Carbon encapsulated iron nanowires

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A study of the structural and magnetic properties of carbon encapsulated iron nanowires is presented. The influence of carbon presence on iron magnetic ordering by means of an *ab initio* computer simulation has been studied. For wires tightly encapsulated, i.e. with large ratio of wires and nanotubes radii, the presence of carbon strongly alters Fe magnetic configuration of free standing wires, in some cases yielding antiferromagnetic ordering. The energy differences between ferromagnetic and antiferromagnetic phases are small enough to allow their coexistence in a nanowire, which is in agreement with the experimental evidence of exchange-bias in such systems.

Key words: *nanowires; nanotubes; magnetism; ab-initio; exchange bias*

1. Introduction

Carbon nanotubes are promising candidates for a variety of applications due to their uncommon and versatile electrical and mechanical properties which recently generated an active area of research [1]. Possible technological applications include, among others, nanotransistors [2, 3], spin-polarized electron sources [4], hydrogen storage [5, 6], flat display panels [7] and magnetic inks. Transition metal (TM) filled nanotubes are expected to have a strong impact on magnetic recording devices since dramatic improvement in memory density could be achieved in quantized magnetic disks, taking advantage of small sizes and magnetic anisotropy of the nanowires. Moreover, experimental works on iron filled nanotubes with shifted hysteresis loops suggest the presence of γ-Fe–α-Fe interfaces, and the existence of the exchange bias phenomenon [8, 9]. Theoretical works on TM-filled nanotubes deal with a small number of iron atoms inside a carbon nanotube [10, 11].

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We present the results of the investigation of structural and magnetic properties of iron nanowires encapsulated by single wall, zigzag type, carbon nanotubes of several diameters. For the iron nanowires, we adopted two different diameters; the smaller unit cell consists of two triangular Fe layers of six atoms each, resembling a part of the hcp structure. For wires of larger diameter, we increase the number of Fe atoms per layer from six to twelve.

2. Simple model

We start with the mentioning of the results of a simpler model presented previously [12]. Here a nanowire with six Fe atoms per layer is surrounded by a rather small number of carbon atoms arranged as six symmetrical lines parallel to the axis of the wire, as shown in Fig. 1. It is not a real nanotube-encapsulated iron nanowire but it may be considered as a first order approximation, suitable for a fast DFT study on the carbon influence on the magnetic behaviour of a nanowire. The system has the diameter of 6 Å.
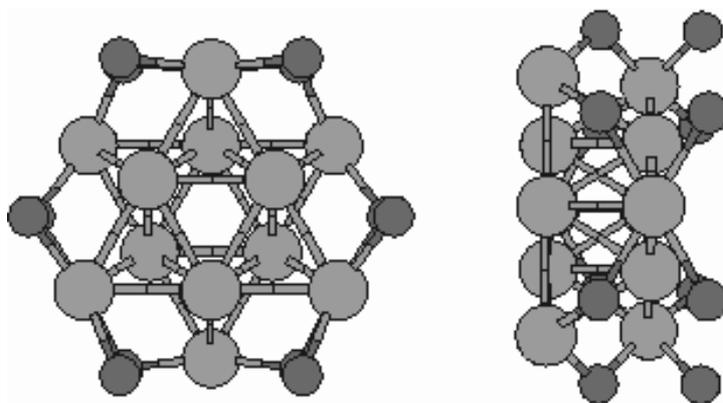

Fig. 1. Unit cell of 6 Fe atoms per layer surrounded by six lines of carbon viewed perpendicular (left) and parallel to the tube axis. The distance between the carbon layers is 2.03 Å and the C–C distance in the same layer is 3.5 Å. The Fe–C distance is taken equal to 2.03 Å, similar to that found in cementite. The AFM phase is energetically favourable for this system, lower than the FM phase energy by 0.014 eV/atom. The energy gain due to encapsulation was estimated as 3.77 eV/atom for the FM and 3.87 for the AFM phase. The magnetic moments present lower values at $2.0\mu_B$ (peripheral Fe), $1.8\mu_B$ (interior Fe) and $-0.1\mu_B$ (C)

