

Spin-dependent electronic conduction along zigzag graphene nanoribbons bearing adsorbed Ni and Fe nanostructures

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Abstract

Using SMEAGOL, an *ab initio* computational method that combines the non-equilibrium Green's function formalism with density-functional theory, we calculated spin-specific electronic conduction in systems consisting of single Fe_n and Ni_n nanostructures ($n = 1-4$) adsorbed on a hydrogen-passivated zigzag graphene nanoribbon. For each cluster we considered both ferromagnetically and antiferromagnetically coupled ribbon edges (Ferro-F and Ferro-A systems, respectively). Adstructures located laterally on Ferro-A ribbons caused significant transmittance loss at energies 0.6–0.25 eV below the Fermi level for one spin and 0.2–0.4 eV above the Fermi level for the other, allowing the potential use of these systems in transistors to create a moderately spin-polarized current of one or the other sign depending on the gate voltage. Ni_3 and Ni_4 clusters located at the centre of Ferro-F ribbons exhibited a strong spin-filtering effect in a narrow energy window around the Fermi level.

Keywords: density functional theory (DFT), electronic transport, spin filtering

1. Introduction

In recent years, growing research attention has been devoted to electronic transport in nanoscale systems with potential technological applications. In addition to the experimental work in this area, intense effort has gone into the development of efficient computational methods. Those proposed so far fall into two broad classes: methods investigating the evolution of electronic charge density in a system perturbed by a time-dependent potential [1–6], and methods calculating the current balance in a steady-state system [1, 7–17]. The latter are conceptually simpler and computationally much less demanding than the former. One of the most efficient of these steady-state approaches is SMEAGOL [16, 17], which combines the non-equilibrium Green's function formalism (NEGF) [18–21] with density functional theory (DFT) [22, 23], as implemented

in SIESTA [24]. SMEAGOL owes its efficiency largely to its algorithm for calculating the surface Green's functions of the leads through which currents enter and leave the system; this algorithm combines generalized singular value decomposition with decimation, and avoids the well-known problems of recursive methods [18]. Also, SMEAGOL's extensively parallel architecture facilitates large-scale simulation of electronically complex atomic and molecular systems. Systems to which it has been applied include parallel-plate capacitors, gold nanowires, molecular spin valves, Ni point contacts, H_2 molecules between platinum electrodes and carbon-based nanostructures [16, 25–37].

A family of systems that continue to attract intense research on their electronic properties is that composed of graphene and its derivatives [38, 39]. Graphene nanoribbons constitute an important subfamily because of properties due to

