

**Size-dependent alternation of magnetoresistive properties in atomic chains**

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Spin-polarized electronic and transport properties of carbon atomic chains are investigated when they are capped with magnetic transition-metal (TM) atoms like Cr or Co. The magnetic ground state of the TM-C<sub>n</sub>-TM chains alternates between the ferromagnetic (F) and antiferromagnetic (AF) spin configurations as a function of *n*. In view of the nanoscale spintronic device applications the desirable AF state is obtained for only even-*n* chains with Cr; conversely only odd-*n* chains with Co have AF ground states. When connected to appropriate metallic electrodes these atomic chains display a strong spin-valve effect. Analysis of structural, electronic, and magnetic properties of these atomic chains, as well as the indirect exchange coupling of the TM atoms through non-magnetic carbon atoms are presented. © 2006 American Institute of Physics. [DOI: 10.1063/1.2354080]

Typical devices based on giant magnetoresistance effect<sup>1</sup> are made of magnetic multilayers, where the relative alignment of the layer magnetizations causes large variations in the resistance of the structure. In such magnetic superlattice structures, the interlayer exchange coupling and the magnetoresistance are found to be oscillating as a function of spacer thickness.<sup>2-4</sup> Recently, efforts in combining spintronics with molecular electronics have focused on lower dimensional analogs of the layer magnetic heterostructures. Along this direction, spin-polarized electronic transport in molecular devices has been investigated extensively.<sup>5-11</sup> Organic and carbon-based molecules are promising in achieving magnetoresistive effects. Linear atomic chains of C have been synthesized,<sup>12</sup> and their impressive properties have been demonstrated.<sup>13</sup> Incorporation of transition-metal (TM) atoms into a C linear chain in the form of impurities, and formation of infinite periodic compound structures are energetically feasible. Such infinite, periodic (TM-C<sub>n</sub>) compound structures are found to be stable and half-metallic.<sup>14</sup> Pati *et al.*<sup>15</sup> have studied atomic wires consisting of C and Co atoms where they have concluded that the ground state of short CoC<sub>n</sub>Co atomic chains is antiferromagnetic.

In this Communication, we find that the isolated TM-C<sub>n</sub>-TM atomic chains or linear molecules (TM denoting Co, Cr, Fe, or Mo) alternate between ferromagnetic (F) and antiferromagnetic (AF) ground states as a function of the number of C atoms *n*. Changing the value of *n* by one modifies the magnetic ground state from F to AF, or *vice versa*. Moreover, whether even- or odd-*n* leads to an AF ground state depends on the type of the TM atom. We also find that the generic electronic properties of these chains are preserved after attaching them to appropriate semi-infinite leads

at both ends. Hence, they act as almost perfect spin valves when they are in a F state.

The oscillatory indirect exchange interaction (known as RKKY) between localized magnetic moments, mediated by the itinerant carriers of a spacer medium, occurs in extended metallic hosts. It is a second order perturbative effect that plays a significant role in determining the magnetic order in low-dimensional structures. Here, owing to the zero-dimensional nature and hence finite level spacing of the TM-C<sub>n</sub>-TM structures and non-perturbative character of the interaction of the TM atoms with the carbon chain an RKKY-type formulation is not appropriate. Rather, one needs to employ self-consistent density functional methods or a direct diagonalization of the spin-dependent model Hamiltonian of the system.

We have performed first-principles plane wave calculations<sup>16</sup> within density functional theory (DFT) using ultra-soft pseudopotentials.<sup>17</sup> The exchange correlation potential has been approximated by generalized gradient approximation.<sup>18</sup> The atomic positions of the structures are optimized by minimizing the total energy as well as the forces on the atoms using spin-relaxed calculations.<sup>19</sup> The results of plane-wave calculations are compared and confirmed with methods which utilize local-basis sets.<sup>20,21</sup> Transition state analysis performed for different reaction paths, extensive stability analysis, and *ab initio* molecular dynamic calculations performed at 1000 K show that CoC<sub>n</sub>Co and CrC<sub>n</sub>Cr isolated atomic chains can be synthesized and are stable. For example, both CoC<sub>n</sub>Co and CrC<sub>n</sub>Cr isolated chains can be formed from a finite, linear C<sub>n</sub> chain by attaching Co or Cr atoms to both ends.<sup>14</sup>

The calculated electronic and magnetic properties of isolated CrC<sub>n</sub>Cr and CoC<sub>n</sub>Co chains are summarized in Table I. The total energy of every structure is calculated for each

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TABLE I. The calculated electronic properties of isolated  $\text{Cr}_n\text{Cr}$  and  $\text{Co}_n\text{Co}$  chains using VASP (Ref. 16). The columns are respectively: The energy difference of the AF and the lowest-energy F states,  $\Delta E_{F \rightarrow AF} = E_T(AF) - E_T(F)$ , magnetic moment  $\mu$  of the ground state in units of Bohr magneton  $\mu_B$  (for AF ground states the moment corresponding to the higher energy F state is given in parenthesis),  $E_g^\sigma$  are the energy gap between the highest occupied and lowest unoccupied levels of spin- $\sigma$  states. The bold numbers denote the spin type of the HOMO levels.