Since in the bulk the fcc structure has the same number of nearest neighbours as the hcp one, we expect similar results for both structures. The Wien2k code [13] has been used in the calculation which is an implementation of the FPLAPW (full potential linear augmented plane aves) method. It uses the exchange and correlation given by Perdew, Burke and Ernzerhoff [19, 20]. The GGA (generalized gradient approximation) was chosen because it gives good results for the bulk bcc Fe lattice parameter

and cohesive energy. The number of plane waves used, given by the parameter RKM = 7, corresponds to the energy cut-off of 206 eV. The calculation is scalar relativistic and includes local orbitals for the 3p states of Fe. Muffin tin spheres radii are 2 a.u. for Fe and 1.8 a.u. for C. A calculation of bulk bcc Fe with these parameters yields the nearest-neighbour distance of 2.48 Å and the magnetic moment of $2.25\mu_B$. For fcc Fe, the nn distance is the same, but the optimal magnetic structure is antiferromagnetic (AFM), with a local magnetic moment of $1.4\mu_B$. In the case of the hcp structure we also obtain an AFM phase, but the energy per atom is 0.01 eV lower than for the fcc. This information is used in the construction of the nanowire unit cell.

For a free standing nanowire, the cohesive energy of such artificial unit cell of 6 atoms per layer is 4.78 eV/atom, surprisingly close to the 6.16 eV/atom for bcc bulk. ferromagnetic (FM) order is favoured over AFM by 0.1 eV/atom. Notice that for bulk fcc or hcp structures, the opposite result is obtained, since with the same Fe–Fe distance the AFM structure has the lowest energy. In the AFM arrangement, the magnetic moments alternate on a single layer with values of 1.1 and $2.9\mu_B$, while for the FM structure the values are $3.0\mu_B$ for the peripheral and $2.5\mu_B$ for the interior atoms. There is a large polarization at the Fermi level since the DOS for the majority iron spin is rather small.

The unit cell of the encapsulated wire is built by adding a layer of six carbon atoms which form a hexagon situated half way between the Fe layers as shown in Fig. 1.

3. Small-diameter nanowires

Now we present the results for nanowires encapsulated in real carbon nanotubes. We considered nanowires of six and twelve Fe atoms per layer, arranged in structures similar to those described in the preceding section. The six-atom per layer wires were introduced in zigzag nanotubes of the (9,0) and (11,0) type. The former case is certainly an extreme situation where the system is in a non-stable repulsive configuration. It was studied, however, as a test case for a very strong interaction between carbon and a wire. The 12-atoms per layer wires will be discussed in the next section. We performed *ab-initio* spin polarized geometry optimization of the structure by means of the SIESTA code within the framework of DFT [14, 15], using a basis set of strictly-localized numerical pseudoatomic orbitals, as implemented in the SIESTA code [16–18] within the generalized gradient approximation (GGA-PBE). The exchange-correlation energy was calculated as parameterized by Perdew, Burke and Ernzerhof [19, 20]. Norm-conserving pseudopotentials [21] in their non-local form were used to describe the electron-ion interactions, including non-linear core corrections [22]. In the SIESTA calculation, we have used a double-zeta basis set including polarization functions (DZP) [17]. Convergence tests have demonstrated that this basis yields reliable results in a variety of cases including covalent, ionic and metallic systems. In fact, tests by Junquera et al. [23] show that the results of DZP calculations are comparable to well converged plane-wave results.

