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## Possible *graphitic*-boron-nitride-based metal-free molecular magnets from first principles study

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### Abstract

We perform first principles calculations based on density functional theory with the generalized gradient approximation (GGA) on the electronic and magnetic properties of carbon dopant in *graphitic* boron nitride (*graphitic*-BN) by the supercell method. It is found that carbon substitution for either boron or nitrogen atoms in *graphitic*-BN favours spin polarization over non-spin-polarization by 0.1 eV. The calculated electronic band structures show a spin-polarized, dispersionless band near the Fermi energy. The spin polarization is found to originate from the carbon dopant and can be attributed to the carbon 2p electron. The lower energies and the resistivity to curvature effect of the spin polarization suggest a possibility of ferromagnetic ordering of the carbon dopants in many realistic BN-based nanostructures which possess a hexagonal network such as nanotubes. Energies required for carbon substitution turn out to be within experimental access. The random substitution and the low doping energy indicate that *graphitic*-BN-based nanostructures can be viewed as candidates for metal-free magnet applications.

(Some figures in this article are in colour only in the electronic version)

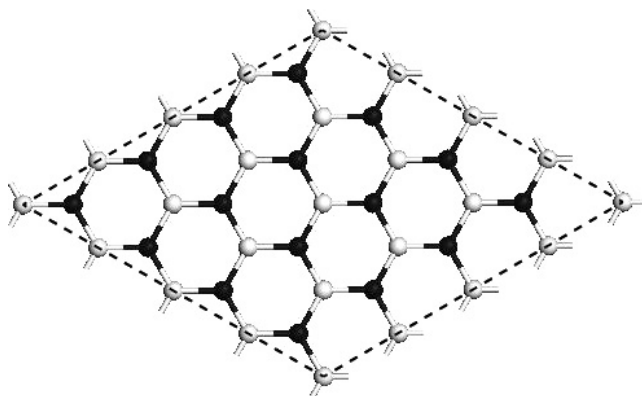
Due to low Curie temperatures, traditional magnetic materials based on magnetic metals have found limited applications. To meet the demands for high temperature applications, there has been a long standing search for novel high temperature magnets [1]. Among the possible materials, metal-free magnets stand out as the most promising candidate. A number of independent experiments have detected and confirmed weak or strong ferromagnetism in some metal-free but mainly all-carbon systems such as graphite, fullerene and carbon nanotubes [2–7]. These novel findings stimulated theoretical investigations on the origin of the unexpected magnetism in these systems and some progress has been made. For example, it was found through the first principles local-spin-density approximation (LSDA) that carbon adatoms and vacancies are responsible for magnetism in graphite [8], and vacancies in carbon nanotubes may be spin polarized, depending on the chirality of the nanotubes and structural configurations [9].

As a more ambitious approach, efforts have been made to design metal-free magnets. An early model based on the nanosized zigzag graphite ribbon was proposed by Fujita *et al* [10], which, however, was unsuccessful. The expected spontaneous spin polarization at the two parallel edges of the ribbon due to the localized edge states was not observed because the magnetic moments cancel out due to the structural symmetry. This problem was solved by Kusakabe and Maruyama [11] who managed to hydrogenate each carbon atom on one side of the ribbon by two hydrogen atoms while hydrogenating each atom on the opposite edge by a single hydrogen atom. In this modified design, a non-zero magnetic moment was observed for the graphite ribbon. Another interesting system proposed recently is the C-BN heterostructured nanotube superlattice [12], in which magnetism originates from the zigzag boundary of the two materials. These models are important because they demonstrated the possibility of designing metal-free magnets. However, no experimental work has been reported to confirm magnetism in these two plausible systems. The reasons can be attributed to the challenges in experimental synthesis as they both require accurate atom-by-atom manipulation. In contrast, doping has become an effective method to induce magnetic properties in non-magnetic materials for its feasibility. A successful case is the ferromagnetism of Mn-doped GaN. Electronic property calculation showed that Mn impurity retains spin-polarization character in GaN while Ga and N atoms remain spin unpolarized [13], yet the magnetic impurities were observed to have a ferromagnetic coupling [14] at room temperature.

