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The electronic structure and ferromagnetism of TM (TM = V, Cr, and Mn)-doped BN(5,5) nanotube: A first-principles study

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ABSTRACT

We study the electronic structure and ferromagnetism of V-, Cr-, and Mn-doped single-wall BN(5,5) nanotube by using polarized spin calculations within first principles. The optimized structures show that the transition-metal atoms move outwards and the calculated electronic properties demonstrate that the isolated V-, Cr-, and Mn-doped BN(5,5) nanotubes show half-metallicity. The total ferromagnetic moments are $2\mu_B$, $3.02\mu_B$, and $3.98\mu_B$ for V-, Cr-, and Mn-doped BN(5,5), respectively. The study suggests that such transition-metal (TM)-doped nanotubes may be useful in spintronics and nanomagnets.

1. Introduction

Since half-metallic ferromagnets in Heusler compounds NiMnSb were first predicted in 1983 [1], the field has attracted increasing research interest for decades because of their promising application to spintronics. Many half-metallic ferromagnets have been reported in theoretical and experimental works, such as metallic oxides, binary transition-metal pnictides, or chalcogenide with zinc-blende (ZB) structure [2–9]. Recently, many researchers paid much attention to transition-metal (TM)-doped III–V and II–VI dilute magnetic semiconductors (DMS) [10–14] and TM-doped metal oxides [15–18], which possess potential application in spintronic devices and half-metallic ferromagnetism.

Though many half-metallic ferromagnets have been predicted, it is still very important to find new half-metallic ferromagnets, especially for nanoscale ferromagnetic materials as magnetic nanostructures are a scientifically interesting and technologically important area of research with many current and future applications in permanent magnetism, magnetic recording, and spintronics [19]. It is well known that BN nanotubes (BNNTs) are insulators independent of their chirality and diameter and possess the potential for nanoscale electronic devices owing to their special properties that are useful in many fields. Their structural and electronic properties can be modified by doping. For example, Tang et al. [20] synthesized F-doped BNNTs and they found that fluorination of BNNTs results in highly curled tubular BN sheets and makes insulating BNNTs semiconducting. In the past 2 years, Hao et al. [21] studied open BNNTs and found that the intrinsic magnetism can be induced by their open ends and the resulting magnetic moment is sensitive to chirality. Zhou and Duan [22] studied C-doped open armchair BNNT, and half-metallic ferromagnetism has been studied in TM-encapsulated zig-zag BNNTs [23]. It is also very important to study the system of TM-doped nanotubes in understanding their potential applications, including nanoelectronic devices and low-dimensional systems. Studies about CNTs indicate that interactions between TM atoms and nanotubes lead to half-metallic behaviour, which is of interest for spintronics devices [24,25]. How about the TM-doped BNNTs? In the present work, we intend to investigate the geometrical structure, electronic structure, and ferromagnetism of V-, Cr-, and Mn-doped BNNT(5,5) by first-principles calculations.

2. Computational model and method

In the present work, a $1\times1\times2$ supercell of BNNT(5,5) is constructed (20 B atoms and 20 N atoms). One B atom is substituted by one TM atom to obtain TM-doped BNNT(5,5). In

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order to prevent any tube–tube interaction, we use a lateral separation of 25 Å between tube centers. Structural optimizations are calculated by the DMol^3 package [26–28], which uses the density functional theory (DFT) [29,30] to obtain high accuracy and is very effective for large systems while keeping the computational cost fairly low for an ab initio method. We use a double numerical basis, including d-polarization function (DND). The generalized gradient approximation (GGA) with the PW91 parameterization [31] is adopted to describe the exchange-correlation interaction. Summation over the Brillouin zone is carried out with a *k*-point sampling using a Monkhorst-pack grid [32] with parameters of $1\times1\times5$. In the case of electronic properties, we employ the plane-wave pseudopotential (PWP) approach implemented in CASTEP [33,34], with a plane-wave kinetic cutoff of 350 eV. The Monkhorst-pack grid parameters and the exchange-correlation interaction are set as those in structural optimizations. Vanderbilt-type ultrasoft pseudopotentials [35] are used to describe valence electron interaction with atomic core.

