Theoretical study of carbon-coated iron nanowires

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Several properties of hybrid systems made of iron nanowires coated with carbon are computed from first principles. In particular, we focus on how the presence of carbon determines the magnetic ordering. A quasi-one-dimensional fcc (or hcp) Fe structure favors ferromagnetic ordering, but when encapsulated into a C tube, antiferromagnetic ordering can become favorable. The spin polarization at the Fermi level is large for the bare nanowires, but it decreases due to hybridization with the carbon coating. Implications of these results for the fabrication of nanodevices, as well as for the appearance of exchange bias, are discussed.

I. INTRODUCTION

Transition-metal carbon-coated nanowires constitute an active and attractive field of research,[1] as these systems are promising materials for use in nanodevices and in the magnetic storage industry. In addition, their potential use in spintronics provides a strong motivation to develop a full understanding of them, since the combination of C nanotubes and ferromagnetic transition metals (TM) has the right ingredients of small size and tailorable magnetic and transport properties.

In particular, recent experimental work has shown that it is possible to produce iron-filled carbon nanotubes and that these have very interesting properties, such as a shift in the hysteresis loop.[2] However, not all the samples present the same properties;[3–5] in fact, these properties appear to depend on the fabrication procedure. All these reasons provide the motivation to study theoretically the effect of carbon coating of quasi-one-dimensional Fe systems.

Previous works on this subject studied carbon nanotubes and only a small number of Fe atoms inside or close to them.[6–8] In this Rapid Communication our purpose is to study Fe nanowires of a reasonable diameter. In order to make the calculation feasible we have not coated them with complete carbon nanotubes but with a smaller number of carbon atoms. We have investigated from first principles the magnetic structure, the conduction-band polarization, and other features of uncoated Fe nanowires and compared them with the carbon-coated ones and also with previous results for other C-encapsulated TM hybrid structures.

II. THE SYSTEM

The nanosystem we have chosen to study is small enough to allow for an *ab initio* calculation but has a larger diameter (5 Å) than that of previous works, and it is therefore more appropriate to compare with experimental results. The nanowires contain two types of Fe atoms, external or peripheral ones with very few nearest neighbors (nn), and interior Fe atoms, with a number of nn that is close to that of bulk Fe.

With respect to the atomic structure of these wires we notice that each Fe atom in a bcc structure nanowire would have a smaller number of neighbors than in a fcc or hcp structure nanowire, thus making it less stable. We must remember that the stability of the bulk bcc structure is due to the presence of six second nearest neighbors, located at almost the same distance as the eight first nn, but these would be absent in systems of a diameter accessible to our calculations. For this reason we decided to use nanowires following the (111) direction of an hcp structure that repeats itself every two planes (ABABA…). This structure is illustrated in Fig. 1. The TM system has six atoms per layer, arranged as an equilateral triangle, with TM atoms on the vertices (which we will refer to as peripheral atoms) and at the midpoints of each side of the triangle (interior atoms); two successive TM layers are rotated relative to each other by 60°. The coating carbon atoms are located outside the TM nanowire and equidistant to two contiguous TM layers, forming straight C chains parallel to the wire axis. This is of course not a carbon nanotube, but we may consider it as a first approximation, to study the influence of carbon coating.

The interior TM atoms have ten nn and the peripheral ones have only four nn. The total number of atoms in the unit
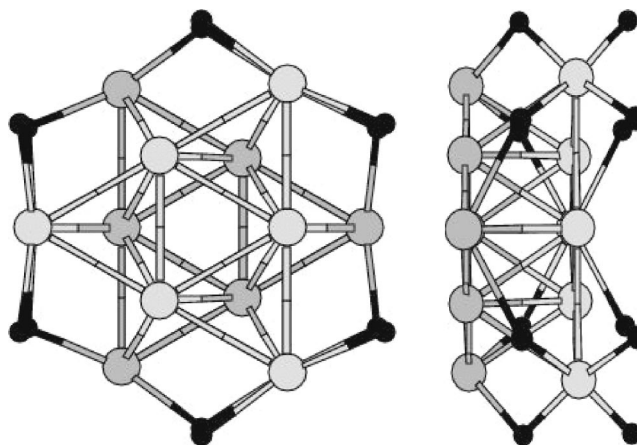

FIG. 1. The unit cell used in the calculation, viewed parallel and perpendicular to the tube axis. The dark circles represent carbon atoms and the two shades of gray represent the two atomic layers of iron. The Fe-Fe nearest-neighbor distances are 2.48 Å and the Fe-C and C-C ones are 2.03 Å.

cell is 24: 12 Fe and 12 C atoms. Thus, the average number of TM nearest-neighbor atoms amounts to seven. This value is intermediate between the bulk fcc or hcp structure (12 nn) and the fcc or hcp monolayer in the (111) direction (6 nn), with the consequent implications for the effective dimensionality of our system.

