First-principles calculations of half-metallic ferromagnetism in zigzag boron-nitride nanoribbons jointed with a single Fe-chain*

Luo Kaiwu(罗开武), Wang Lingling(王玲玲)†, Li Quan(李权), Chen Tong(陈桐), and Xu Liang(许梁)

Key Laboratory for Micro-Nano Physics and Technology of Hunan Province, School of Physics and Electronics, Hunan University, Changsha 410082, China

Abstract: First-principles calculations have been used to research the electronic structure and magnetic properties of zigzag boron nitride nanoribbons (ZBNNRs) terminated/jointed by armchair dimer-Fe chains (respectively called Fe-terminated ZBNNRs and Fe-jointed ZBNNRs). The Fe-terminated ZBNNRs is a semiconductor for different ribbon widths, and the Fe-jointed ZBNNRs become half-metallic regardless of the ribbon width. The magnetism of both structures mainly stems from the Fe atoms. It is found that the self-metallicity of the Fe-jointed ZBNNRs results from the strong interaction between the 3d orbitals of Fe atoms and the 2p orbitals of N atoms. The stability of the Fe-jointed ZBNNRs under room temperature has been confirmed by molecular dynamics simulation. This kind of half-metal property means a selectivity for the two different electrons, it can be applied to spintronics devices. Other transition-metal jointed ZBNNRs are also studied, which can be metals, half-metals or semiconductors with different ground states.

Key words: first-principles calculations; electronic structure; boron nitride nanoribbons

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1. Introduction

In the last decade, graphene and the corresponding nanoribbons have always been a hot topic due to their charming electronic, magnetic and mechanical characteristics[1–6], and recently, extensive studies on the isoelectronic and isostructural analogues of carbon-based nanomaterials of boron nitride (BN) nanostructures have been reported[7–9]. Unlike the semimetallic graphene sheet, the electrical measurements and UV–visible absorption spectrum find the BN sheet is a wide-band gap semiconductor[10–12]. Its low-dimensional nanostructure is well known as BN nanoribbons (BNNRs), which are similar to graphene nanoribbons (GNRs) in geometry, and can be obtained through plasma etching or alkali metal intercalation by longitudinally unzipping the BN nanotubes to form narrow BNNRs[13,14].

As we all know, the GNRs are either nonmagnetic or antiferromagnetic semiconductors, depending on their edge geometries. The armchair GNRs are semiconductors with hierarchically changed gap size, and the zigzag GNRs are either metal at the nonmagnetic state or semiconductor under the antiferromagnetic state[3,15–17]. However, BNNRs are semiconductors regardless of their edge shapes and widths. With increasing the width, the band gaps of armchair BNNRs exhibit family dependent oscillations, and for the ribbons wider than 3 nm, they converge to a constant value about 0.02 eV, which is smaller than the bulk band gap of a BN sheet for the existence of extraordinary weak edge states. Meanwhile the band gaps of zigzag BNNRs monotonically decrease and converge to a gap about 0.7 eV as width increases, and it is smaller than the bulk gap due to the presence of strong edge states[18]. Although the BN nano-materials are semiconductors with wide gaps, their gaps can turn into various values by chemical functionalizations, for example, the electronic structures of BNNRs can be spin-polarized by atomic doping or defects[19–22]. Due to the large ionicity of B-N bonds, BNNRs possess different properties with GNRs, which suggests a great potential application in nanoscale electronic devices.

Many works on the tunable electronic structures of BNNRs have been performed, and it is obvious to see doping and modification of edges are two of the most effective ways to tail the electronic and magnetic properties of the ribbons[23–25]. For instance, the promising half-metallicity can be found in ZBNNRs with non-passive N edges or fully passivated B edges. In addition, the system shows a giant spin splitting, the electrons at the Fermi level are 100% spin polarized[26]. Then, Lai et al.[27] have demonstrated that the ground states of the fully bare BNNRs, the BNNRs with one bare N edge and the BNNRs with H-terminated B edge are half-metallic. The alignment of the spin at the bare B edge is antiferromagnetic, while it is ferromagnetic at the bare N edge in the ground states both for the fully bare and for half-bare ZBNNRs. Ding et al.[28] have investigated the stabilities of BNNRs with different hydrogen-terminated edges: five and three kinds of stable edges are considered in their ZBNNRs and ABNNRs, respectively. They conclude that the ZBNNRs are ferromagnetic metal under the condition of a rich hydrogen environment, yet the ABNNRs are nonmagnetic semiconductors. Moreover, Chen et al.[29] have

