Ab-Initio Calculation of the Magnetic Properties of Metal-Doped Boron-Nitrogen Nanoribbon

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Abstract. The field of spintronics has been continuously attracting researchers. Tremendous efforts have been made in the quest to find good candidates for future spintronic devices. One particular type of material called graphene is under extensive theoretical study as a feasible component for practical applications. However, pristine graphene is diamagnetic. Thus, a lot of research has been performed to modify the graphene-based structure to achieve meaningful magnetic properties. Recently, a new type of graphene-based one-dimensional material called Boron Nitrogen nanoribbon (BNNR) has been of interest, due to the theoretical predictions that this type of material shows half-metallic property. Here we present the results of the theoretical and computational study of M-doped (M = Cr, Mn) Zigzag BNNR (ZBNNR), the objective of which is to determine whether the presence of these dopants will give rise to ferromagnetism. We have found that the concentration and the atomic distance among the dopants affect the magnetic ordering of this type of material. These results provide a meaningful theoretical prediction of M-doped ZBNNR as a basic candidate of future spintronic devices.

1. Introduction
The exploration of new materials for spintronic [1] – electronics based on electron spin rather than charge – continues to attract great interests. From the practical point of view, any candidates of spintronic materials need to have room-temperature ferromagnetism. In addition, it would also be a major advantage if these new materials already have an existing technology-base in other applications (e.g. optoelectronic). Among the many materials fitted as candidates for spintronic devices, graphene-based and other light p-block elements nanostructures have received considerable attention. This all began in 2004 with the first isolation of a truly two-dimensional structure of sp²-bonded densely packed Carbon graphene [2-3] which has a unique electronic structure (linear band dispersion at the Fermi level). The discovery of graphene has since attracted attention due to its many important technological applications

Although the ideal graphene is non-magnetic, its nanostructures and derivative materials show promising magnetic properties. One of these materials, the quasi one-dimensional graphene nanoribbons (GNRs), have been experimentally synthesized and characterized successfully. Due to its honeycomb structure, the edges of the GNRs may exhibit either the armchair edge or the zigzag edge. Naturally, depending on the type of edge and the combination of elements connected to them, the electronic structure and magnetic properties of these two types of GNRs are different. Thus, the rich variations of these edges will affect the physical and chemical properties of the nanostructures. It also has been shown that applied external stimuli could affect the spin-transport properties of these
materials. Applied electric fields might generate half-metallicity in zig-zag graphene nanoribbons according to theoretical investigation [4]. Additionally, it also has been predicted that a high transition temperature might be naturally generated in materials containing sp-elements due to the high spin-wave stiffness [5-6].

In recent years, however, experimental as well as theoretical investigations of nanoribbons have shifted to other types of materials. Examples of materials include nanoribbons of Boron Nitride (BN) [7], mixed of graphene/BN [8], BNC [9], etc. Recent theoretical and experimental studies showed, e.g., edge modified Boron Nitrogen Nanoribbon (BNNR) has a wide range of magnetic, electronic, as well as optical characteristics [10-12]. While modifying the edges could change their physical properties, the present investigations of possible ferromagnetism in graphene and nanoribbon structures are also focused in defect vacancies [13] and doping of foreign atom(s) [14-15]. The doping of transition metal atoms in this type of structure is especially interesting because of the possible generation of ferromagnetism due to the unpaired d (or f) electrons of the atoms. Recently, the realization of well isolated, high spin state, transition metal atoms at the edge or divacancy of the graphene layer was demonstrated [15]. This has opened up an avenue to control the spin state in metal-doped graphene and nanoribbon structures for future spintronic devices.

In a recent paper Luo et. al. [16] presented a study of M-chain-embedded (M = Fe, Cr, Mn, Co) Zigzag BNNR (ZBNNR) with different dimers in pentagon-octagon-pentagon line defects and found some of their ground states to be ferromagnetic. They have also predicted that the hydrogen-passivated systems with C2 dimer result in half-metallic behavior. Even though the present paper and Ref. [16] have a similar spirit, i.e. to investigate the occurrence of ferromagnetism in ZBNNR systems, they differ in several important points: Firstly, we have used different structures to substitute the atoms, i.e. an M-doped ZBNNR (this paper) vs an M-chain-embedded ZBNNR with line defects (Ref. [16]); secondly, the locations of metal dopants in our study are arbitrary vs the more centered M-chain-embedded dopants in Ref. [16]; thirdly we also studied the effect of dopant concentrations and distance on the ferromagnetism of the M-doped ZBNNR system which had not been done in Ref. [16]. However, since the system we considered in this paper is small in term of the number of atoms, we are not able to compare the results of more dopant concentration levels.