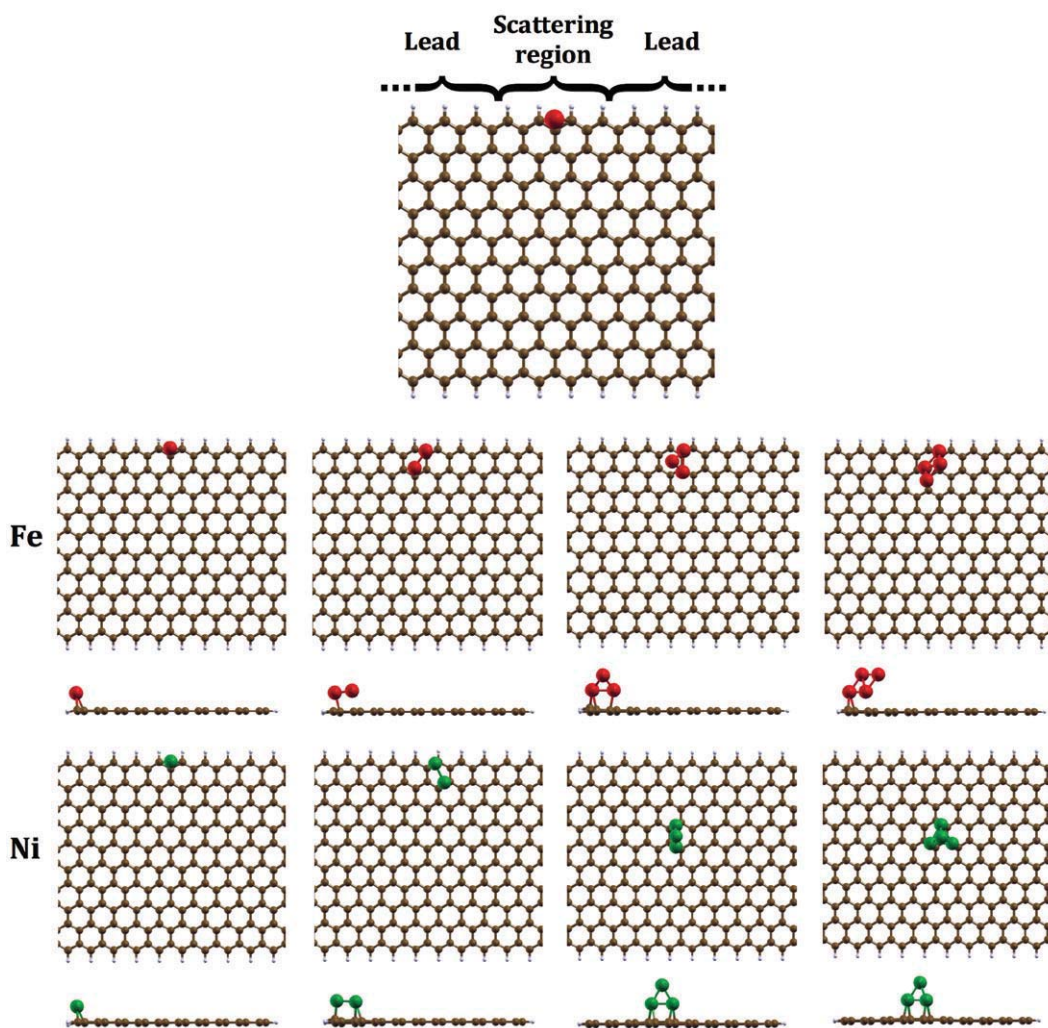


Figure 1. Schematic representations of the system used for electronic transport calculations (upper panel), and of the locations of the relaxed Fe_n and Ni_n adstructures ($n = 1-4$) on the hydrogen-passivated 10-ZGNR (lower panels, with lateral views included).

the existence of their edges. In particular, special attention has been afforded to hydrogen-passivated zigzag graphene nanoribbons (ZGNRs), i.e. ZGNRs with hydrogen atoms bound to the carbons at their edges. In these nanoribbons all the edge carbons on the same edge have the same magnetic moment. The Ferro-F form, in which the moments on the two edges are the same, is metallic, while the Ferro-A form, in which the edges have opposite moments, is semiconducting [40]. The Ferro-F form is marginally the less stable because in this configuration antiferromagnetic coupling between nearest neighbors is frustrated at the center of the ribbon.

Several recent studies have shown that the properties of ZGNRs are modified in potentially useful ways by adsorption of adstructures such as organic magnets [41], atoms or small clusters of transition metals (TMs) [42–49] (see also [50, 51] and references therein). However, such studies have generally modeled the modified ZGNR as an infinite periodic system, and their results may therefore not be valid for the corresponding finite structures, at least as regards electronic transport. As far as we know, scattering in a finite TM-modified ZGNR segment has only been studied in a few cases, including single Ni atoms adsorbed at lateral sites on a Ferro-F ribbon [52]

and single Co atoms adsorbed at central or lateral sites on a Ferro-A ribbon [53]. In both these cases spin-selective depression of transmittance was observed at certain energies (in the latter case more markedly with Co at lateral sites, where it binds more strongly). In the case of Ni, however, these energies were too far from the Fermi level for spin-polarized electron transport at low bias.