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† Corresponding author. Email: llwang@hnu.edu.cn

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found the way to modulate the electronic and magnetic properties of BNNRs via controlling the hydrogenation ratio. They have investigated the fully and partially hydrogenated BNNRs, and then they find the fully hydrogenated ABNNRs are non-magnetic semiconductors regardless of the widths. However, the ZBNNRs exhibit diverse electronic properties of semiconductor→half-metal→metal transition accompanied by a non-magnetic→magnetic transfer by controlling the hydrogenation ratio. Recently, Wang et al.\textsuperscript{[29]} performed a first-principles study on the Fe-terminated ABNNRs. They found that the Fe-ABNNRs were antiferromagnetic metals, and half-metals appeared in their ABNNRs as one edge terminated by Fe atoms and another edge terminated by H atoms. At the same time, the other transition-metal terminated ABNNRs were also presented, which displayed diverse magnetic states of semiconductors as well as half-metals depending on the types of metals. What is more, the electronic and magnetic properties of Fe-terminated GNRs and BNNRs also have been explored in detail by others\textsuperscript{[30–33]}. Nonetheless, there is still no any discussion about the characteristics of metal-jointed BNNRs up to now, so in this paper, we investigate the electronic and magnetic properties of Fe-jointed ZBNNRs in some detail.

2. Computational details

The electronic structure and magnetic properties of the Fe-jointed ZBNNRs and Fe-terminated ZBNNRs are calculated by spin-polarized density functional theory (DFT) implemented in the VASP code within a plane-wave basis set\textsuperscript{[34, 35]}. The plane-wave cutoff energy is set to be 500 eV, and the convergent force on each atom is less than 0.01 eV/Å. The nanoribbons are simulated by using a supercell image of Fe-connected ZBNNRs with a large vacuum spacing of 15 Å between two periodic adjacent images. The generalized gradient approximation (GGA) exchange and correlation functional in combination with projector augmented wave pseudopotentials are adopted, and the GGA plus the multiorbital mean-field Hubbard model (GGA + U) calculations are used for describing the Fe atoms. The Monkhorst-Pack scheme is used to sample the Brillouin zone. On the basis of the equilibrium structures, 25,000 points are used to compute spin-related band structures. All the lattice constants and the positions of the atoms in the supercell are fully relaxed during the geometry optimizations.

Based on the previous work on Fe-terminated nanoribbons\textsuperscript{[30]}, the Fe terminations dimerize at the edge of the ribbon due to the Peierls distortion. In the same way, the dimerization of the Fe chain then connects two ZBNNRs and form a Fe-ZBNNRs hybrid junction. Figure 1 shows the atomic structures of Fe-jointed-8ZBNNRs and Fe-terminated-8ZBNNRs. In Figure 1(a), both edges are passivated by hydrogen atoms. However, for Fe-terminated-8ZBNNRs as illustrated in Figure 1(b), only one edge has the normal H-termination and the other edge is terminated with Fe atoms. From Figure 1(c) for the Fe-jointed-8ZBNNRs, we can see the angles of the N–B–N in the octagonal and pentagonal rings are 122° and 118°, respectively, and the angle of B–N–Fe in octagon is 129°. Meanwhile, the bond length of Fe atoms dimerized armchair chain is larger than the Fe–N and the B–N in ZBNNRs, and all the bond lengths are also labeled in Figure 1(c). Similarly, the corresponding angles and bond lengths for the Fe-terminated-8ZBNNRs are shown in Figure 1(d). Here, Figure 1(e) represents a profile of the binding process of Fe-jointed-8ZBNNRs. The binding energies of the two structures are defined as $E_b = E_{\text{Fe-ZBNNRs}} - E_{\text{pristine ZBNNRs}} - n_{\text{Fe}}E_{\text{Fe-atomes}}$. Herein the $E_b$ of Fe atoms is about $-2.93 \text{ eV/Fe}$ in Fe-ZBNNRs, which is much more stable than isolated Fe chains with only $-1.54 \text{ eV/Fe}$. The large energy difference between Fe-ZBNNRs and Fe chains manifests the robustness of N–Fe bond, which implies a great stability of Fe-jointed-8ZBNNRs.