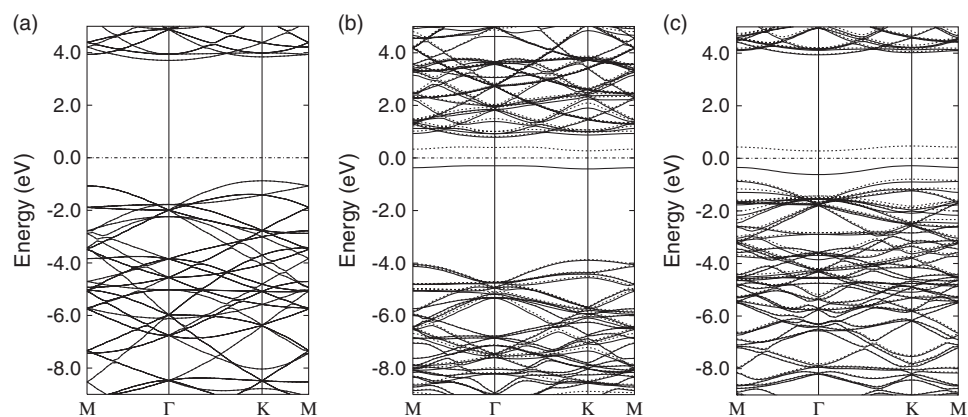
In this paper, we investigate the electronic and magnetic properties of pristine and carbon-doped *graphitic*-BN. This system is interesting because *graphitic*-BN has a melting temperature  $> 1,700$  K, which makes it suitable for high temperature applications, and *graphitic*-BN can form different nanoscale structures such as nanotubes [15], fullerenes [16] and fullerites [17]. The BN-based magnetic nanostructures can be used as molecular magnets. Most importantly, in the hexagonal network, a carbon atom may form three bonds with either boron or nitrogen atoms and thus leave one electron unpaired, making spin polarization possible in such a carbon-containing boron nitride system. The interlayer interaction is only weak van der Waals interaction and can be ignored.

Our calculation is based on the spin-polarized density functional theory (DFT). The generalized gradient approximation (GGA) of Perdew and Wang [18] is used for the exchange–correlation potential. The projector augmented wave (PAW) potentials are used to represent the electron–ion interactions. All 2s and 2p electrons are considered explicitly as valence electrons. A kinetic energy cut-off of 520 eV is used to ensure a convergence better than 1 meV for total energy per atom. A supercell consisting of a *graphitic*-BN sheet made of  $4 \times 4 \times 1$  unit cells is used in the calculation as shown in figure 1. The adjacent layers are separated by a vacuum region 12 Å thick. A gamma-centred  $4 \times 4 \times 1$   $k$ -mesh was used to sample the irreducible Brillouin zone (IBZ). The structure is fully relaxed using the conjugate-gradient algorithm [19]. The structural parameters are adjusted to reduce the external pressure to less than 1 kbar along all three lattice directions. All the calculations are done using the plane wave basis VASP package [20]. The structural and electronic properties of *graphitic*-BN are calculated using similar parameters. The equilibrium lattice constant of 2.52 Å and an indirect bandgap of 4.61 eV for *graphitic*-BN are in good agreement with those obtained by similar calculations [21, 22]. Of course the predicted bandgap is underestimated. Upon each carbon substitution, we calculate the total energies for both the spin-polarized and the non-spin-polarized states. The results suggest that in each case spin polarization is favoured by 0.1 eV over non-polarization. Due to the periodic boundary condition, our calculations are done in a ferromagnetic ordering configuration. This indicates a possibility of ferromagnetic ordering in BN-based nanostructures.