In view of the above findings with single Ni and Co atoms, we decided to investigate whether more pronounced or more exploitable effects might result from the use of small clusters of ferromagnetic elements instead of single atoms, since the total magnetic moments of such clusters are considerably larger than those of single adatoms when all the atoms in the cluster have similarly oriented spins. An additional reason for investigating the transport-modulating effects of clusters was that, in regard to their preparation, ZGNRs bearing clusters are more feasible and stable than ZGNRs bearing single atoms. In the work described here we used SMEAGOL to investigate electronic transport in hydrogen-passivated ZGNRs bearing isolated Fe_n or Ni_n ($n = 1-4$), i.e. in systems in which a finite ZGNR segment bearing a single adstructure was sandwiched between two semi-infinite ZGNR leads. Calculations with

single Fe or Ni adatoms were included for comparison with the larger clusters and with the results of Rigo *et al* [52]. Since our aim was to explore the possibilities of clusters rather than to carry out an exhaustive analysis, and given the heavy computational burden of these calculations, we did not perform calculations for all possible cluster configurations at all possible adsorption sites, but instead concentrated on lateral sites (where the adstructures bind more strongly) and configurations obtained in previous work [42, 44]. However, we did consider central adsorption sites for Ni₃ and Ni₄, and we systematically investigated adsorption on both the Ferro-A and Ferro-F forms of the ZGNR. Computational details are briefly described in section 2, our results are presented and discussed in section 3, and our main conclusions are summarized in section 4.

2. Method

We considered systems consisting of an Fe_n or Ni_n cluster ($n = 1 - 4$) borne by a hydrogen-passivated 10-ZGNR, i.e. a ZGNR ten zigzag C chains wide (figure 1). The specific adsorption sites and initial cluster configurations considered (the lower panel of figure 1 shows the corresponding relaxed configurations) were selected from among the sites considered and configurations obtained by Longo *et al* [42, 44] for infinite periodic Fe_n/ZGNR and Ni_n/ZGNR systems. Apart from the single-adatom system Ni/ZGNR, the selected systems were not chosen as being likely to relax to ground-state structures, but probably do lead to metastable forms in which the system might be trapped under favorable experimental conditions: as noted above, most of the adsorption sites considered are in the lateral region, where TM atoms generally bind most strongly to ZGNRs [42, 44]. Calculations were in each case performed with the ZGNR initially in both Ferro-A and Ferro-F configurations; in what follows the magnetic moments of the C atoms of the edge nearer the adstructures are treated as positive (spin up).

In the present work, only the finite cluster-bearing segment (the scattering region) was relaxed, not the leads on either side (see figure 1). Relaxation was performed within SMEAGOL [16, 17] using SIESTA [24] with the same components as used by Longo *et al* [42, 44]: the Perdew–Burke–Ernzerhof form of the generalized gradient approximation (GGA) [54], Troullier–Martins pseudopotentials [55] generated using the valence configuration 4s¹ 3d⁹ for Ni and 4s¹ 3d⁷ for Fe, triple- ζ doubly polarized basis sets, and an energy cutoff of 250 Ry to define the real-space grid for calculations involving electron densities.

Electronic transport calculations were likewise performed using SMEAGOL [16, 17], which for this purpose employs the retarded Green's function of an extended molecule comprising the scattering region together with short adjacent lead segments on either side:

$$G_M^R(E) = [e^+ S_M - H_M - \Sigma_L^R(E) - \Sigma_R^R(E)]^{-1}, \quad (1)$$

where H_M and S_M are the Hamiltonian and overlap matrices of the extended molecule and $\Sigma_L^R(E)$ and $\Sigma_R^R(E)$ are the retarded self-energies of the left- and right-hand leads, respectively. Since $G_M^R(E)$ contains all the information about the electronic