Structure	$\Delta E_{F \rightarrow AF}$ (eV)	$\mu$ ( $\mu_B$ )	$E_g^\uparrow$ (eV)	$E_g^\downarrow$ (eV)
$\text{CrCr}$	1.12	8	<b>0.97</b>	2.37
$\text{Cr}_2\text{Cr}$	-0.10	0 (10)	1.43 ( <b>0.82</b> )	1.43 (3.56)
$\text{Cr}_3\text{Cr}$	0.87	8	1.33	<b>1.83</b>
$\text{Cr}_4\text{Cr}$	-0.08	0 (10)	1.26 ( <b>0.91</b> )	1.26 (2.97)
$\text{Cr}_5\text{Cr}$	0.70	8	1.43	<b>1.79</b>
$\text{Cr}_6\text{Cr}$	-0.06	0 (10)	1.17 ( <b>0.88</b> )	1.17 (2.77)
$\text{Cr}_7\text{Cr}$	0.58	8	1.32	<b>1.63</b>
$\text{CoCo}$	-0.17	0 (2)	0.24 (1.41)	0.24 ( <b>0.40</b> )
$\text{Co}_2\text{Co}$	0.32	4	1.80	<b>0.55</b>
$\text{Co}_3\text{Co}$	-0.12	0 (2)	0.87 (1.67)	0.87 ( <b>0.86</b> )
$\text{Co}_4\text{Co}$	0.28	4	1.72	<b>0.26</b>
$\text{Co}_5\text{Co}$	-0.13	0 (2)	0.88 (1.48)	0.88 ( <b>0.85</b> )
$\text{Co}_6\text{Co}$	0.24	4	1.62	<b>0.48</b>
$\text{Co}_7\text{Co}$	-0.13	0 (2)	0.79 (1.34)	0.79 ( <b>0.75</b> )

possible value of its magnetic moment  $\mu$ . The AF state ( $\mu = 0$ ) arises as the ground state of the  $\text{Cr}_n\text{Cr}$  chains only for even  $n$ . In this case, the state with  $\mu = 10\mu_B$  is the lowest-energy F configuration. Chains with odd  $n$ , however, have a F ground state with  $\mu = 8\mu_B$ . Therefore, the quantity  $\Delta E_{F \rightarrow AF} = E_T(AF) - E_T(F)$ , defined as the energy difference of the AF and the lowest F states of the structures, displays an alternating variation with  $n$ . Interestingly, a similar alternation for  $\Delta E_{F \rightarrow AF}$  in  $\text{Co}_n\text{Co}$  chains is found with an inverted form; the AF ground state is obtained only for odd- $n$  cases as seen in Fig. 1. The variation of  $\Delta E_{F \rightarrow AF}$  in chains with terminal Mo and Fe atoms resembles to the Cr and Co cases, respectively. On the other hand, with Ti or Sc, for instance, such regular alternations are not found. Apparently, the electronic configuration of the outer  $d$ -orbitals of the TM atoms

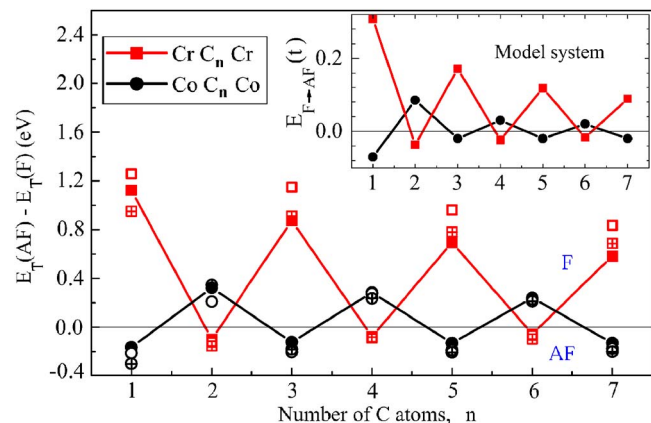


FIG. 1. (Color online) Energy difference of the AF and the F states in the  $\text{Cr}_n\text{Cr}$  and  $\text{Co}_n\text{Co}$  atomic chains as a function of the number of C atoms. The ground state is AF for negative values of the energy difference. The solid, open, and crossed symbols represent the results of VASP,<sup>16</sup> SIESTA,<sup>20</sup> and GAUSSIAN03<sup>21</sup> calculations, respectively. The inset shows similar variations obtained in a model system.

