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Magnetic Properties of Carbon Chains Doped with 4d Transition Metals

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The structural and magnetic properties of functionalized carbon chains doped with 4d transition metals, such as Ru, Rh, and Pd, were investigated using the full-potential linearized augmented plane wave (FLAPW) method. The carbon nanowire doped with Ru exhibited a ferromagnetic ground state with a sizable magnetic moment, while those doped with Rh and Pd had nonmagnetic ground states. For the Ru-doped chain, the density of states at the Fermi level showed large spin polarization, which suggests that the doped nanowire could be used for spintronic applications.

Keywords : carbon chain, 4d transition metal, magnetic moment, FLAPW method

1. Introduction

Low-dimensional carbon systems, such as carbon nanotubes (CNTs), fullerenes, carbon stripes etc., have been the focus of a great deal of scientific research, due to their possible device applications [1, 2]. For instance, a linear chain of carbon atoms (C-LC) has been investigated theoretically, in order to understand the physical properties of the carbon system in an ideal one-dimensional structure [3]. In another study, it was found that an ideal C-LC is a better conductor than a linear gold chain [4]. Furthermore, first-principles pseudopotential calculations have shown that C-LCs have lower energies than equivalent zigzag structures, which is contrary to most other LCs consisting of metal atoms [5, 6].

A theoretical attempt to functionalize the C-LC by adding transition metal (TM) atoms [7] calculated the electronic structures of the C-LCs with adsorbed 3d magnetic TM atoms, such as Mn, Fe, Cr, and Co. The magnetic moments of the adsorbed TM atoms were found to be very close to those of the isolated atoms themselves. The spin polarization, defined as the ratio of the difference and sum of the majority and minority density of states (DOS) at the Fermi level, was also large enough for practical applications in spintronics.

It is well known that low-dimensional 4d transition metal systems may exhibit magnetism [8]. Therefore, in this study, the electronic and magnetic properties of functionalized C-LC doped with 4d transition metals, such as Ru, Rh, and Pd, were investigated using the full-potential linearized augmented plane wave (FLAPW) method [9], with the generalized gradient approximation (GGA) [10].

2. Computational Method

The systems we investigated here are linear carbon chains, where one 4d transition atom is adsorbed periodically per every five carbon atoms in the chain. The unit cell therefore contains five carbon atoms and one 4d transition atom, as illustrated in Fig. 1, which displays Ru adsorbed on a C-LC (Ru-C-LC). The one-dimensional lattice constant along the chain (6.25 Å) was taken from a previously reported calculation [7].

Firstly, we determined the optimized structure of each TM (Ru, Rh, and Pd)-C-LC using the pesudopotential method [11]. For our pseudopotential calculation, the wavefunctions were represented by plane waves up to an energy cut-off 400 eV. The Brillouin zone was sampled using the Monkhorst-Pack sampling scheme with a $1 \times 1 \times 21$ mesh.

Subsequently, we used the FLAPW method [9] to calculate the electronic structures for the optimized structures. Lattice harmonics up to $l = 8$ were used to expand the charge density, potential, and wavefunction inside muffin-tin spheres with radii of 1.1 a.u. for C atoms, and

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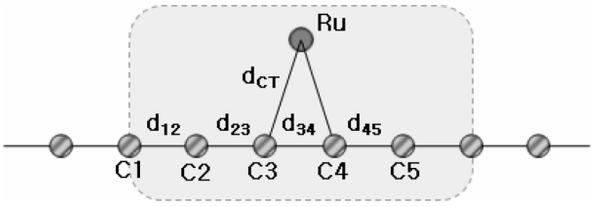

Fig. 1. A schematic structure of a C-LC with an adsorbed Ru atom.

2.3 a.u. for Ru, Rh, and Pd atoms. Around 1000 plane waves were used to describe the interstitial region. Self-consistency was assumed when the difference between the input and output charge density was smaller than 1×10^{-4} e/a.u.^{3}.