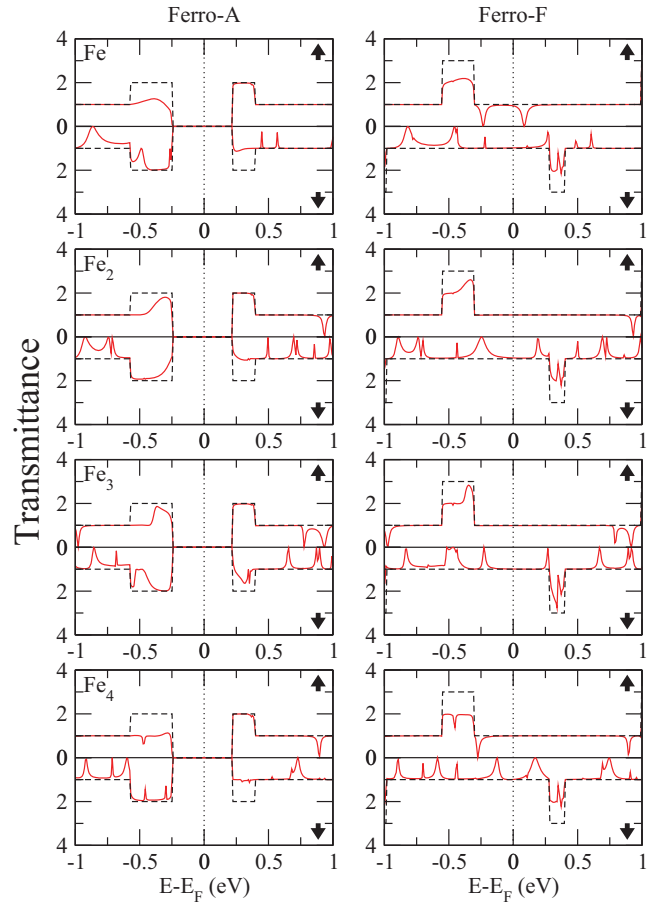


Figure 2. Spin-up (↑) and spin-down (↓) electronic transmittances of the Fe_n/ZGNR ($n = 1 - 4$) systems in Ferro-A and Ferro-F configurations (continuous red lines), and of the pristine ZGNR (dashed black lines).

structure of the extended molecule in equilibrium with the leads, application of the Fisher–Lee relation [18, 56] directly affords the zero-bias conductance G :

$$G = \frac{2e^2}{h} \text{Tr}[T_L G_M^{R\dagger} T_R G_M^R], \quad (2)$$

where e is the electron charge, h the Planck constant, and $T_\alpha(E) = i[\Sigma_\alpha^R(E) - \Sigma_\alpha^{R\dagger}(E)]$. All the quantities in equation (2) are evaluated at the Fermi energy E_F , and $\text{Tr}[T_L G_M^{R\dagger} T_R G_M^R]$ is the energy-dependent total transmission coefficient $T(E)$.

3. Results and discussion

Figure 2 shows the spin-specific electronic transmittances of the Fe_n/ZGNR systems ($n = 1 - 4$), in each case together with the transmittance of the pristine nanoribbon, a step-like function giving the number of bands (transmission channels) at each energy. Figure 3 shows the corresponding projections of the density of states (DOS) on the s , p and d orbitals of the Fe atoms. In the Ferro-A configuration, all the Fe_n/ZGNR systems retain the semiconducting nature of the pristine nanoribbon. The Fe clusters acquire strong positive atomic spin magnetic moments [42] because most Fe states near the Fermi level are spin-down while the corresponding spin-up states are well below the Fermi level. Fe d -type DOS peaks are associated

