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_n-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 magneto resistance effect 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. 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. Organic and carbon-based molecules are promising in achieving magneto resistive effects. Linear atomic chains of C have been synthesized, and their impressive properties have been demonstrated. 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_n) compound structures are found to be stable and half-metallic. Pati et al. have studied atomic wires consisting of C and Co atoms where they have concluded that the ground state of short CoC_{n}Co atomic chains is antiferromagnetic.

In this Communication, we find that the isolated TM-C_n-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_n-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 within density functional theory (DFT) using ultra-soft pseudopotentials. The exchange correlation potential has been approximated by generalized gradient approximation. 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. The results of plane-wave calculations are compared and confirmed with methods which utilize local-basis sets. Transition-state analysis performed for different reaction paths, extensive stability analysis, and ab initio molecular dynamic calculations performed at 1000 K show that CoC_{n}Co and CrC_{n}Cr isolated atomic chains can be synthesized and are stable. For example, both CoC_{n}Co and CrC_{n}Cr isolated chains can be formed from a finite, linear C_n chain by attaching Co or Cr atoms to both ends.

The calculated electronic and magnetic properties of isolated CrC_{n}Cr and CoC_{n}Co chains are summarized in Table I. The total energy of every structure is calculated for each
The calculated electronic properties of isolated CrC\textsubscript{n}Cr and CoC\textsubscript{n}Co chains using VASP (Ref. 16). The columns are respectively: The energy difference of the AF and the lowest-energy F states, \( \Delta E_{F-\text{AF}} = E_F(\text{AF}) - E_F(\text{F}) \), 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), \( E_F^\uparrow \) are the energy gap between the highest occupied and lowest unoccupied levels of spin-\( \uparrow \) states. The bold numbers denote the spin type of the HOMO levels.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( \Delta E_{F-\text{AF}} ) (eV)</th>
<th>( \mu ) (( \mu_B ))</th>
<th>( E_F^\uparrow ) (eV)</th>
<th>( E_F^\downarrow ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrCCr</td>
<td>1.12</td>
<td>8</td>
<td>0.97</td>
<td>2.37</td>
</tr>
<tr>
<td>CrC\textsubscript{2}Cr</td>
<td>-0.10</td>
<td>0 (10)</td>
<td>1.43 (0.82)</td>
<td>1.43 (3.56)</td>
</tr>
<tr>
<td>CrC\textsubscript{3}Cr</td>
<td>0.87</td>
<td>8</td>
<td>1.33</td>
<td>1.83</td>
</tr>
<tr>
<td>CrC\textsubscript{4}Cr</td>
<td>-0.08</td>
<td>0 (10)</td>
<td>1.26 (0.91)</td>
<td>1.26 (2.97)</td>
</tr>
<tr>
<td>CrC\textsubscript{5}Cr</td>
<td>0.70</td>
<td>8</td>
<td>1.43</td>
<td>1.79</td>
</tr>
<tr>
<td>CrC\textsubscript{6}Cr</td>
<td>-0.06</td>
<td>0 (10)</td>
<td>1.17 (0.88)</td>
<td>1.17 (2.77)</td>
</tr>
<tr>
<td>CrC\textsubscript{7}Cr</td>
<td>0.58</td>
<td>8</td>
<td>1.32</td>
<td>1.63</td>
</tr>
<tr>
<td>CrC\textsubscript{8}Cr</td>
<td>-0.01</td>
<td>0 (2)</td>
<td>0.24 (1.41)</td>
<td>0.24 (0.40)</td>
</tr>
<tr>
<td>CoCCo</td>
<td>0.32</td>
<td>4</td>
<td>1.80</td>
<td>0.55</td>
</tr>
<tr>
<td>CoC\textsubscript{3}Co</td>
<td>-0.12</td>
<td>0 (2)</td>
<td>0.87 (1.67)</td>
<td>0.87 (0.86)</td>
</tr>
<tr>
<td>CoC\textsubscript{4}Co</td>
<td>0.28</td>
<td>4</td>
<td>1.72</td>
<td>0.26</td>
</tr>
<tr>
<td>CoC\textsubscript{5}Co</td>
<td>-0.13</td>
<td>0 (2)</td>
<td>0.88 (1.48)</td>
<td>0.88 (0.85)</td>
</tr>
<tr>
<td>CoC\textsubscript{6}Co</td>
<td>0.24</td>
<td>4</td>
<td>1.62</td>
<td>0.48</td>
</tr>
<tr>
<td>CoC\textsubscript{7}Co</td>
<td>-0.13</td>
<td>0 (2)</td>
<td>0.79 (1.34)</td>
<td>0.79 (0.75)</td>
</tr>
</tbody>
</table>

The possible value of its magnetic moment \( \mu \). The AF state \((\mu = 0)\) arises as the ground state of the CrC\textsubscript{n}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 \( \Delta E_{F-\text{AF}} = E_F(\text{AF}) - E_F(\text{F}) \), 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 \( \Delta E_{F-\text{AF}} \) in CoC\textsubscript{n}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 \( \Delta E_{F-\text{AF}} \) 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 is essential in the form of the carbon-mediated interaction between them.