The spin-polarized band structures of pristine and carbon-doped *graphitic*-BN are given in figure 2. In the band structure of pristine *graphitic*-BN (figure 2(a)), we can see that all



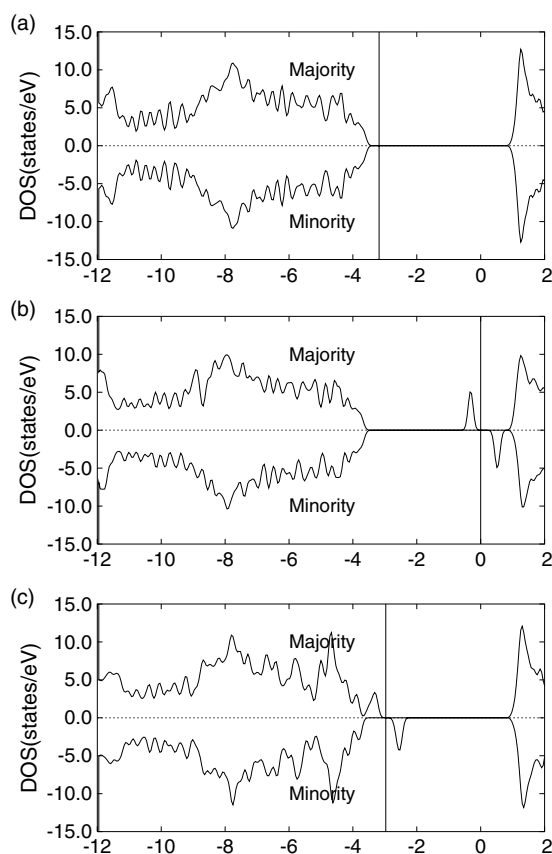
**Figure 1.** The ball-and-stick model of the supercell of pristine BN sheet. Nitrogen atoms are indicated by black balls and boron atoms by white balls. A carbon impurity is introduced by replacing either a nitrogen atom or a boron atom with a carbon atom.



**Figure 2.** The calculated band structures of the pristine *graphitic*-BN (a), with a boron atom (b) and a nitrogen atom (c) substituted by a carbon atom. The solid lines represent the spin-up branches while the dotted lines represent the spin-down branches. The Fermi level is set to zero.

states are in twofold degeneracy, indicating no spin polarization in the pristine *graphitic*-BN. Figure 2(b) shows the band structure of *graphitic*-BN with a boron atom substituted by a carbon atom. The carbon substitution resulted in a lift-up of the Fermi level of the system and emergence of a flat band near the Fermi level, which is due to the fact that the carbon atom acts as a n-type dopant. All bands with energies lower than  $-4.0$  eV are fully occupied and thus do not contribute to spin polarization. However, the flat band near the Fermi level is split into two branches. The spin-up branch is occupied and the spin-down branch is left empty, leading to a spontaneous polarization in the doped system with a net magnetic moment of around  $1.0 \mu_B$ . The same effect is observed when a nitrogen atom is substituted by a carbon atom (figure 2(c)). The only difference is that the Fermi level is pushed down, since in this case carbon acts as a p-type dopant.

In figure 3 we present the majority and minority density of states (DOS) of the three systems. We can see that they share very similar character. For energy lower than  $-3.6$  eV, it is obvious that in each system the majority DOS and the minority DOS counteract quantitatively