We start with perfect structures as shown in Fig. 2. Notice a large distortion suffered by the wire and the nanotube upon relaxation. The wire maintains the FM phase and there is very little charge transfer from the iron atoms to the carbons. The peripheral Fe atoms show a larger magnetic moment than the inner ones, while the opposite situation occurs for more tightly encapsulated wires. The results are shown in Table 1.
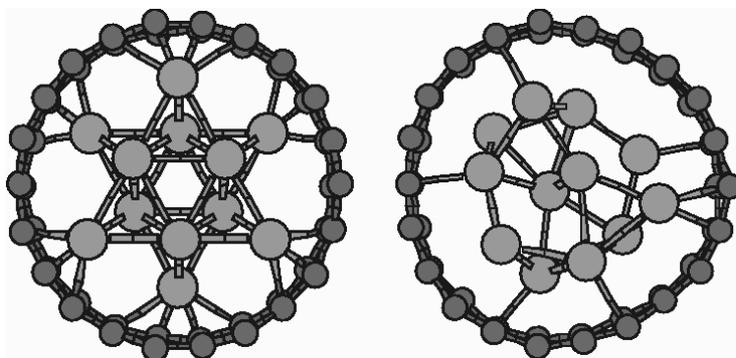

Fig. 2. Unit cell of six Fe atoms per layer encapsulated
in a (11,0) nanotube viewed perpendicular to the tube axis. Both the unrelaxed (left)
and relaxed configurations (right)are illustrated

Table 1. Magnetic moments per atom μ_{at}, in Bohr magnetons (μ_B), and charge transfer $\Delta\rho$
from Fe to C atoms in a.u. for relaxed nanowires of 6 or 12 Fe atoms per layer encapsulated
in a (n,0) carbon nanotube (CNT). The last two rows refer to free standing iron wires
with 6 and 12 atoms per layer, respectively

Nanowire	μ_{at}		$\Delta\rho$		Order
	Peripheral	Interior	Peripheral	Interior	
(9,0)-6 Fe	0.40	1.87	0.05	0.02	FM
(11,0)-6 Fe	2.6	2.36	0.046	−0.052	FM
(13,0)-12 Fe	−1.16	2.07	0.058	0.0	−
(15,0)-12 Fe	2.62	2.62	0.0	0.0	FM
6 Fe	3.20	2.65	−	−	FM
12 Fe	2.34	1.96	−	−	FM

4. Larger diameter nanowires

In this section, we present the results for nanowires with 12 Fe atoms per layer encapsulated in a (13,0) and in a (15,0) nanotube. We have performed an optimization of the geometry of the structure by means a DFT spin polarized calculation with the SIESTA code within the generalized gradient approximation (GGA-PBE). We started with perfect structures shown in Figs. 3(a) and (c).
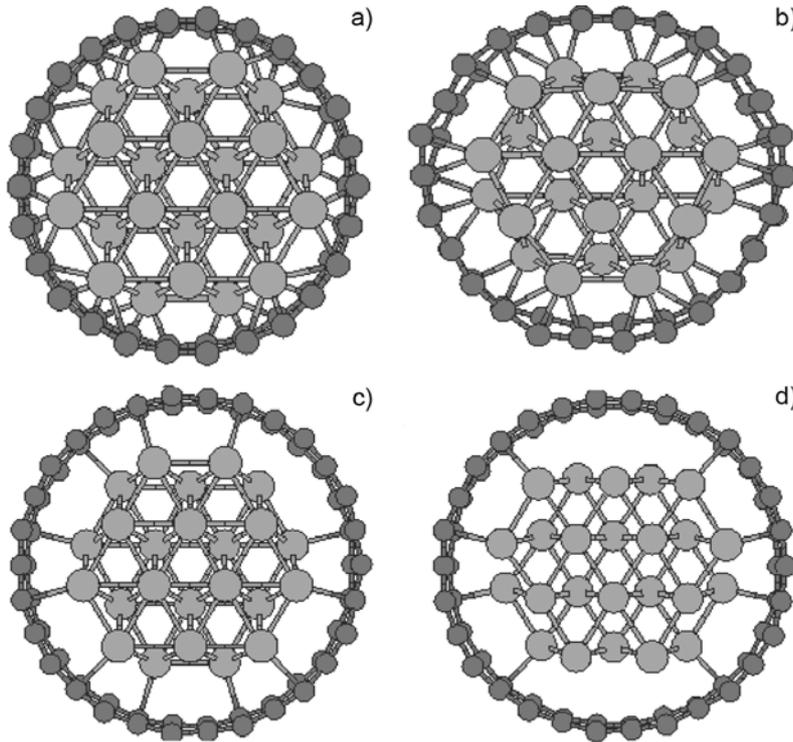
Fig. 3. Unit cell of 12 Fe atoms per layer encapsulated in a (13,0) nanotube (a, b)
and in a (15,0) nanotube (c, d) viewed perpendicular to the tube axis. The unrelaxed
configurations are shown on the left and relaxed configurations on the right