As is well known, the fcc and hcp structures have the same number of nearest neighbors and thus we expect that the results would not differ significantly for a nanowire with the fcc structure.

The ferromagnetic (FM) structure is unique. However, the antiferromagnetic (AFM) structure is not, and we have chosen, among several possibilities, the most AFM one. More precisely, within each atomic TM layer we assume an equal number of up and down spins, and in addition, consecutive layers are antiferromagnetically oriented relative to each other.

III. METHOD OF CALCULATION AND RESULTS

For the calculations we used the WIEN2K code,[9] which is an implementation of the FPLAPW (full potential linear augmented plane waves) method. It uses the local spin-density approximation (LSDA) and the exchange and correlation given by Perdew, Burke, and Ernzerhoff.[10,11] 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 corresponds to an energy cutoff of 204 eV. The calculation is scalar relativistic and includes local orbitals for the $3p$ states of Fe. The atomic sphere radii (muffin tins) were taken as 2 au for Fe and 1.8 au for C. The number of k points in the Brillouin zone was 100 (with C) and 200 (without C).

Under these conditions we calculated the optimal lattice parameter of FM bcc Fe and obtained a nearest-neighbor distance of 2.48 Å and a magnetic moment of 2.25 μ_B. For fcc Fe the optimal nearest-neighbor distance is the same, but the optimal magnetic structure is AFM, with a local magnetic moment in each muffin tin of 1.4 μ_B. For hcp Fe the result is also AFM, and the energy difference with the fcc structure is only 0.01 eV. All this information was incorporated in the construction of the unit cell used in our calculations. It is worth mentioning that small changes in the atomic volume of fcc iron produce important changes in the magnetic structure, while this is not the case for ordinary bcc iron.[12]

In the context of nanoparticle magnetization an interesting issue was recently raised by Mørup and Fransden.[13] They pointed out that there is a thermoinduced contribution to the magnetic moment of nanoparticles, which increases with temperature. This effect could wipe out the zero-temperature AFM order, but its consequences for finite systems as ours deserves additional careful scrutiny.

A. Pure TM nanowire

The cohesive energy of the artificial 12 Fe hcp wire is quite large, 4.78 eV/atom, as compared with the Fe bcc bulk value of 6.16 eV/atom calculated under the same conditions. The energies of the FM and AFM magnetic ordering differ by 0.1 eV/atom and favor the FM structure. This contrasts with the lowest-energy configurations for the bulk fcc and hcp structures which, for the same interatomic Fe-Fe distance, clearly favor antiferromagnetism. In the AFM arrangement the staggered magnetic moments alternate between 1.1 and 2.9 μ_B, while in the FM case the magnetic moments of the peripheral and interior atoms are 3.0 and 2.5 μ_B, respectively. The same results for the 6 Fe hcp nanowire are cohesive energy 4.5 eV and magnetic moment 2.8 μ_B per Fe atom.

The pure iron metal nanowire in the FM configuration turns out to have a very large polarization at the Fermi energy, since the majority band does not contribute significantly to the density of states at the Fermi level. This is also the case for linear chains,[14] but constitutes a relevant result due to the fact that here we are dealing with a system several angstroms in diameter and with an average number of nn that is intermediate between the two- and three-dimensional systems.

B. Carbon-encapsulated TM nanowire

Having determined the properties of the bare Fe metal nanowires we now surround them by carbon atoms. As mentioned above, and as illustrated in Fig. 1, we locate the C atoms halfway between two successive TM layers forming linear chains along which the C atoms are 2.03 Å apart. This way the interchain nearest-neighbor C-C distance amounts to 3.50 Å. We adopted the value 2.03 Å for the nearest-neighbor Fe-C distance, as found experimentally in some Fe-C compounds such as Fe_3C (cementite).[15] To avoid extensive computations on an artificial structure, such as the one we put forward in this paper, we did not perform a geometrical optimization of this distance.