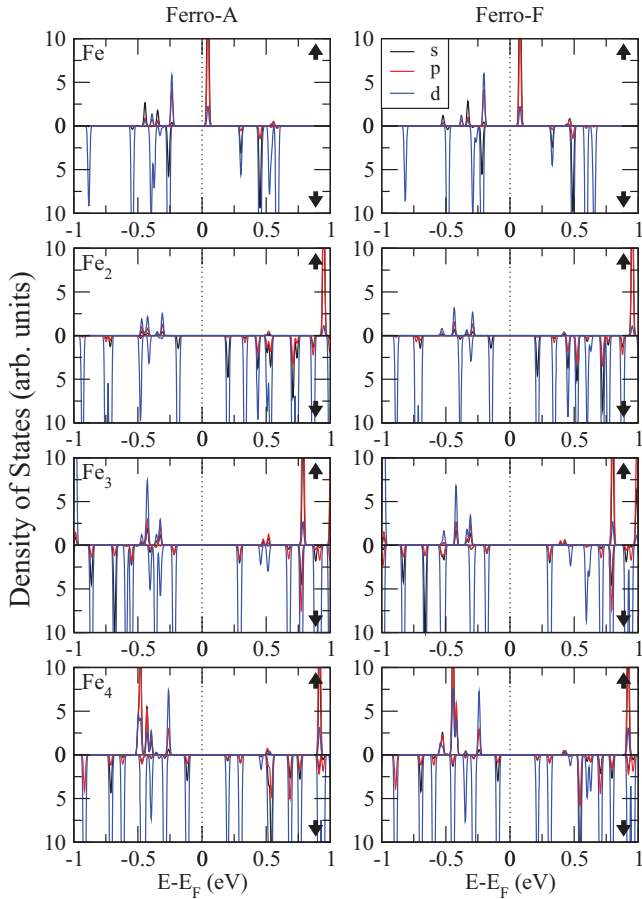


Figure 3. Density of states of the $Fe_n/ZGNR$ ($n = 1-4$) systems projected on the s , p and d orbitals of the Fe atoms.

with reduced transmittance with respect to pristine Ferro-A ZGNR, while the size of the reduction and the energy interval affected depend on the intensity of the Fe sp contribution: the greater this contribution, the greater the delocalization of the electronic states and hence the greater the interaction with the ribbon and the efficiency of electron capture. The broadest energy intervals affected in this way cover the regions near the Fermi level where the leads provide two conduction channels for each spin component, -0.6 – 0.25 eV and 0.2 – 0.4 eV. However, above the Fermi level it is only the spin-down component that is affected, and below the Fermi level mainly the spin-up component. Thus these systems could potentially be used as substrates in a transistor to create a moderately spin-polarized current of one or the other sign depending on the gate voltage. As mentioned above, spin transport selectivity in Ferro-A ZGNRs bearing a Co adatom, attributed to backscattering from localized Co states, has been predicted by Cocchi *et al* [53], who found this effect to be more pronounced at lateral than at central adsorption sites.

The Ferro-F $Fe_n/ZGNR$ systems also all retain the conductivity type of the pristine ZGNR, which in this case is metallic. As in the Ferro-A systems, transmittance is reduced mainly where more than one channel is provided by the leads, namely, between -0.6 eV and -0.3 eV for the spin-up component and between 0.25 eV and 0.40 eV for the spin-down component.