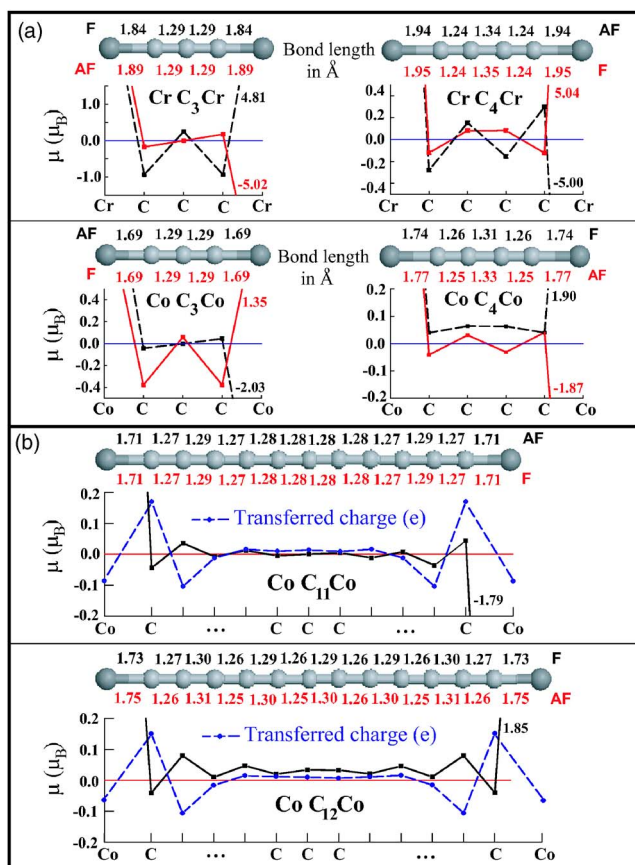


FIG. 2. (Color online) (a) Molecular structure and atomic magnetic moments in isolated  $\text{Cr}_n\text{Cr}$  and  $\text{Co}_n\text{Co}$  chains for  $n=3$  and 4 in their AF and F states. The values of the moments on the TM atoms are also denoted. (b) Same for longer chains. The charge transfer and induced atomic moments are plotted only in the ground states.

is essential in the form of the carbon-mediated interaction between them.

The quantity  $\Delta E_{F \rightarrow AF}$  is related to the strength of the indirect exchange interaction between the TM atoms. It is the energy required to invert the magnetic moment of one of the TM atoms in the F state. The situation bears some resemblance to the case of indirect exchange coupling of two Co adatoms on a metallic carbon nanotube. Costa *et al.*<sup>7</sup> have obtained an oscillatory variation of the exchange coupling between the Co adatoms as a function of their separation. The indirect exchange interaction was extremely long-ranged, and the period of oscillations was larger than the structural period of the carbon nanotube. In our case, however, the period of alternation of magnetic ground state is shorter; its type is altered when the number of C atoms is changed by one. It is the  $\text{C}_n$  atomic chain that mediates the interaction in an involved manner. In the F and AF states, the variation of the induced magnetic moments on the C atoms changes, and the atomic structures of the molecules are also slightly modified.

In Fig. 2, we display the equilibrium atomic structure and the variation of atomic magnetic moments in  $\text{Cr}_n\text{Cr}$  ( $n=3, 4$ ), and  $\text{Co}_n\text{Co}$  chains ( $n=3, 4, 11, 12$ ) as representative samples. In the even- $n$  cases the C atoms tend to dimerise, whereas for odd- $n$  the C-C bonds are almost uniform (this property is more evident for larger  $n$  cases). The atomic

magnetic moments are calculated based on an orbital-resolved Mulliken analysis.<sup>20</sup> The magnetic TM atoms induce moments throughout the C chain which set up an indirect exchange interaction between them. Owing to the chain geometry and quantum interference effects, the induced magnetization of C atoms is quite long-ranged; for instance, in the F ground state of the Cr C<sub>15</sub> Cr structure all the C atoms have alternating magnetic moments of  $|\mu| \sim 0.1\mu_B$ . The effect is somewhat weaker for the Co cases; in Fig. 2(b) the chains with  $n=11$  and 12 have higher induced charge and magnetic moments on the two nearest-neighbor C atoms, but they get damped deeper in the chain. Our results are in accord with a recent experimental study on contact induced magnetism in metallic carbon nanotubes,<sup>22</sup> where they find that spin-polarized charge transfer at the interface between a flat ferromagnetic metal substrate (Co) and a multiwalled carbon nanotube leads to a spin transfer of about  $0.1\mu_B$  per contact C atom.

