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Effect of Low Dimensionality and Encapsulation on the Magnetic and Hyperfine Properties of Iron Nanowires

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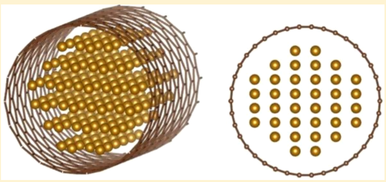

ABSTRACT: Ab initio calculations were performed for a very thin iron nanowire, both free-standing and enclosed in a carbon nanotube with the same size and structure of available experiments. Our interest was to study the effects of low dimensionality and the influence of the Fe−C interaction on the magnetic and hypefine properties of these systems. Our main finding was that the interfacial region between the nanowire and the carbon nanotube is of fundamental importance, as an iron atom close to the carbon atoms has a magnetic moment and a local hyperfine field very different from that at the surface of a free-standing iron nanowire. In fact, the properties of the calculated iron nanowire, of only 1 nm in diameter, when encapsulated inside a carbon nanotube result close to those of bulk iron.

I. INTRODUCTION

Magnetic nanowires are promising candidates for many applications: in spintronics, magnetic data storage, sensors for magnetic force microscopy, containers for biomedical use, etc.[1,2] Many experimental and theoretical studies have been performed recently on this subject, as extremely small nanowires with diameters of only a few nanometers have been fabricated. The properties of these nanowires are different from those of the bulk materials. Of the many experimental methods to obtain them, the enclosure in carbon nanotubes has the advantage of providing both chemical and mechanical stability.[1,3−7] Also, their metallic character has been experimentally proved to be long lasting,[8] meaning that the carbon nanotubes act as inert containers for storage of otherwise quickly oxidizing systems.

The changes in the magnetic properties of the nanowire due to the carbon environment have not been very much discussed. For example, for the case of iron nanowires, Mossbauer spectroscopy has been frequently used to characterize the phases found inside the carbon nanotube: both BCC and FCC iron have been found, also Fe_3C and some Fe-oxides.[3,4] These characterizations involve a comparison of spectra from bulk materials with that of the nanosystem, therefore, neglecting all low dimensionality effects. However, this approach could be dangerous, as in a nanoparticle or a nanowire a large proportion of the atoms are at the surface, and, therefore, do not have the same number of nearest neighbors as in the bulk material. The interface between the nanowire and the encapsulating carbon nanotube determines the movement of the nanowire inside it and even allows it to move through a constriction, as was shown in ref 9.

In this paper, as in previous work,[10] we study the magnetic properties of an infinitely long iron nanowire encapsulated in a single-walled carbon nanotube (SWCNT) but now using a wire thickness comparable to the experimental one and paying special attention to the hyperfine properties at the interfacial and internal Fe atoms. Our results distinguish the contributions from the surface atoms of the nanowire from those of the internal irons. The system studied can be taken as representative of different nanowire aggregates, as dipolar interactions among nanowires have been shown experimentally to play a small role in dense materials based in magnetic nanowires.[11] The optimization of macroscopic materials made of filled nanotubes can, therefore, be deduced from the properties of individual wires.

II. SYSTEMS STUDIED AND METHOD OF CALCULATION

For the calculations, we used the Wien2k code,[12] which is an implementation of the FP-LAPW (full potential linear augmented plane waves) method. The calculations were scalar relativistic, within the GGA approximation, and the parameters used are listed in ref 13. As this code requires three-dimensional periodicity, the unit cell considered consisted of infinitely long iron nanowires of approximately 10 Å in diameter, encapsulated or not in carbon nanotubes, with enough empty space between them so that neighboring wires would not interact with each other. The wire diameter and the structure (BCC along the (110) direction) were chosen to be comparable with available experiments.[4] As the calculations require that the iron nanowire and the SWCNT share a unit cell of reasonable size, which is repeated periodically along the wire axis, a zigzag $(n, 0)$

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nanotube was chosen. In fact, there is a small misfit between the separation of (110) planes in BCC-Fe (4.06 Å) and the periodicity of a carbon nanotube of that type (4.36 Å) (Figure 1). The unit cell size was kept fixed to the experimental periodicity of carbon nanotubes as these are very strongly bound and changing their interatomic distance requires a large amount of energy. The iron nanowire was, therefore, stretched with respect to its optimal structure, and this leads to a small systematic increase in the magnetic moment of all the Fe atoms. Atomic positions were allowed to relax along coordinates normal to the wire direction.