The consequences of C encapsulation are important, since now the energetically most favorable magnetic structure is the AFM one, with an energy lower by 0.014 eV per Fe atom relative to the FM configuration. The presence of carbon also brings about a reduction of the magnetic moments. For the FM case they now amount to 2.0, 1.8, and −0.1 μ_B, for the peripheral, interior and C atoms, respectively. These results are not so much of a surprise since they agree with previous calculations that investigated the structure and stability of other FM structures that contain Fe and C atoms, such as Fe_3C-cementite bulk and surfaces, from first principles.[15] On the other hand, the lower-energy AFM configuration has magnetic moments of 1.9 and 1.4 μ_B, for the peripheral and interior Fe atoms, respectively, while the C moment is negligible.

It is worth mentioning that when the lowest energy of the C-encapsulated nanowire is subtracted from the lowest energy of the bare TM wire, to which the energy of 12 C atoms is added, one obtains a cohesive energy of 6.13 eV/atom, which is remarkably close to the 6.16 eV/atom bulk bcc Fe value. This binding energy is also considerably larger than that of the wire without the C atoms surrounding it, which constitutes an indication of the stabilizing effect of C coating.[15]

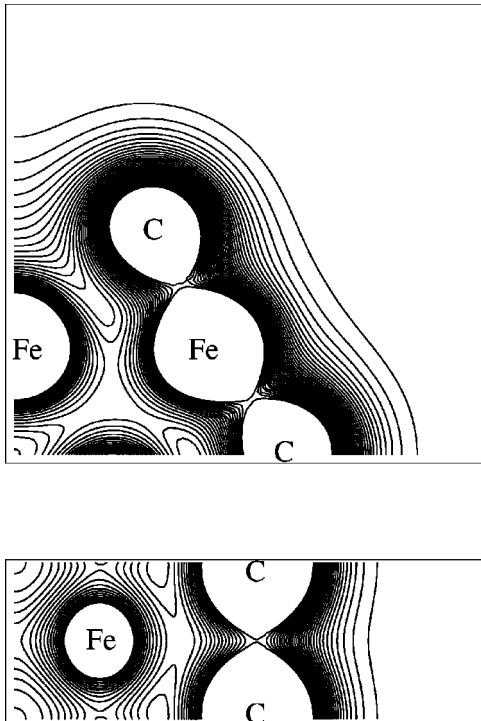We also performed some other related calculations. For example, we computed the energies of the Fe wire (without

FIG. 2. Electronic density around the iron and carbon atoms in the ferromagnetic configuration. The top figure corresponds to a plane perpendicular to the nanowire axis located halfway between two contiguous C and Fe layers. In the bottom figure the plane contains the nanowire axis, while one Fe and two C atoms are near to the plane. In both figures only one-fourth of the cell is represented. Each successive line in the graph represents an increment of 0.0183 electrons/$Å^3$. In the top figure the constant electron density lines that correspond to 0.55 electrons/$Å^3$ or more were suppressed for the sake of clarity. In the bottom figure densities larger than 0.66 electrons/$Å^3$ were omitted.
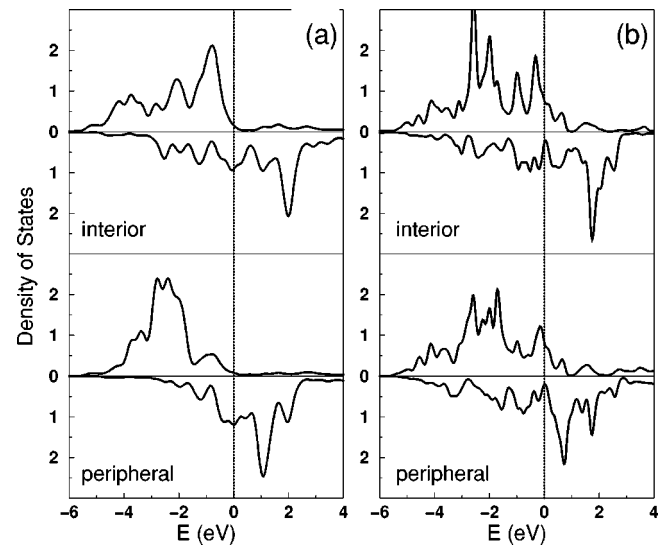

FIG. 3. Majority (upper) and minority (lower) spin iron density of states for ferromagnetic alignment. The upper panels correspond to the local density of states at the interior iron atoms and the lower ones to the peripheral iron. The more strongly polarized densities of states on the left (a) correspond to a bare iron nanowire, while the ones on the right (b) describe the carbon-coated Fe case.

the C) and of the C tube (without the Fe filling). This yields an estimate of the energy that is gained by the encapsulation, which amounts to 3.77 eV/Fe atom for the FM configuration, and 3.87 eV/Fe atom for the more favorable AFM ordering of the 24-atom cell.