3. Results and discussion

3.1. Geometrical structure

Firstly, pure BNNT(5,5) is optimized and the electronic band structure is calculated considering spin as restricted. B–N bond lengths of pure BNNT(5,5) range from 1.436 to 1.453 Å and the mean length is 1.441 Å. Then the isolated V-, Cr-, and Mn-doped BNNT(5,5) are optimized considering spin as polarized. From the fully relaxed structure (as shown in Fig. 1), we can find that the structure changes a lot and the TM atoms move outwards due to interactions between TM and N atoms. Typically, the hexagonal rings that include the TM atom experience serious distortion with respect to the pure nanotube. The bond angles of the hexagonal rings including V atom change greatly, while those of the pure nanotube are about 120°. The bond lengths of TM–N and B–N are shown in Table 1. B–N bond lengths of TM-doped BNNT(5,5) have a larger range than those of the pure tube (1.436–1.453 Å). TM–N bond length is longer that that of B–N, and the bond that is vertical to the nanotube axis is longer than the other two TM–N bonds. Obviously, the introduced TM atom changes the interaction between B and N atoms and the resulting geometric structure changes significantly.

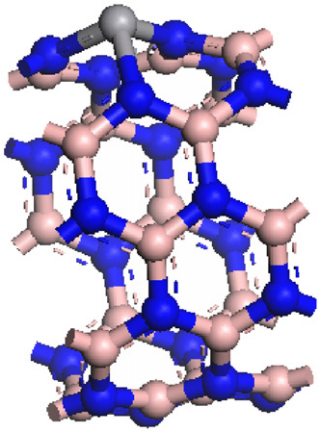

Fig. 1. The optimized structure of TM-doped BNNT(5,5).

Table 1
The bond lengths of TM–N and B–N bonds

		$B_{19}VN_{20}$	$B_{19}CrN_{20}$	$B_{19}MnN_{20}$
B_{TM-N}	$B_\perp$	1.942	1.895	1.888
	$B_\parallel$	1.849	1.820	1.795
B_{B-N}		1.426–1.477	1.425–1.466	1.422–1.468

The $B_\perp$ and $B_\parallel$ indicate that the bond is and is not vertical to the nanotube axis, respectively.

3.2. Electronic structure

Fig. 2(a) shows the partial density of states (DOS) of pure BNNT(5,5) and Fig. 2(b) shows the spin-polarized total DOS of TM-doped BNNT(5,5). For pure BNNT(5,5), the calculated band gap in this work is 4.325 eV, which is slightly larger than the result of Rubio et al. [36], who pointed out that the band gap is underestimated on using the tight binding (TB) method. By doping with a single TM atom, the peaks of total DOS shift to a lower energy level and spin splitting is induced around the Fermi level. For V-, Cr-, and Mn-doped BNNT(5,5), the majority spin electronic band cuts the Fermi level, which indicates metallic behaviour, while the minority spin electronic band is semiconducting because there is an energy gap around the Fermi level. Therefore, V-, Cr-, and Mn-doped BNNT(5,5) are all half-metals, which is similar with TM-doped CNTs [25]. The energy gaps in the band of minority spin electrons are 1.774, 2.397, and 1.774 eV for V-, Cr-, and Mn-doped BNNT(5,5), respectively, and these values are smaller than that of pure BNNT(5,5) (4.325 eV).

In order to further understand the electronic structure, we show the spin-dependent partial DOS of V-, Cr-, and Mn-doped BNNT(5,5) in Fig. 3. Clearly, the spin splitting comes from N2p, B2p, and TM3d states, and the peak that cuts the Fermi level consists mostly of TM3d states and also contains some B2p and N2p states, and the TM3d states hybridize with the B2p and N2p states strongly. From the figures of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO, as shown in Fig. 4), it can be found that the HOMO and the LUMO main originate from the B and N atoms, which are the nearest or next nearest neighbors to the doped TM atom and the other N (or B) atoms are not polarized. That is to say, the polarized electrons are decided by the distance between the N (or B) atom and the TM atom.

In covalent semiconductor crystals, impurities can produce deep-gap states because breaking of covalent bonds leads to a strong perturbation of the valence charge distribution, and the charge transfer must affect the spin configuration. (In this work, bond population is calculated and can be used to assess the covalent or ionic nature of a bond. A high value of the bond population indicates a covalent bond, while a low value indicates an ionic interaction.) The mean population of B–N for pure tube is 0.9, but the population of TM–N is close to 0.25. Obviously, TM–N possesses a stronger ionic interaction. For the pure nanotube, because of the large overlap between the electron clouds of B and N atoms, the spin configuration of the nearest two unpaired electrons is antiparallel, following the Pauli principle. Thus, pure BNNT never possesses net spin. After doping, the charge transfer between atoms or different shells results in the contribution of net spin. Table 2 lists the net spin values and the ferromagnetic moments of every type atom and total spin of the supercells. Every B atom neighboring the TM atom can provide 0.01, 0.02, or $0.04\hbar$ positive spin, while the polarized N atoms can provide some negative or positive spin. For V-, Cr-, and Mn-doped BNNT(5,5), the total spin is 1, 1.51, and $1.99\hbar$, respectively, which is very close