The qualitative features of the peculiar magnetic ordering in these chain structures can be understood through a Hückel-type “toy” model. Consider the Hamiltonian of a chain structure having  $n+2$  sites:  $H = \sum_{i,\sigma} \varepsilon_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - \sum_{i,\sigma} (t_{i,i+1,\sigma} c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.})$ , where  $\varepsilon_{i,\sigma}$  is local site energy,  $t_{i,i+1,\sigma}$  is the spin-dependent nearest-neighbor hopping integral,  $c_{i,\sigma}^\dagger$  and  $c_{i,\sigma}$  denote fermion creation and annihilation operators for site  $i$  (from 0 to  $n+1$ ) with spin  $\sigma$ , respectively. The nonmagnetic sites ( $i=1$  to  $n$ ) are represented by spin-degenerate on-site energies of zero, and  $t_{i,i+1,\sigma} = t$ . To mimic the magnetic sites ( $i=0$  and  $i=n+1$ ), however, we take both the on-site energies and their coupling to nearest nonmagnetic sites as spin-dependent:  $\varepsilon_{0,\uparrow} = \varepsilon_1$  and  $\varepsilon_{0,\downarrow} = \varepsilon_2$ ;  $t_{0,1,\uparrow} = t_1$  and  $t_{0,1,\downarrow} = t_2$ . For the sake of simplicity, we model the magnetic sites with only two spin-dependent states. In the F state of the molecules the two magnetic sites are equivalent, and the AF configuration can be represented by taking one of the magnetic sites ( $i=n+1$ ) to have on-site energies and hopping terms with inverted spin labels:  $\varepsilon_{n+1,\uparrow} = \varepsilon_2$ ,  $\varepsilon_{n+1,\downarrow} = \varepsilon_1$ ,  $t_{n,n+1,\uparrow} = t_2$ , and  $t_{n,n+1,\downarrow} = t_1$ . Diagonalizing the Hamiltonian, the total energy of the molecule is calculated at half-filling for the F and AF configurations separately. Depending on the parameter set  $\{\varepsilon_1, \varepsilon_2, t_1, t_2\}$  the variation of the total energy difference  $\Delta E_{F \rightarrow AF}$  with  $n$  shows several distinct patterns, including the type of alternations compatible with the DFT calculations of the Cr and Co cases. For instance, the sets  $\{0.0, -1.0, 1.0, 1.5\}$  and  $\{-0.3, -1.0, 0.5, 1.5\}$  in units of  $t$  reproduce Cr- and Co-like variations, respectively (see Fig. 1). The model is capable of simulating the DFT results, since it can mimic the dominant mechanisms of charge and spin induction on the nonmagnetic spacer, as well as the quantum interference effects. The magnetic TM atoms certainly have strong spin polarizations justifying different on-site energies for electrons of each spin type in the model. That asymmetry is expected to be stronger for Cr than for Co due to Hund's rule. When the TM atoms are in contact with the nonmagnetic C chain, the couplings of the TM spin-dependent states with the carbon states are also different. The resulting effect is to create a charge and spin polarization on the C network which also sets up the indirect exchange interaction between the TM atoms. The analysis of the DFT results show that not

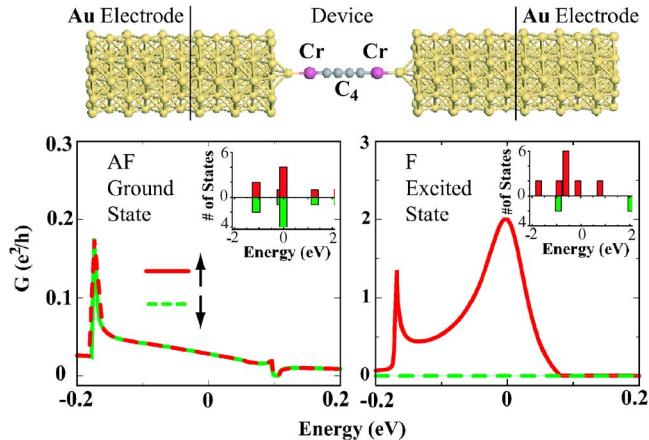


FIG. 3. (Color online) Spin polarized conductance of CrC<sub>4</sub>Cr molecular spin-valve device when connected to semi-infinite Au electrodes. The insets show the molecular energy levels of the isolated chains.

only the  $\pi$ -conjugated states of the carbon chain but also the lower-energy  $\sigma$ -bonding states contribute significantly to the indirect interaction.