For the (13,0) nanotube, the optimized geometry of the wire appears slightly distorted when compared with the initial ones (Figs. 3a, b). The average diameter of the nanotube increases from 10.28 Å to 10.81 Å but the width of the wire shrinks from 7.57 Å to 7.29 Å. The distance between Fe layers stretches from 2.023 Å to 2.138 Å. The average magnetic moment for the innermost iron atoms is $2.07\mu_B$, while for the outermost atoms it is $-1.16\mu_B$. The average magnetic moment of the carbon atoms is less than $0.1\mu_B$. These values are summarized in Table 1.

After relaxation, the nanowire inside the (15,0) nanotube changes its structure into a bcc configuration. The initial diameter of 7.57 Å stretches to 8.5 Å after relaxation. The nanotube also increases its diameter to about 12.2 Å.

The isocurves of the charge density distribution are shown in Figs. 4 and 5, where the darker lines represent net spin up charge, and the lighter ones – net spin down charge. In a more tightly encapsulated nanowire (13,0), the charge densities of the outermost iron atoms have opposite polarizations to the inner ones. Notice that in this case there is a charge transfer from Fe to C atoms (see Table 1). The (15,0) nanotube is quite different since all the iron atoms are polarized in the same direction, with almost the same charge, and there is a negligible charge transfer.
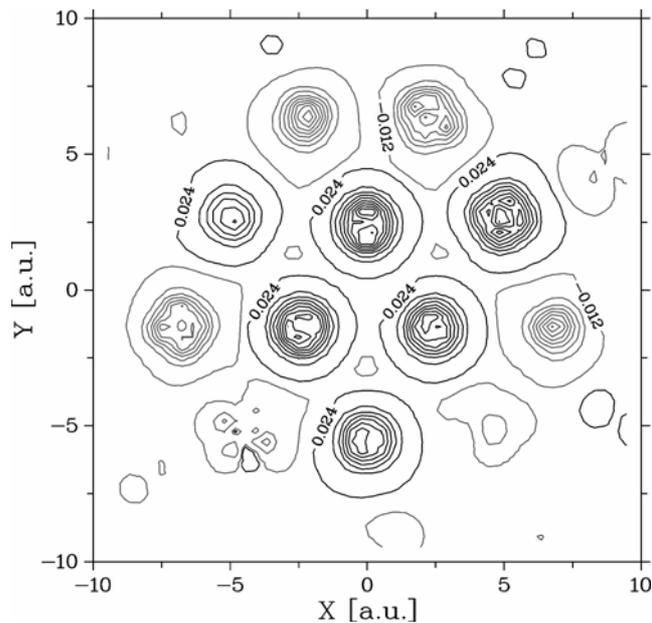
Fig. 4. Isocurves of the difference between the spin up and the spin down charge densities for a 12 Fe atom per layer wire encapsulated in a (13,0) carbon nanotube. The darker lines represent a net spin up and the lighter ones a net spin down charge
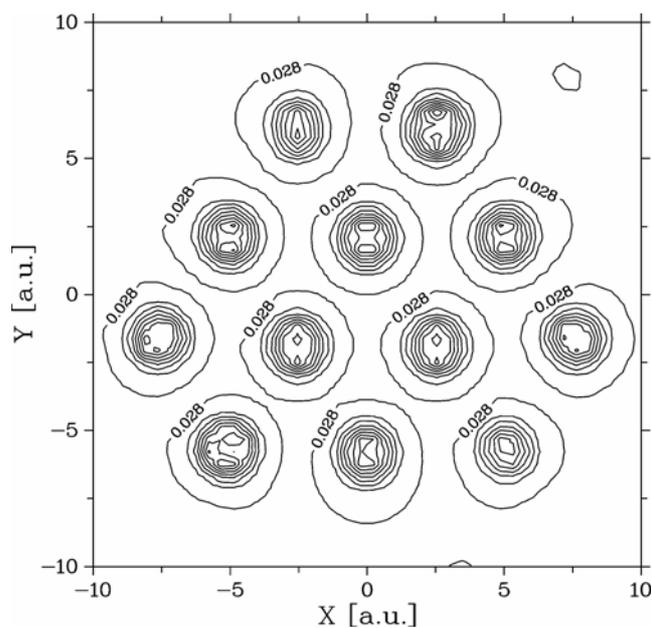