The electronic density in real space, shown in Fig. 2, helps to visualize the characteristics of the Fe-C and C-C bonds, both of which display some degree of covalency. A certain degree of covalency between the three iron atoms in the top figure is apparent from the fact that there is no clearcut discontinuity in the constant charge contours between them.

The changes in the magnitude of the magnetic moments reported above are due to the shape and width alteration of the d bands, as illustrated in Fig. 3 for the FM case. The plots display the iron majority (up) and minority (down) spin partial densities of states, both for peripheral and interior Fe atoms. It is always the case that between 5.65 and 5.7 electrons of d symmetry, plus between 0.25 and 0.4 electrons of $4s$ and $4p$ symmetry, are found inside the Fe muffin tin. In the pure C tube each muffin tin contains 2.6 electrons, while in the encapsulated case it reduces to just 1.4 electrons, due to covalent bonding with s- and p-Fe states. Hybridization

with C broadens the bands of the pure Fe nanowires and alters the spin splitting. This has important physical consequences, as the magnetic moment reduction and the decrease of polarization at the Fermi level.

The spin density is illustrated in Fig. 4. Large values of spin-up density are represented by white areas and the spin-down direction by dark regions. The values of the magnetic moment on each atom were indicated above.
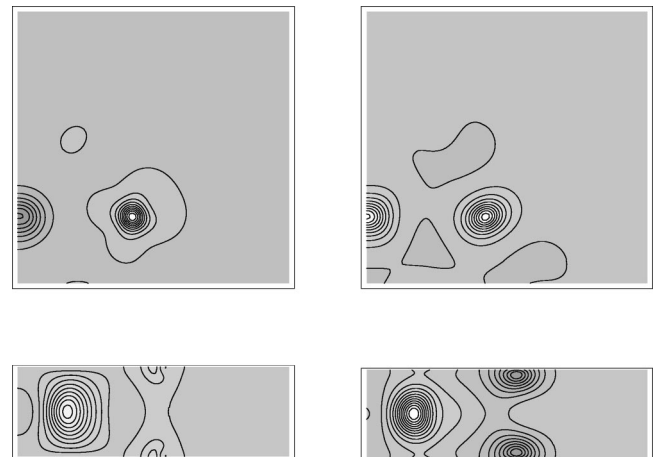

FIG. 4. Spin density for the same planes and atoms of Fig. 2. The AFM configuration is depicted on the left and the FM one on the right. Fully aligned values of spin up and down are represented by the white and dark regions, respectively, at the atomic sites. In both figures only one-fourth of the cell is represented. Each successive line in the upper two graphs represents an increment of 0.018 spins/$Å^3$, while in the lower plots the increment is of 0.12 spins/$Å^3$.

IV. CONCLUSION

Calculations performed with the parameters specified in Sec. II yield an antiferromagnetic ordering for fcc and hcp bulk iron. When the same procedure is implemented for a quasi-one-dimensional system the ordering becomes ferromagnetic, but, when the nanowire is encapsulated within a carbon tube once again the system orders antiferromagnetically.

For our encapsulated system the energy difference between the FM and AFM is slightly favorable to the latter, but it amounts only to 0.014 eV per Fe atom. In contrast, the energy difference in favor of the FM structure for the uncoated nanowire is 0.1 eV/atom. This suggests that a metastable equilibrium, with both FM and AFM (α- and γ-Fe) encapsulated in C nanotubes is possible, as has been reported by some authors.[2,5] This, in turn, opens the possibility for the fabrication of interesting nanosize exchange-bias systems.[16,17]

The dominant factors that govern properties like the magnitude of the magnetic moments, the spin ordering, and the spin polarization at the Fermi level (including possible half metallicity), seem to depend in a subtle way on the effective dimensionality of the system and the way the C encapsulation is achieved. The magnetic ordering is very sensitive to, and mainly determined by, the nearest-neighbor distances of the atoms that surround the Fe, and by the number and atomic species of these nn atoms. The nontrivial dependence on these parameters allows to understand the significant differences between our results and other work already reported in the literature.[6] This fundamental fact should be kept in mind when interpreting calculations on these nanosized magnetic systems.

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