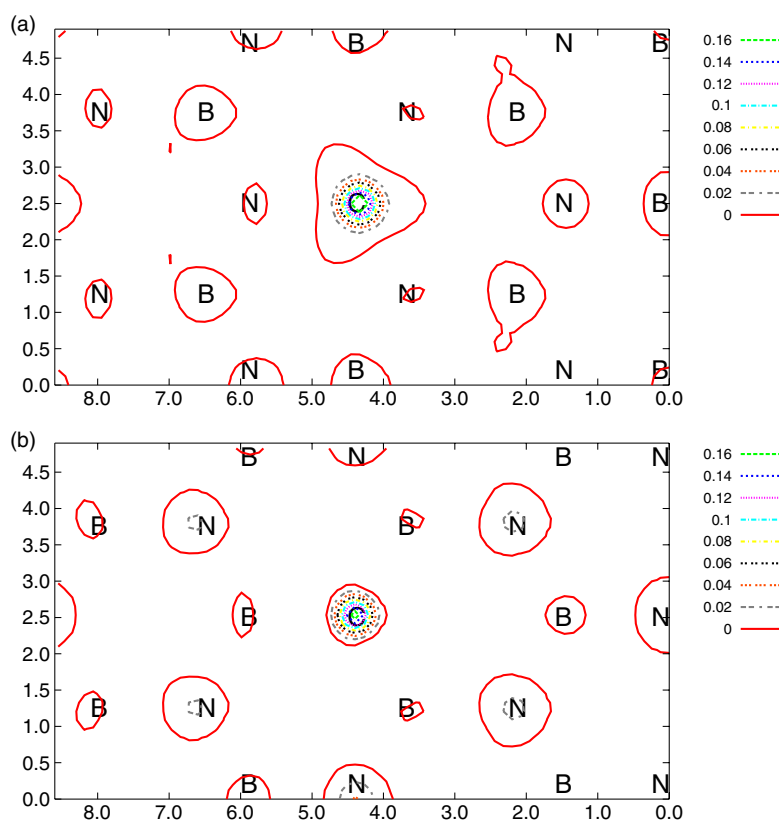


**Figure 3.** The calculated majority and minority DOS for (a) pristine, (b) a boron atom, and (c) a nitrogen atom substituted by a carbon atom systems. The Fermi level is denoted by the vertical lines.

at any energy position, indicating no contribution to spin polarization. Thus the pristine *graphitic*-BN system is non-polarized (figure 3(a)). Yet for the doped *graphitic*-BN system (figures 3(b) and (c)), we can see that the majority DOS exceeds the minority DOS by the occupied peak just below the Fermi level. The minority DOS peak near the Fermi level, however, is unoccupied. Thus both doped systems are spin polarized.

To find out the origin of the magnetism, we show the magnetization density (difference in densities of majority and minority spins) of both systems using a contour map in figure 4. It is clear that the magnetization density originates from the carbon atom. The magnetization density at other atomic sites is negligibly small. This suggests that the spin polarization results from the unpaired electron of the carbon atom. This is reasonable, since in the hexagonal network a single carbon atom can form bonds with its three nearest neighbours, leaving one electron unpaired. It is obvious that in both cases the magnetization results from one of the carbon 2p electrons.

The total charge distribution in the graphite sheet is shown in figure 5 for both carbon substitutions at the boron site and the nitrogen site respectively. In both systems we can see that the carbon dopant forms bonds with its three nearest neighbours. When carbon is surrounded by nitrogen atoms (figure 5(a)), the electron density is higher near the nitrogen atoms. Due to



**Figure 4.** The magnetization density (difference in charge densities of majority and minority spins) distribution of the *graphitic*-BN with a boron atom (a) and a nitrogen atom (b) substituted by a carbon atom. Unit: spins Å<sup>-3</sup>.