3. Results and discussions

The Fe-jointed ZBNNRs and Fe-terminated ZBNNRs in our work are schematically illustrated in Figure 1, where the Fe atoms form a dimerized armchair chain in the middle of two H-terminated ZBNNRs and on the right edge of a half-H-terminated ZBNNRs, respectively. Here, The ZBNNRs are labeled by the number of zigzag chains which denotes the width of the ribbon, and the ZBNNRs with $n$ B–N chains can be called NzZBNNR. The outmost atoms at both edges are hydrogen passivated B atoms since the middle Fe–N bonds are more stable than corresponding Fe–B bonds. Therefore, the symmetric structure of Fe-jointed-NzZBNNRs is formed by linking two perfect ZBNNRs with Fe atoms in the center, which results in octagonal and pentagonal rings between the two ZBNNRs. In this work, we represent the spin-polarized density functional calculations of Fe-jointed-8ZBNNRs to research the electronic structures and the magnetic moments of the ribbons. The total energy calculation of nonmagnetic (NM) state, the ferromagnetic (FM) state and the antiferromagnetic (AFM) state are performed to estimate the ground states of the magnetic structures. We have calculated the Fe-jointed-8ZBNNRs as well as the Fe-terminated-8ZBNNRs with the width of Nz = 1–8 for all these states, and then we find that the ground state for both are FM, and it has nothing to do with the widths of ZBNNRs.
Figure 2. (Color online) (a) The spin polarized band structures and (b) the spin densities of the Fe-terminated-8ZBNNRs.

Figure 3. (Color online) (a) The spin polarized band structures and (b) the spin densities of the Fe-jointed-8ZBNNRs.

Figure 2(a) demonstrates the band structures of Fe-terminated-8ZBNNRs under the FM state. Both for the spin up electrons and spin down electrons, there are no bands crossing the Fermi level, suggesting a semiconductor property for this system, and the gaps for spin up electrons and spin down electrons are 0.3466 eV and 0.1035 eV, respectively. Figure 2(b) indicates the spin densities of the Fe-terminated-8ZBNNRs, from which we can know the total magnetic moment of this structure is mainly from the Fe-termination. Likewise, Figure 3(a) shows the band structures of Fe-jointed-8ZBNNRs at the ground FM state. One can see that the Fe-jointed-8ZBNNRs display half-metallicity behaviors. Three spin-up electrons’ bands cross the Fermi level, representing an obvious metallic behavior. While none of the spin-down electrons’ bands pass through the Fermi level, which means a band gap exists for spin down electrons, and the value (about 0.52 eV) of the half-metal gap can be obtained by the distance between the Fermi level and the topmost occupied band of spin down electrons. This value is larger than the previously reported half-metallic GNR under the high electric field and other functional ZBNNRs\cite{3, 26, 27}. The spin densities of an Fe-jointed-8ZBNNRs unit cell are plotted in Figure 3(b); one can see the magnetic moments are mainly located on the Fe dimerization and few of them distribute on the Fe-connected N atoms, which means the total magnetic moment of each unit cell (about 6.02 $\mu_B$) is mainly from the Fe atoms. Also, from the Bader charge analysis we can know that each Fe atom has a magnetic moment of about 3.03 $\mu_B$.

In order to understand the half metallicity of Fe-jointed-8ZBNNRs, we have studied their spin-resolved projected density of states (DOS) as shown in Figure 4. We can see the charge transports are totally dominated by the spin-up electrons (according to the distribution of the spin resolved DOS in Figure 4(a)), while the spin-down electrons are absolutely suppressed around the Fermi level, which is in line with the half metallicity
Figure 4. The spin resolved density of states (DOS) of Fe-jointed-8ZBNNRs. (a) The total DOS of the system. (b) The 3d orbitals of center dimerized Fe atoms. (c) The 2p orbitals of Fe-connected N atoms.