The quantity \( \Delta E_{F-\text{AF}} \) 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.\textsuperscript{7} 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 alteration of magnetic ground state is shorter; its type is altered when the number of C atoms is changed by one. It is the C\textsubscript{a} 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 isolated CrC\textsubscript{n}Cr and CoC\textsubscript{n}Co chains for \( n = 3, 4 \), and CoC\textsubscript{n}Co chains \((n = 3, 4, 11, 12)\) as representative samples. In the even-\( n \) cases the C atoms tend to dimerize, whereas for odd-\( n \) the C–C bonds are almost uniform (this property is more evident for larger \( n \) cases). The atomic interactions 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.

FIG. 1. (Color online) Energy difference of the AF and the F states in the CrC\textsubscript{n}Cr and CoC\textsubscript{n}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,\textsuperscript{26} SIESTA,\textsuperscript{20} and GAUSSIAN03\textsuperscript{21} 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 CrC\textsubscript{n}Cr and CoC\textsubscript{n}Co chains for \( n = 3, 4 \) 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.
magnetic moments are calculated based on an orbital-
resolved Mulliken analysis. The magnetic TM atoms in-
duce moments throughout the C chain which set up an in-
direct exchange interaction between them. Owing to the chain
geometry and quantum interference effects, the induced mag-
netization of C atoms is quite long-ranged; for instance, in
the F ground state of the Cr C15 Cr structure all the C atoms
have alternating magnetic moments of $|\mu| \sim 0.1 \mu_B$. The ef-
fect 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 ac-
cord with a recent experimental study on contact induced
magnetism in metallic carbon nanotubes, where they find
that spin-polarized charge transfer at the interface between a
flat ferromagnetic metal substrate and a multiwalled car-
bon nanotube leads to a spin transfer of about $0.1 \mu_B$ per
contact C atom.

The qualitative features of the peculiar magnetic order-
ing in these chain structures can be understood through a Hückel-type “toy” model. Consider the Hamiltonian of a
chain structure having $n+2$ sites: $H=\sum_{i=0}^{n} E_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} -\sum_{i=0}^{n} t_{i+1,\sigma} c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}$, where $E_{i,\sigma}$ is local site energy,
$t_{i+1,\sigma}$ is the spin-dependent nearest-neighbor hopping integ-
ral, $c_{i,\sigma}$ and $c_{i,\sigma}^\dagger$ 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 $t_{i+1,\sigma}=t_i$. To mimic
the magnetic sites ($i=0$ and $i=n+1$), however, we take both
the on-site energies and their coupling to nearest nonmag-
netic sites as spin-dependent: $E_{0,\uparrow}=E_1$ and $E_{0,\downarrow}=E_2$; $t_{0,1,\uparrow}=t_1$
and $t_{0,1,\downarrow}=t_2$. For the sake of simplicity, we model the mag-
netic 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: $E_{n,n+1,\uparrow}=E_2$, $E_{n,n+1,\downarrow}=E_1$,
$t_{n,n+1,\uparrow}=t_2$, 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 $\{E_1,E_2,t_1,t_2\}$ the variation of the total energy
difference $\Delta E_{F-AF}$ 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 in-
duction 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 Hunds
rule. When the TM atoms are in contact with the nonmag-
netic 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
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 prop-
erties 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$_n$-TM structures having an AF ground state remained
AF with smaller $|\Delta E_{F-AF}|$ values in cases of Au electrodes,
whereas the ground states were changed to F upon connect-
ing 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$_n$-TM
chains. Consequently, we obtain a prominent spin-valve ef-
fect that is compatible with the spin-relaxed energy config-
urations 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 $\mu_f$
$=10 \mu_B$, 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, 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 for-
malism, $G(E)=(e^2/h)\text{Tr}(T^aG^R T^bG^L)$, for each spin configuration. In Fig. 3, we show our results for the CrC$_3$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 −60 for the Cr₄C structure. This is a clear indication of a strong spin-valve effect through the TM-Cₜₐₜ-M 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 Cr₄C that dominantly contributes to the conduction.

We should note that Pati et al. have also studied Co₄ₐₗ-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-Cₜₐₜ-TM chains have been consistently reproduced by the calculations using three independent codes. 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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16 Most of the numerical computations have been carried out using VASP software: G. Kresse and J. Hafner, Phys. Rev. B 54, 11169 (1996).
19 All molecular chain structures have been treated in tetragonal supercells using periodic boundary conditions. A large vacuum spacing ( ~10 Å) has been taken in all directions. K-point sampling of the TM-Cₜₐₜ-TM molecules is performed at the Γ 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.
21 M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 03, Revision C. 02, Gaussian Inc., Wollongong CT, 2004. The UB3PW91 functional with 6-31G* basis set has been employed. The results are subjected to wave function stability analysis.