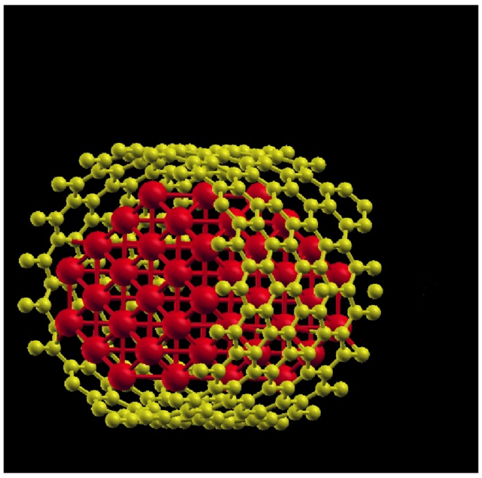

Figure 1. View of the system Fe nanowire encapsulated in the (19, 0) carbon nanotube.

A question that arised was which nanotube of type (n, 0) was adequate to encapsulate the Fe nanowire. To answer it, we calculated the optimal Fe−C distance using the same code and parameters for a simpler system. We performed a slab calculation, using an 11 layer iron slab with a BCC(111) structure covered with a graphene layer. Again, enough empty space was added so that the different slabs did not interact with each other. To make both systems commensurable, the cell parameter for BCC iron had to be stretched from 4.05 to 4.21 Å to match graphene. The slab unit cell had only one Fe atom per layer and 6 carbon atoms from graphene (Figure 2). We found that the most stable structural arrangement after relaxation was that with one carbon atom atop an Fe atom at 2.20 Å.

Using the information obtained from the slab calculation, we found that the nanotube (19, 0) was the best suited for our nanowire. For $n > 19$, all the Fe−C distances were considerably larger than the optimal 2.20 Å so that the effect of carbon would be almost negligible. For $n < 19$, there would be some Fe−C distances shorter than the optimal one, and therefore, the interaction would be repulsive.

We will report, therefore, the particular example of a nanowire with 36 Fe atoms in the unit cell (18 per plane) inside the carbon nanotube (19, 0) that has 76 C atoms in the unit cell so that there is a total of 112 atoms in it.

III. RESULTS

Before considering the interaction between an iron nanowire and a carbon nanotube, we studied the free-standing nanowire with 36 Fe atoms in the unit cell. The atoms were allowed to relax in directions normal to the wire axis, so as to decrease the force on each one, but the total deformation was not large if care was taken to avoid any symmetry restrictions. The atoms at the surface have fewer nearest neighbors than those of bulk iron and, therefore, have larger magnetic moments and hyperfine fields. These properties of low coordinated atoms in the nanowires have been carefully described in ref 14. In fact, the magnetic moments within the muffin tin spheres, which are 2.27 μ_B for bulk BCC-Fe, in our example range from 2.45 to 2.81 μ_B and average 2.62 μ_B in the unit cell. There is also a large magnetization of the interstitial region. The hyperfine fields (HFFs) clearly separate between those corresponding to atoms having all their neighbors, with HFFs around −350 kG (−331 kG for bulk BCC-Fe), and the surface ones with HFFs between −160 and −220 kG. These values correspond to the Fermi contact term, as the dipolar and orbital ones, which were also calculated with the same Wien2k code, are at least one order of magnitude smaller. The Fermi contact term is divided in the calculation into a core ($\mathrm{HFF^{core}}$) and a valence ($\mathrm{HFF^{val}}$) part, the core one being usually related to the magnetic moment (m) of each atom, which is due to the polarization of d electrons. As can be seen in Figure 3, the dependence of $\mathrm{HFF^{core}}$ with m is almost linear in this low-dimensional system. Lately, a more detailed study showed that the small contribution of the polarization of the s electrons to the magnetic moment, which can be either of the same or of the opposite sign to that of the d electrons, is related to the valence part of the hyperfine field.[15] This was also true for our free-standing wire, as shown in Figure 3.

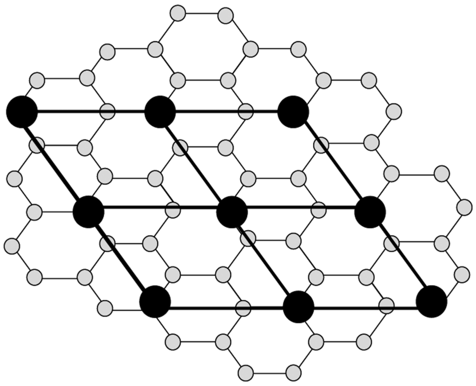

Figure 2. Geometry of the Fe(111)/graphene slab. Small circles are C atoms adsorbed over the iron slab. Large circles indicate the position of the Fe atoms in the surface layer.