in Figure 3. Figures 4(b) and 4(c) respectively denote the DOS of 3d orbitals of dimerized Fe atoms and the 2p orbitals of Fe-connected N atoms. It is clear that the large spin-polarization phenomenon appears in Fe-jointed-8ZBNNRs and the most of total DOS around the Fermi level are attributed to the Fe 3d orbitals and N 2p orbitals. Furthermore, the large spin-up peaks of Fe 3d and N 2p orbitals around the Fermi level are in the same location. A strong interaction exists between the Fe and N atoms, which results in the large binding energies in Fe-jointed-8ZBNNRs. In combination with the two structures in Figures 1(a) and 1(b), we can find the number of the N atoms bonded with the Fe atoms in Figure 1(b) is twice that in Figure 1(a), which are 4 and 2, respectively. The interaction of Fe atoms and N atoms in Fe-jointed-8ZBNNRs is strong enough to generate the half metallicity, while in Fe-terminated-8ZBNNRs the interaction is not strong yet. This is the origin of the half metallicity for Fe-jointed-8ZBNNRs.

Then, the stability of Fe-jointed-8ZBNNRs has been evaluated by carrying out molecular dynamics (MD) simulations at room temperature (T = 300 K) with a time step of 1 fs. During the progress of simulation, the bonding interatomic interaction is calculated by the many-body Tersoff-Brenner potential, and the Van de Waals interaction is described by a Lennard-Jones potential. In Figure 5, we graph the variations of temperature versus time. One can see that during the running time of 500 fs, the geometry is always stabilized. Besides that, we demonstrate the structure of Fe-jointed-8ZBNNRs after 500 fs of the MD simulation in Figure 6, suggesting the Fe-jointed-8ZBNNRs is stable at room temperature. This structure is in very good agreement with the results of our relaxed structure as illustrated in Figure 1(a) except for some distortion. In Figure 6, this structure contains 18 hydrogen atoms, 72 boron atoms, 72 nitride atoms as well as 8 iron atoms. Therefore, the interesting electronic and magnetic properties of these Fe-jointed ZBN-NRs may have actual potential application in nano-spintronics devices.

Finally, we research the cases of other transition-metals (M = Co, Cr, Cu, Mn, Ni, Zn) briefly by replacing the Fe atoms in the Fe-jointed-8ZBNNRs. The results reveal different metals could induce various electronic and magnetic properties for this kind of structure. The data are listed in Table 1. Like the Fe-jointed-8ZBNNRs, the Cr-jointed-8ZBNNRs is also an FM half-metal with a half-metal gap of 0.07 eV, and the Co-jointed-8ZBNNRs as well as the Cu-jointed-8ZBNNRs are FM metals. However, the Ni-jointed-8ZBNNRs and the Mn-jointed-8ZBNNRs prefer the AM magnetic state. As a special case, the Zn-jointed-8ZBNNRs is an NM semiconductor with the biggest gap of 2.02 eV.

4. Conclusion

In conclusion, we have investigated the electronic and magnetic properties of Fe-terminated-8ZBNNRs and Fe-jointed-8ZBNNRs, and the results of calculation demonstrate that the Fe-terminated-8ZBNNRs display a semiconductor behavior. However, for the Fe-jointed-8ZBNNRs, there are several spin-up electrons’ bands across the Fermi level, while none of the spin-down electrons’ bands across the Fermi level, and the value of the gap is about 0.52 eV. It shows a classical half-metallicity behavior. Through analyzing the DOSs of this structure, it is found the self metallicity of the Fe-jointed-8ZBNNRs results from the strong interaction between the 3d orbitals of Fe atoms and the 2p orbitals of N atoms. Moreover,
first-principles calculations have shown that the magnetic moments of the two structures are mainly derived from the Fe atoms. Ultimately, we employ the molecular dynamic simulations to verify the stability of the Fe-jointed-8ZBNNRs at room temperature. From above, we can regard the Fe-jointed-8ZBNNRs as excellent candidates for spintronic devices. In addition, the half-metal behaviors also occur in the Cr-jointed-8ZBNNRs, and we can obtain semiconductor properties in Mn-jointed-8ZBNNRs or metal characteristics in Cu-jointed-8ZBNNRs, and so on. These abundant electronic and magnetic characteristics of the M-jointed ZBNNRs have a giant application in spintronics and electronics.

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