3. Results and Discussion

The optimized structures, obtained by use of the pseudopotential method, are summarized in Table 1. As can be seen from Table 1, the bond length between the central C atoms (C3 and C4) was slightly longer than those between the other adjacent C atoms (C1, C2, and C3). It is also longer than the bond lengths between the C atoms of bare C-LC (1.27 Å). These results are considered to be due to the interaction between the C atoms and the attached transition metal.

Even though the previous calculation for the adsorption of 3d TMs (e.g. Fe and Co) [7] considered asymmetric configurations, thereby creating two different distances between the TM atom and the two nearest carbon atoms, the shorter distances that were calculated for adsorbed Fe and Co [7] are nearly the same as the currently calculated distances for 4d TM atoms adsorbed in symmetric configurations. From Table 1, it can be seen that the d_{CT} for Pd is slightly greater than that for Ru or Rh. This can be explained by their ionic radii. The slightly larger ionic radius for Pd [12], compared with Ru or Rh, means that the outer electrons of Pd give stronger repulsion if the center of Pd atom is located at the same position as that of Ru or Rh atom, therefore may result in a longer distance.

Table 1. The bond lengths (d_{12}, d_{23}, d_{34}) between adjacent carbon atoms, and the distance (d_{CT}) between the 4d transition metal atom (Ru, Rh, Pd) and the nearest carbon atoms of the C-LC.

4d atom	d_{12} (Å)	d_{23} (Å)	d_{34} (Å)	d_{CT} (Å)
Ru	1.255	1.271	1.299	2.028
Rh	1.256	1.271	1.297	2.010
Pd	1.260	1.271	1.289	2.141

With the structural parameters, we calculated the electronic structures using the FLAPW method. We first calculated the paramagnetic states, and the DOS plots are shown in Fig. 2. The general shapes of DOS are similar