The comparison of the HFF obtained in our calculations with the Mossbauer spectra in ref 4 suggests that the effect of carbon on the magnetic properties should be important, as hyperfine fields between −160 and −220 kG were not obtained when fitting those experimental results.

Another interesting hyperfine property, related to the anisotropy of the charge distribution, is the electric field gradient (EFG) at the Fe nucleus. For atoms at the surface of the nanowire, it is around 6 × 10^{21} V/m^2, whereas, at the interior atoms, it is considerably smaller, tending to the value for bulk iron that is zero.

The calculations considered a single domain magnetic structure and predicted a total magnetic moment (easy axis) normal to the wire axis, as in ref 16, although the magnetic anisotropy energy (MAE) was very small, within the error of the calculations (0.03 meV/Fe). Noncollinear spins were not considered.

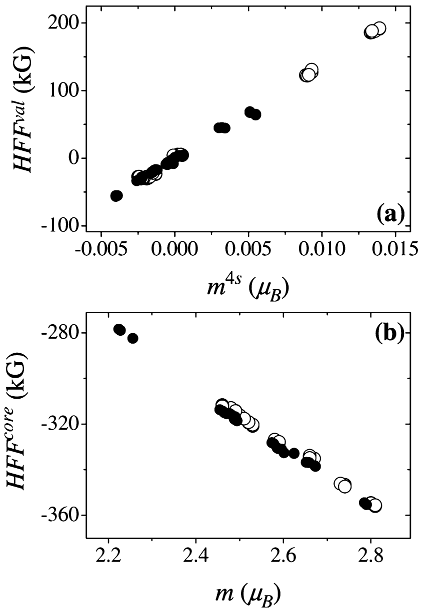

Figure 3. Hyperfine fields (HFFs) versus magnetic moments m of Fe atoms in the nanowire, free-standing (open circles), and inside the carbon nanotube (filled circles): (a) valence contribution ($\mathrm{HFF}^{\mathrm{val}}$) to the HFF versus the s orbital polarization; (b) core contribution to the HFF ($\mathrm{HFF}^{\mathrm{core}}$) versus total magnetic moment.

The next system studied was the Fe-BCC(111) slab covered with a graphene layer (Figure 2). We show in Figure 4 the magnetic moments and hyperfine fields layer by layer, in the free-standing and coated slabs. It is clear that hybridization of the graphene π orbitals with the Fe-3d ones affects the magnitude of the interfacial magnetic moments and hyperfine fields. The free-standing slabs show a well-known large surface effect[17] that decreases when the slab is covered with the carbon atoms. The binding energy between graphene and the iron slab (per Fe atom) was calculated as

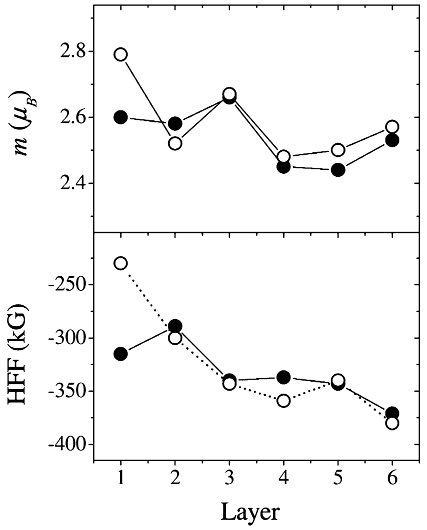

Figure 4. Magnetic moments and hyperfine fields of Fe atoms in each layer of a symmetric 11 layer Fe(111) slab. Filled circles represent the slab coated with a graphene layer and open ones the free-standing slab.

$$E_{\mathrm{Fe}} = (E_{\mathrm{gr+Fe\ slab}} - E_{\mathrm{gr}} - E_{\mathrm{Fe\ slab}})$$

where $E_{\mathrm{gr+Fe\ slab}}$, E_{gr}, and $E_{\mathrm{Fe\ slab}}$ are the energies of the coated Fe slab, the graphene layer, and the free-standing slab, respectively. As mentioned in ref 18, the cohesive energy is surprisingly large, in this case, about 2 eV. A similar system was studied recently, both experimentally and theoretically, searching for possible spintronics applications. It consists of thin cobalt films on graphene,[19] and the results are very similar to the present ones. In both cases, the interaction of carbon with the magnetic ions affects the magnetic properties of the whole system.