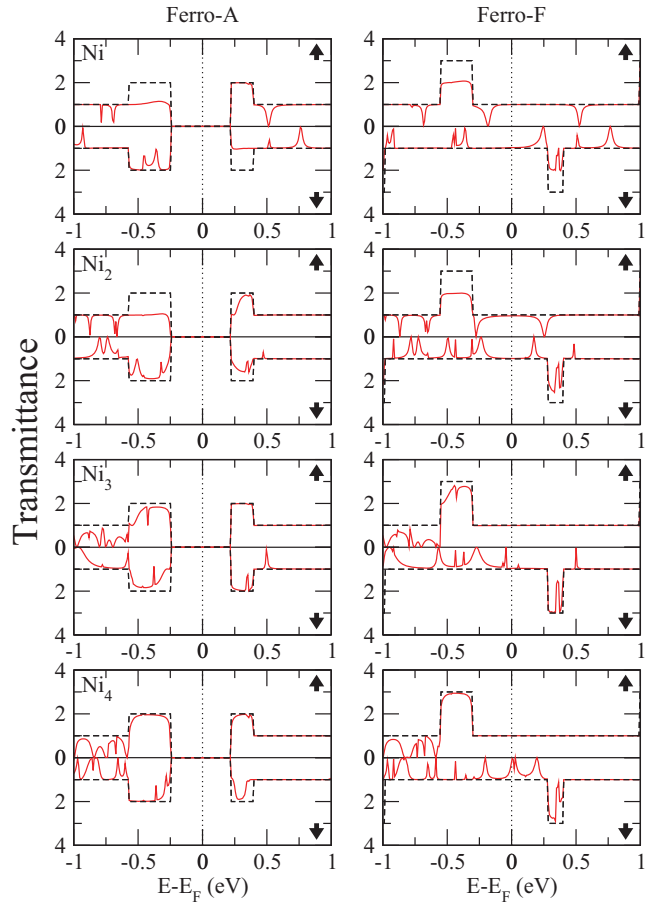


Figure 4. Spin-up (\uparrow) and spin-down (\downarrow) electronic transmittances of the $Ni_n/ZGNR$ ($n = 1-4$) systems in Ferro-A and Ferro-F configurations (continuous red lines), and of the pristine ZGNR (dashed black lines).

As in the Ferro-A systems, other transmittance reductions, associated with Fe d -type states (mainly spin-down), are narrow and too far from the Fermi level to produce significant spintronic effects, at least at low bias.

Since the Fe atom has three unpaired d electrons and the Ni atom only one, the adstructure atoms of the $Ni_n/ZGNR$ systems have much smaller spin magnetic moments than those of the $Fe_n/ZGNR$ systems, e.g. 0.51 as against $3.08\mu_B$ for the single adatom, and $0.42/0.44$ as against $3.40/3.43\mu_B$ for the dimer [42]. Figure 4 shows the spin-specific electronic transmittance curves of the $Ni_n/ZGNR$ systems and the pristine nanoribbon, and figure 5 the DOS projections on the Ni s , p and d orbitals. Ferro-A $Ni/ZGNR$ and Ferro-A $Ni_2/ZGNR$ behave very like their Fe analogs, but not so Ferro-A $Ni_3/ZGNR$ and Ferro-A $Ni_4/ZGNR$, possibly because, unlike Fe_3 and Fe_4 , Ni_3 and Ni_4 are located near the centre of the ribbon. In these cases the reduction in transmittance in the energy window -0.5 – 0.5 eV is much smaller than in the Fe analogs because of the smaller contribution of the TM sp states. Thus Ferro-A $Ni_3/ZGNR$ and Ferro-A $Ni_4/ZGNR$ behave much more like the pristine Ferro-A ZGNR than do Ferro-A $Fe_3/ZGNR$ and Ferro-A $Fe_4/ZGNR$, at least at low bias.

Like Ferro-A $Ni/ZGNR$ and Ferro-A $Ni_2/ZGNR$, Ferro-F $Ni/ZGNR$ and Ferro-F $Ni_2/ZGNR$ behave quite like their