Fig. 5. Isocurves of the difference between the spin up and the spin down charge densities for a 12 Fe atoms per layer wire encapsulated in a (15,0) carbon nanotube. All the Fe atoms show a net spin up charge
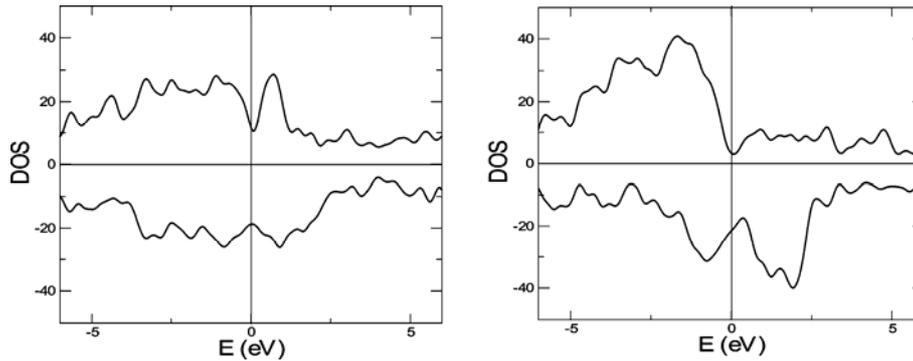
Fig. 6. Densities of states of wires with 12 Fe atoms encapsulated in a (13,0) nanotube (left) and in a (15,0) nanotube (right) for the majority and the minority bands. Notice a large difference in the DOS at the Fermi level for the wire in the (15,0) nanotube

The average magnetic moment of the innermost iron atoms of a (13,0) nanotube is $2.07\mu_B$, while for the outermost atoms it is $-1.16\mu_B$. The average magnetic moment of carbon atoms is less than $0.1\mu_B$. For the (15,0) nanotube all the iron atoms have similar magnetic moments of $2.62\mu_B$. The densities of states for these structures, for the majority and the minority band, are shown in Fig. 6. The density of states at the Fermi level for the (15,0) nanotube greatly differs for the spin up and the spin down bands. This could be interesting in a possible application of these systems in electron spin injection.

5. Conclusions

We have studied several configurations of iron nanowires inside a carbon nanotube structure. Within a very simple static model, we found that the energy difference between the FM and the AFM phases is very small, and therefore we conclude that they could coexist in an encapsulated nanowire, a fact that could explain the observation of exchange-bias in these systems [8, 9].

The spin polarization of an iron atom in an encapsulated wire depends on the number of neighbouring carbon atoms and the Fe–C distance. We also found that iron magnetic configuration in a carbon encapsulated nanowire strongly depends on the ratio of the diameters of the nanotube and the wire. If this ratio is large, the iron spin polarization of the peripheral iron atoms decreases, and in some cases the whole structure tends to an AFM configuration. On the other hand, if this ratio is small, the charge transfer from Fe to C is small. In this case, however, the densities of states at the Fermi level greatly differ between spin up and spin down bands. This fact could be of interest in a possible use of these systems in spin injection. We also observe that for large ratios of the diameters of the nanotube and the wire, the layers of the wires prefer the [110] bcc structure.

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