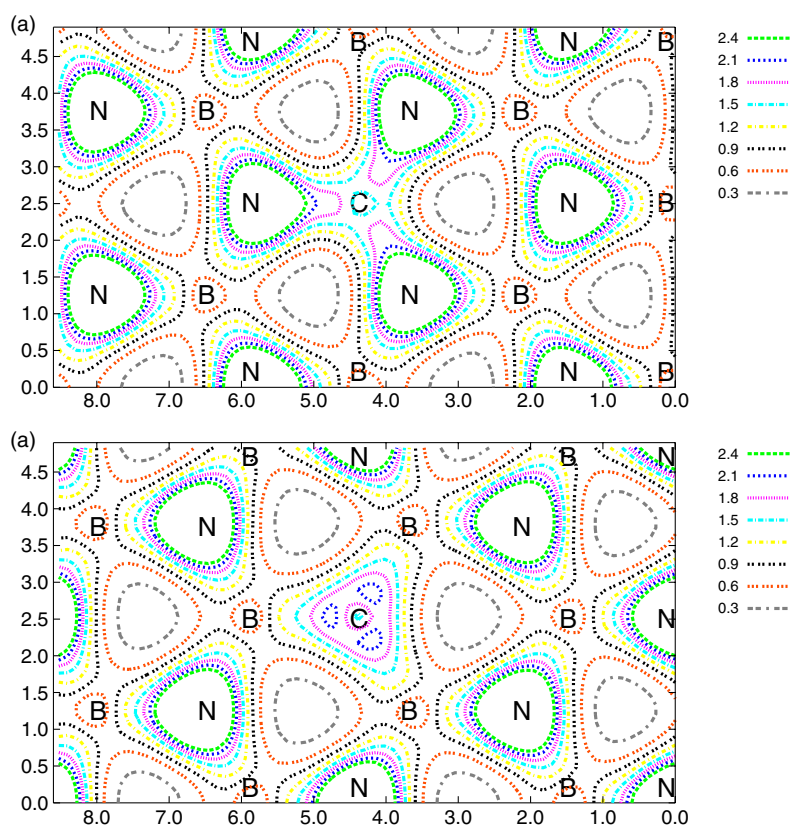
the difference in their electronegativities, the carbon atom loses part of its valence electrons to nitrogen atoms. In the case of carbon substitution for nitrogen (figure 5(b)), the carbon atom attracts electrons from boron atoms. In both case, the nature of the bonds is covalent. Actually, upon geometry optimization, no structural distortion has been induced by carbon doping. This means that the doped system still remains in fine *graphitic* structure.

We also find that the structural perfection and the spontaneous spin polarization survive the curvature effect in the BN nanotubes [23]. Although we cannot give a direct study on the exchange coupling between carbon impurities, experimental observations of ferromagnetism in metal-free systems induced by impurities have been frequently reported [2–7, 24]. Thus various nanostructures originating from *graphitic*-BN promise to act as molecular magnets when doped with carbon. Moreover, we find that other elements like Si, Ge and Sn can also introduce magnetism in the *graphitic*-BN. This means that the magnetic properties of doped BN can be adjusted by different dopants.

To evaluate the feasibility of experimentally synthesizing the carbon doped *graphitic*-BN, we calculated its formation energy  $E_{\text{form}}$ , which is defined as

$$E_{\text{form}} = E_{\text{total}}^{\text{doped}} - E_{\text{total}}^{\text{perfect}} - (E_{\text{A}}^{\text{isolated}} - E_{\text{B}}^{\text{isolated}}), \quad (1)$$

where  $E_{\text{A}}^{\text{isolated}}$  and  $E_{\text{B}}^{\text{isolated}}$  are the energy of the doping atom and the substituted atom at isolated states respectively. The calculated  $E_{\text{form}}$  is 1.95 eV for carbon substitution of boron



**Figure 5.** The charge distribution of the *graphitic*-BN with a boron atom (a) and a nitrogen atom (b) substituted by a carbon atom. Unit: electrons  $\text{\AA}^{-3}$ .

and 3.46 eV for carbon substitution of nitrogen. Compared to the energy required to dope a silicon atom in  $C_{60}$  by substitution, which is 5.77 eV [25], and the fact that  $C_{59}Si_1$  has been experimentally produced [26], the energy required for a carbon atom to substitute a boron or nitrogen atom in *graphitic*-BN is within experimental access.

In summary, the electronic and magnetic properties of carbon dopant in *graphitic*-BN have been calculated by the first principle plane wave basis set calculation. It shows that the carbon dopant in *graphitic*-BN is in a spin-polarized state. More interestingly, the doped BN-based nanostructures may act as molecular magnets. That the magnetism results from random substitution and the energies required to dope a carbon atom are not very high compared to  $C_{59}Si_1$  suggest the experimental feasibility of *graphitic*-BN-based metal-free molecular magnets. Of course, spin polarization does not ensure the occurrence of ferromagnetism, which results from magnetic moment coupling. Further investigations are still needed to get insight into how these dopants interact.

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