2. Computational Method
First-principles total energy calculations of transition metal (Mn, Cr)-doped ZBNNR were performed using the ABINIT code [17-18]. ABINIT is a plane-wave-based pseudopotential density functional theory (DFT) code. Specifically, the generalized gradient approximation (GGA) of DFT is used in our calculations. The GGA is a widely used approximation for the exchange correlation functional in DFT and has proven to be very successful in predicting many material properties.

For our calculations, the GGA-PBE from Fritz-Haber-Institute (Troullier-Martins scheme) [19] has been used for all elements. The automatic generation of k points in the Irreducible Brillouin Zone of 5 X 1 X 1 Monkhorst-Pack grids has been performed. The cutoff energy of the plane-wave basis set was fixed at 70 Ha.

For our calculations, the supercell of ZBNNR is flat in the x-y plane. The two edges are passivated by Hydrogen atoms. In our notation, the ZBNNR consists of N atoms of Boron Nitrogen and 2 atoms of Hydrogen. For example, a 8-ZBNNR contains 8 atoms of Boron, 8 atoms of Nitrogen and 2 atoms of Hydrogen. Figure 1 shows an example of the structure of ZBNNR with N = 5. The dashed line in the figure represents the supercell of the nanoribbon being considered.

3. Results and Discussion
We substituted (Mn, Cr) atoms to replace only the Boron atoms: (Mn_x, Cr_y) B_{1-x}N with the consideration that in the limit of x = 100% we should have MnN or CrN compounds. For each case, the total energy for the ferromagnetic (FM), antiferromagnetic (AFM) and non-magnetic spin alignment were computed. We have performed calculations for N = 8 (i.e. a system with 8 atoms of Boron, 8 atoms of Nitrogen and 2 atoms of Hydrogen). To study the effect of metal concentration on
ZBNNR, we considered the following two cases: (i) $x = 12.5\%$ (equal to 2 dopants per 16 atoms in the supercell) and (ii) $x = 25\%$ (equal to 2 dopants per 8 atoms in the supercell). Note that since the number of atoms used in the present study is small it is not possible to study more dopant concentration levels (e.g. $x = 3.125\%$ or $x = 6.25\%$).

Table 1 shows the results of our calculations. The table lists the relative total energy per atom for Mn and Cr dopants. The relative total energy was calculated as the difference of total energy (for each magnetic structure): $\Delta E = E_{\text{total}}^{\text{FM or AFM}} - E_{\text{total}}^{\text{non-magnetic}}$. For both dopants the FM state is the preferred state. However, as the dopant concentration is increased from 12.5\% to 25\% the FM energy difference also increases.

![Figure 1](image-url) An example of ZBNNR structure with $N = 5$. Dashed line is the supercell.

The occurrence of ferromagnetism can be explained as follows. Assuming that metal atoms are $M^{3+}$ when they substitute for Boron atom, $Mn^{3+}$ and $Cr^{3+}$ have 4 and 3 d electrons, respectively. In this case, FM state is preferred because there are plenty of donors available.

To investigate the interaction between two dopants, we vary the locations of two dopants in the supercell with 25\% concentration. Increasing the distance by $\sim 1.84$ Angstrom, we found, significantly reduces the relative total energy of Mn-doped ZBNNR from 0.213 eV/atom to $10^{-7}$ eV/atom, while for Cr-doped BNNR the relative energy decreases from 0.242 eV/atom to 0.017 eV/atom. This result shows the source of ferromagnetism originates from the interaction among dopants located closely.

**Table 1.** The relative total energy per atom (in eV/atom) for (Mn or Cr)-doped ZBNNR. FM means ferromagnetic configuration and AFM means antiferromagnetic configuration. The preferred state is given in bold.

| Dopant | Concentration = 12.5\% | Concentration = 25\% |
|--------|-------------------------|------------------------|
| Mn     | 0.002 (FM); $< 10^{-3}$ (AFM) | 0.213 (FM); $< 10^{-4}$ (AFM) |
| Cr     | 0.010 (FM); $< 10^{-3}$ (AFM) | 0.242 (FM); $< 10^{-4}$ (AFM) |

4. **Conclusion**

Using the first-principles DFT within the GGA, we have calculated the magnetic properties of (Mn, Cr)-doped ZBNNR. Our calculations show that increasing the concentration of the dopants will increase the chance of obtaining ferromagnetism in this type of nanoribbon. This result provides a meaningful theoretical prediction of M-doped ZBNNR as a candidate for future spintronic devices.

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