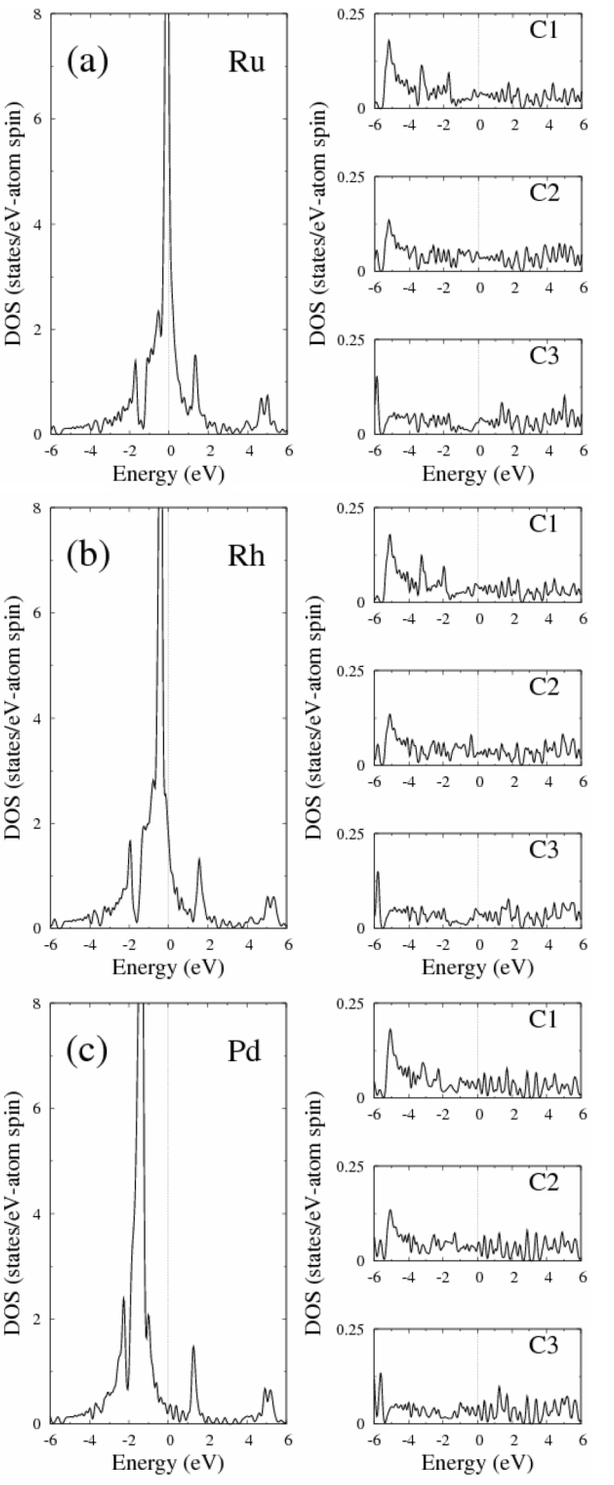

Fig. 2. The density of states for a paramagnetic C-LC doped with: (a) Ru, (b) Rh, and (c) Pd atoms.

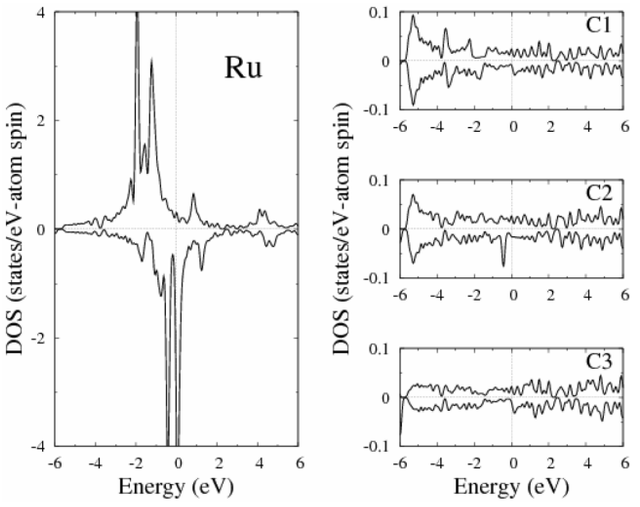

Fig. 3. The density of states for a ferromagnetic C-LC doped with an Ru atom.

but with different locations of Fermi levels. This is due to the different number of d electrons: as the number of d electrons of the TM is increased, the Fermi level moves up to a higher energy.

We found that the DOS values for the Rh- and Pd-C-LC systems, as given in Fig. 2(b) and (c), are small at the Fermi level. It is expected that these systems are paramagnetic because the DOS value at the Fermi level is not large enough to satisfy the Stoner criterion. Figure 2(a) shows, contrary to the cases of C-LCs doped with Rh and Pd, that the Fermi level for C-LC doped with Ru is located near the DOS peak, which implies that the ferromagnetic state could be stable.

We also performed the spin polarized calculation for all three TM-C-LC systems. As expected from the calculations for paramagnetic states, the converged results for the Rh- and Pd-C-LC systems adopt paramagnetic states. Only the Ru-C-LC system turned out to be ferromagnetic. The DOS plot for a ferromagnetic C-LC doped with Ru is presented in Fig. 3.

We can see that the exchange splitting causes shifts of both majority and minority bands. Therefore, the number of occupied electrons with majority spin is larger than that with minority spin thus gives ferromagnetic states. Furthermore, the DOS of majority spin at the Fermi level is smaller than that of minority spin, which leads to a large spin polarization of about −85.5% at the Fermi level as in previous calculation for C-LCs doped with Fe or Co [7], contrary to the positive spin polarization for Cr and Mn.