We now report the results for the system shown in Figure 1, an iron nanowire encapsulated in a single-walled carbon nanotube. The geometrical stability of this system was verified calculating the binding energy of the nanowire with the carbon nanotube, per Fe atom as follows

$$E_{\mathrm{Fe}} = (E_{\mathrm{SWCNT+Fe}} - E_{\mathrm{SWCNT}} - E_{\mathrm{Fe\ wire}})/36$$

where $E_{\mathrm{SWCNT+Fe}}$, E_{SWCNT}, and $E_{\mathrm{Fe\ wire}}$ are the energies of the encapsulated Fe nanowire, the empty carbon nanotube, and the free-standing nanowire, respectively. For the calculation of the binding energy, the size of the basis sets (energy cutoff) and number of K-points were the same for the three systems. The cohesive energy was again large, as in the graphene-slab case, but to obtain its precise value, a larger basis set and, therefore, a much more time-consuming calculation would be required.

We again consider a single domain ferromagnet and look at the individual magnetic moments of the atoms. We find that, due to proximity and orbital effects, a small magnetic moment (smaller that 0.02 μ_{B}) appears in some of the carbon atoms, in agreement with experimental information.[20,21] Concerning the polarization of the Fe atoms, Figure 3 shows the correlation of the total magnetic moment of each Fe atom with the core contribution to the HFF and also the proportionality of the small s contribution to the magnetic moment with the valence contribution to the HFF. Almost the same linear relation than for the free-standing wire is obtained. However, there are important differences. The average value of the magnetic moment is 2.55 μ_{B}, larger than that of pure iron, but lower than that of the free-standing nanowire. Contrary to the case of the bare nanowire, there is a very small magnetization of the interstitial region. The total HFF ranges between −277 and −373 kG, with an average value of −321 kG quite different from the result of the free-standing Fe nanowire, as the valence contributions are considerably smaller in magnitude. HFFs with an absolute value less than 300 kG are obtained in this calculation for Fe atoms not close enough to C atoms and are also found by fitting some experimental results, for example, for nanoparticles composed of iron and carbon. These HFFs have been associated with $\mathrm{Fe_3C}$ and other carbide structures,[5,22] but we believe that they may also be interpreted as due to surface atoms that have a nearest-neighbor coordination smaller than the bulk atoms. Of course, not all pairs Fe−C are at the optimal distance so that, as stated in ref 23, the magnitude of the local magnetic moments and, in consequence, of the HFFs will depend on the specific location of the Fe atoms. Some representative results are shown in Table 1. The local magnetic moment and the hyperfine properties of iron atoms located at the center of the wire and at two different positions on the surface are displayed. The EFGs range from -4×10^{21} to $+6 \times 10^{21}$ V/m^2, being larger in the surface atoms and tending to zero inside the nanowire, when the atoms have a neighborhood close to that in bulk iron. Evidently, the effect of coating is very

Table 1. Magnetic Moment, Electric Field Gradient, Asymmetry Parameter, Isomer Shift, Core and Valence Contributions, and Total Hyperfine Field for Three Representative Iron Atoms[a]

atom	mag. moment μ_B	EFG 10^{21} V/m^2	η	isomer shift mm/seg	HFF^{core} kG	HFF^{val} kG	HFF^{total} kG
				free standing			
central	2.46	0.8	0.94	−0.10	−311	−30	−341
Surface1	2.80	5.4	0.22	0.28	−355	190	−165
Surface2	2.74	6.9	0.43	0.13	−347	130	−217
				encapsulated			
central	2.52	1.1	0.95	−0.19	−322	−25	−347
Surface1	2.30	−2.9	0.98	−0.71	−296	−0.1	−296
Surface2	2.70	6.5	0.68	−0.16	−347	68	−279
				bulk iron			
	2.27	0	0	0	−289	−42	−331

[a] The central one has all its nearest neighbors as in the bulk material, which is shown for comparison. Surface1 is close to a carbon atom when encapsulated, whereas Surface2 is further away from the carbon nanotube.

important, the encapsulated Fe nanowire being much more like bulk iron than the free-standing one.

We have shown here only one example of a coated nanowire, but calculations performed for other examples gave qualitatively similar results. The interfacial region between a nanowire and a nanotube will certainly differ in different cases, and therefore, a variable proportion of surface HFF values should be expected and will be averaged in the experiments.

IV. CONCLUSIONS

The main conclusion of this work is that properties of very thin encapsulated wires are quite similar to those of bulk iron, especially when compared with those of bare wires. We have considered not only the local magnetic moments but also the hyperfine properties, which can be measured with Mossbauer and other spectroscopies. The interpretation of these experimental results should not be made simply from spectra of bulk materials, as the interfacial region is important and must be considered.

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Notes

The authors declare no competing financial interest.

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