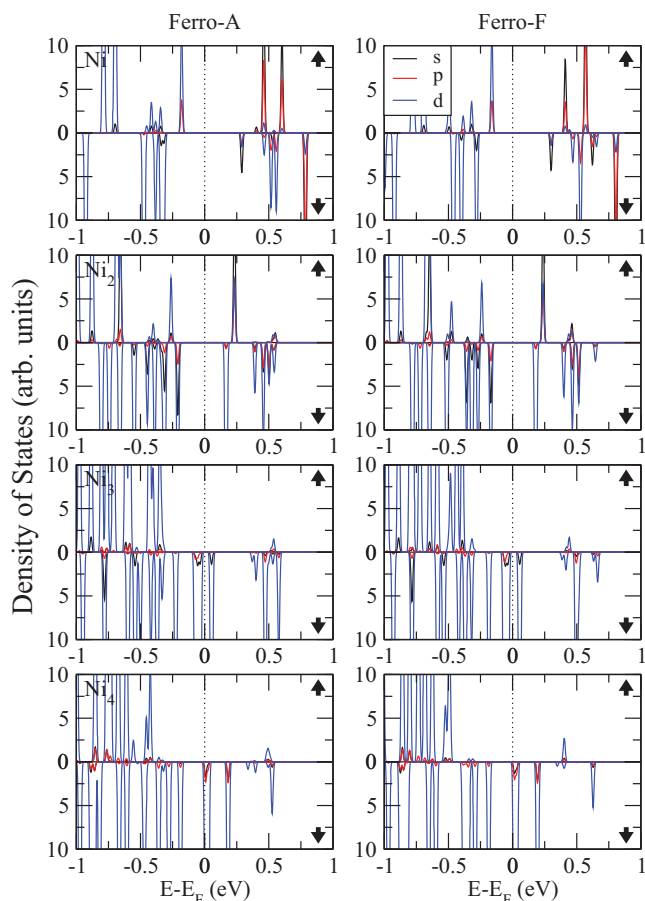


Figure 5. Density of states of the $Ni_n/ZGNR$ ($n = 1-4$) systems projected on the s , p and d orbitals of the Ni atoms.

Fe analogs; the only difference of note is that around the Fermi level there is a somewhat wider energy window with no loss of transmittance, there being no Ni states closer than 0.2 eV to the Fermi level (similar behavior was reported by Rigo *et al* [52] for a Ferro-F Ni/ZGNR system). However, although Ferro-F $Ni_3/ZGNR$ and Ferro-F $Ni_4/ZGNR$ behave like Ferro-A $Ni_3/ZGNR$ and Ferro-A $Ni_4/ZGNR$ at energies at which the pristine ZGNR has multiple transmission channels, showing little or no transmittance loss at these energies, their spin-down transmittance is significantly reduced near or around the Fermi level due to d -type spin-down DOS peaks. In particular, at the Fermi level of $Ni_4/ZGNR$ the spin-up and spin-down transmittances are respectively 1.0 and about 0.01 G_0 , where $G_0 = e^2/h$ is the quantum of conductance for magnetic systems. In these systems there will therefore be strong spin selection at low bias, although this effect will tend to disappear at higher bias.

4. Conclusions

In this work we investigated spin-specific electronic transmittance in $Fe_n/ZGNR$ and $Ni_n/ZGNR$ systems ($n = 1-4$) using SMEAGOL [16, 17], an *ab initio* computational package that combines the NEGF formalism [18–21] with the DFT method SIESTA [24]. In all these systems there were energies at which

transmittance was less than in the pristine ZGNR. In those in which the Fe or Ni atom or cluster, was located in the lateral region of the ribbon ($Ni/ZGNR$, $Ni_2/ZGNR$ and all the $Fe_n/ZGNR$ systems), these losses were most significant in energy windows in which the pristine ribbon has more than one transmission channel, which in Ferro-A ribbons made spin-down transmittance greater than spin-up transmittance 0.6–0.25 eV below the Fermi level and *vice versa* 0.2–0.4 eV above the Fermi level. This behavior would potentially allow the use of these systems in transistors to create a moderately spin-polarized current of one or the other sign, depending on the gate voltage. When Ni_3 or Ni_4 clusters were centrally located on Ferro-F ribbons, a large concentration of spin-down Ni d -type states around or close to the Fermi level produced a strong spin-filtering effect.

Acknowledgments

We are grateful to R. C. Longo for useful information. This work was supported by the Spanish Ministry of Science and Innovation (Project Nos. FIS2011-22957 and FIS2012-33126) and by the Xunta de Galicia (Project GPC2013-043) in conjunction with the European Regional Development Fund (FEDER). AG-F acknowledges the Swiss National Science Foundation for financial support.

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