The charge and spin density contours for ferromagnetic C-LC doped with Ru are shown in the upper and lower panels of Fig. 4, respectively. The number of majority and minority electrons inside the muffin-tin sphere of Ru, together with their sums and differences, are summarized in Table 2. The first and second rows of each cell represent majority and minority spins and their sums and

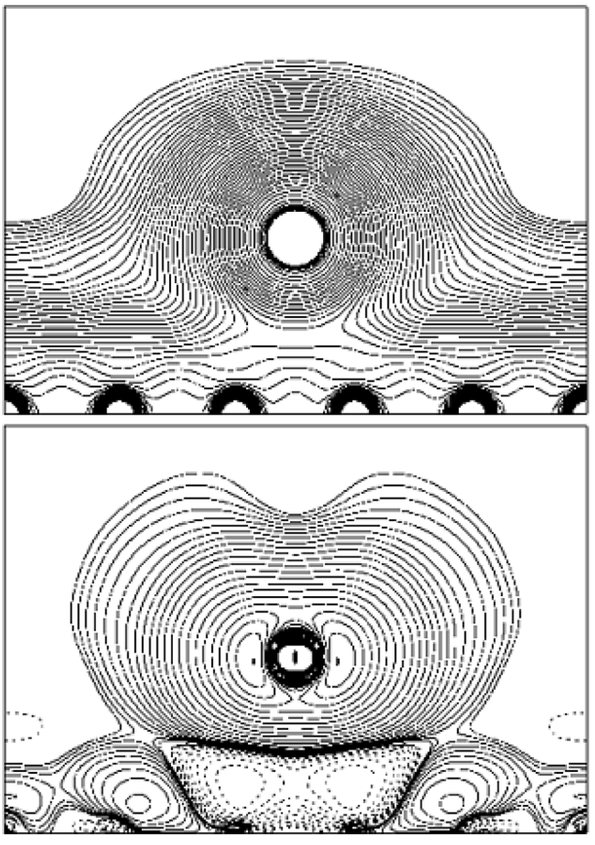

Fig. 4. The charge (upper panel) and spin (lower panel) density contours for a C-LC doped with Ru. The solid and dotted lines represent majority and minority spins, respectively.

Table 2. The number of electrons and magnetic moments (in μ_B) inside the muffin-tin sphere of the carbon atoms and Ru atom. The first and second rows of each cell represent majority and minority spins and their sums and differences, respectively.

atom	s	p	d	total	magnetic moments
C1	0.22/0.22 0.44/0.00	0.34/0.34 0.68/0.00	0.01/0.01 0.02/0.00	0.57/0.57 1.14/0.00	0.00
C2	0.22/0.22 0.44/0.00	0.33/0.33 0.66/0.00	0.01/0.01 0.02/0.00	0.56/0.56 1.12/0.00	0.00
C3	0.22/0.22 0.44/0.00	0.33/0.33 0.66/0.00	0.01/0.01 0.02/0.00	0.56/0.55 1.11/0.01	0.01
Ru	0.10/0.07 0.17/0.03	0.05/0.04 0.09/0.01	3.65/2.23 5.88/1.42	3.82/2.36 6.18/1.46	1.46

differences, respectively. We can see that the calculated magnetic moment of the Ru atom (1.46 μ_B) has considerable magnitude. This can be inferred from the DOS and spin density contours.

The charge density contour shapes in Fig. 4 show different bonding characteristics around C2, C3, and Ru, due to the p electrons from C and the d electrons from Ru. This can also be confirmed from the slight deficiency of p electrons for C2 and C3 in Table 2.

The spin density surrounding the Ru atom indicates that it can be ferromagnetic. Furthermore, it can be seen that there are regions of negative spin density between the C3 and Ru, and around C1 and C2, which are mostly due to the p electrons from the C atoms. The adsorbed Ru atom in the C-LC behaves like a ferromagnetic impurity in a metal, which causes a spin density oscillation similar to the RKKY-Friedel oscillation. This behavior is indicated by the alternating sign of spin densities along the line from Ru to C2.

4. Summary

The structural and magnetic properties of C-LCs doped with 4d transition metals, such as Ru, Rh, and Pd, were investigated using the FLAPW method. The C-LC doped with Ru exhibited a ferromagnetic ground state with a considerable magnetic moment (1.46 μ_B), while those doped with Rh and Pd had nonmagnetic states. The DOS at the Fermi level for the Ru-doped chain showed a large spin polarization of −85.5%.

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