Conductance properties of molecular devices depend not only on their intrinsic structure but also on the electrodes. In particular, if the coupling of the device to the electrodes is strong, the electronic structure and hence the transport properties of the device can be quite different, and cannot be inferred from the electronic structure of the isolated device. We have examined Au and Al atomic chains, and Au leads with finite cross section to model the electrodes. The TM-C<sub>n</sub>-TM structures having an AF ground state remained AF with smaller  $|\Delta E_{F \rightarrow AF}|$  values in cases of Au electrodes, whereas the ground states were changed to F upon connecting to Al electrodes. Here, we choose to discuss the case of finite cross-section Au electrodes with single-atom sharp tips, which couples weakly to the device and preserves the generic electronic structure of the isolated TM-C<sub>n</sub>-TM chains. Consequently, we obtain a prominent spin-valve effect that is compatible with the spin-relaxed energy configurations of the isolated molecules.

To calculate the transport characteristics, the effective device region with a long buffer of Au layers (see Fig. 3) is first solved within periodic boundary condition for both AF and F states. We considered the Cr cases for  $n=4$  and 6, and found that the ground state is AF, and the F state has  $\mu = 10\mu_B$ , same as in the case of isolated chains. For the Co cases, the chains studied for  $n=3$  and 5 also preserved their AF ground states when attached to the Au leads. The self-consistent calculations lead to spin-up and spin-down Hamiltonians,<sup>20</sup> which are used to calculate the transmission coefficient for each spin state in the AF as well as in the higher energy F configurations. The surface Green's function of the contacts is calculated recursively. Following this, we calculate the conductance of the device within Landauer formalism,  $G(E) = (e^2/h) \text{Tr}(\Gamma^L \mathbf{G}^T \mathbf{R}^R \mathbf{G}^a)$ , for each spin configuration.<sup>23</sup> In Fig. 3, we show our results for the CrC<sub>4</sub>Cr molecule. In the AF state of the device, the conductance of majority-spin (spin-up) electrons coincides with that of minority-spin (spin-down). However, if the system is in the excited F state, the conductance through the spin-down lev-

els is substantially reduced while it is enhanced through the spin-up levels. The equilibrium conductance value is enhanced by a factor of  $\sim 60$  for the  $\text{CrC}_4\text{Cr}$  structure. This is a clear indication of a strong spin-valve effect through the TM- $\text{C}_n$ -TM molecular structures. Consistent with the energy levels of the isolated chain given in the insets of Fig. 3, it is the spin-up HOMO level in  $\text{CrC}_4\text{Cr}$  that dominantly contributes to the conduction.

We should note that Pati *et al.*<sup>15</sup> have also studied  $\text{CoC}_n\text{Co}$  atomic chains, predicting that the ground state of these isolated structures are AF for all  $n=1-15$  (except  $n=14$ ). However, the alternating variation found in this study is novel and dramatically different than theirs. We believe that in the calculations of Ref. 15, the true ground states of the structures have not been found. The present results concerning with the alternating magnetic ground states of TM- $\text{C}_n$ -TM chains have been consistently reproduced by the calculations using three independent codes.<sup>16,20,21</sup> Furthermore, they have been explained successfully by a simple analytical model that produces the same F-AF alternations of the ground states (see Fig. 1).

In summary, we find that the magnetic ground state of TM-atom-capped C atomic chains alternates between AF and F states depending on the number of C atoms in the chain. The indirect exchange interaction of the TM atoms is mediated by the induced spin polarizations on the C atoms which is due to the asymmetric coupling of the spin states of the TM atoms with the C states. Furthermore, we showed that an almost perfect spin-valve effect is present in these simple molecular structures. These properties can be engineered by selecting the type of the TM atom and the number of C atoms in the chain which lead to odd-even disparities in their magnetic and transport properties. These impressive characteristics are of fundamental and technological interest in the promising fields of spintronics and molecular electronics.

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<sup>19</sup>All molecular chain structures have been treated in tetragonal supercells using periodic boundary conditions. A large vacuum spacing ( $\sim 10$  Å) has been taken in all directions.  $\mathbf{k}$ -point sampling of the TM- $\text{C}_n$ -TM molecules is performed at the  $\Gamma$  point. A plane-wave basis set with kinetic energy cutoff of 350 eV has been used. The energy tolerance for self-consistency is taken as  $10^{-6}$  eV and the maximum force allowed on each atoms is 0.05 eV/Å.

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