduced both from its initial ($\eta=0$) value and from the free-standing-wire value of $\mu=6.8\mu_B$. For the on-center configuration in which the initial interaction among C and Ni atoms is weak, the magnetic moment steadily decreases (apart from small fluctuations) with the deformation. In the off-center case, the larger interaction substantially reduces the magnetic moment at the very beginning of the process, and a further decrease is observed for larger values of η.

The minima for $\eta>0$ of Fig. 2(a) were obtained under the geometrical constraints of the radial compression. We removed such constraints, and obtained the unconstrained metastable energy minima shown in Figs. 1(d) and 1(e). Interestingly, the self-flattened structure of Fig. 1(e) is the second most stable in Fig. 1, only 0.35 eV (0.04 eV/Ni atom) above that of Fig. 1(b), which is the most stable one. This raises the interesting possibility of achieving metastable flattened structures of Ni-filled nanotubes through compression by the tip of an atomic force microscope, for instance. Further, the geometry shown in Fig. 1(e) presents an average C-Ni bond length of 2.09 Å, which is in the range of typical C-Ni distances that have been reported in previous calculations for Ni interacting with carbon structures (2.07–2.20 Å).[10]

Previous modeling of the experimental results[6] suggest that, for the diameter range that includes the $(n,0)$ nanotubes with $9<n<14$, a metallic wire diameter such as the one employed in our models is consistent with the observed data.[6] A particular situation occurs for the (9,0) structure since the model wire perfectly fits into the nanotube, making covalent bonds with the walls even without deformation. In this case, the energy is a monotonically increasing function of the flattening distance, and the filled nanotube is harder than the empty one, as represented in the plots of Fig. 3(a). Interestingly, even in this case, the magnetic moment is initially nonzero ($2.40\mu_B$), and decreases as a function of the flattening parameter, reaching a null value for $\eta=0.21$ ($d=5.79$ Å), as shown in Fig. 3(b). Notwithstanding the lower formation energy per Ni atom for the filling of this nanotube [−0.44 eV/atom versus −0.24 eV/atom for the (11,0) nanotube], the kinematics of the process should be more favorable for the larger ones ($9<n<14$) since the Ni atoms tend to block the entrance of the narrowest (9,0) nanotube, hindering the uniform filling of the tube.

Since the experimental results[5,6] concern double-wall nanotubes, we have also considered the encapsulation of a Ni wire inside a (11,0)@(20,0) structure. Figure 1(f) shows the relaxed geometry (without constraints) for an outer-tube flattening distance of 13.1 Å, which resulted in a distance of 6.2 Å between the inner-tube flat walls. We notice that practically all charge transfers take place among the inner C atoms and the Ni atoms, the magnetic moment decreases to $4.04\mu_B$, and the nanotube (both walls) maintains the flat

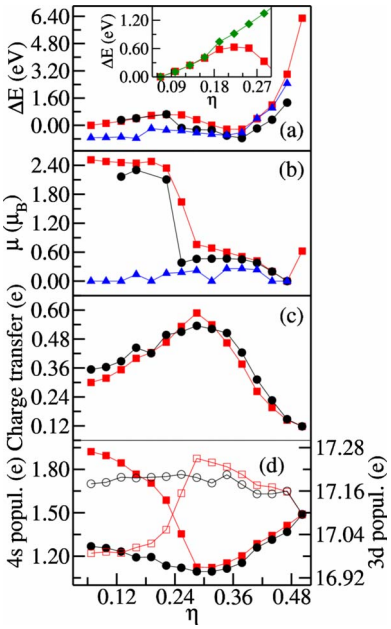

FIG. 4. (Color online) Energy, magnetic moment, charge transfer, and electronic population for a linear Ni wire inside a carbon nanotube as a function of flattening. Red squares, black circles, and blue triangles correspond to the on-center, and the OFF1 and OFF2 off-center configurations, respectively. In (a), the inset shows a comparison between empty and filled nanotube responses to flattening. In (d), the filled symbols represent the *s* population while open symbols represent the *d* population.

cross section, upon removal of the constraint.

In order to investigate whether the above results are more generally valid, and thus not restricted to the above geometries, we study a single Ni atomic chain encapsulated by the narrower (8,0) nanotube (diameter of 6.43 Å). Again, we consider on-center and off-center configurations. In this case, as shown in Fig. 4(a), we find two off-center minima, which we call OFF1 and OFF2, corresponding to off-center displacements between 0.50 and 0.87 Å in the OFF1, and 1.48 and 1.74 Å in the OFF2, depending on the degree of flattening. The results presented in Fig. 4(b) indicate a sharp decrease in the magnetic moment in these three metastable configurations. Note that in the OFF2 case, the wire is close enough to the nanotube wall for the magnetic moment to be totally suppressed (or nearly so) by encapsulation, even without flattening. For the on-center and OFF1 configurations, the magnetic moment is strongly suppressed after a critical degree of flattening is reached.

The inset in Fig. 4(a) shows a comparison between the elastic responses of empty and metal-filled nanotubes. We observe that for $\eta > 0.16$, the metal-filled tube is softened by interaction with the encapsulated wire, in contrast with the case of the (9,0) tube filled with a thicker wire. The effect is even more dramatic for the OFF2 case, for which the energy changes very mildly with flattening for $\eta \leq 0.38$. As mentioned before, the interpretation of these results may be pursued by looking at the variations in charge transfer between the wire and the tube, and also the intra-atomic charge transfer from *s* to *d* orbitals of the wire atoms. Figures 4(c) and 4(d) show both charge-transfer mechanisms for the on-center and lowest-energy off-center configurations as a function of η. It is clear that both are maximum at the η value where the strong quenching of magnetic moment kicks in. Also, upon increasing the confinement, Ni *s* electrons are transferred to *d* orbitals, quenching the magnetic moment, as can be seen in Fig. 4(d). Basically, the same reasoning applies to the wider wire-nanotube system discussed above.

In summary, we predict that metastable flattened configurations of filled nanotubes may be achieved through radial deformation. Also, the deformation induces a decrease in the magnetic moment, which may cause a sharp transition to a nonmagnetic state for sufficiently narrow wires.

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