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Computations of the quadrupole coupling constants in aluminum doped boron nitride nanotubes

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ABSTRACT

We performed a computational study to calculate the quadrupole coupling constants (C_Q) in the aluminum doped (Al-doped) boron nitride nanotube (BNNT) based on the density functional theory (DFT). The Al-doped forms of representative (6,0) zigzag and (4,4) armchair models of BNNTs are considered in this study. Comparison with the available data on the pristine BNNTs reveals the influence of Al-doping on the C_Q parameters of ^{11}B and ^{14}N atoms in the Al-doped structures. For most lattice sites, the magnitude of influence on the C_Q parameters of the zigzag model is larger than that of the armchair model. Similar values of the C_Q parameters of ^{27}Al atoms are obtained for the armchair and zigzag BNNTs when the same element is replaced with Al, but the C_Q parameter is larger for Al when it forms an Al–B bond than when it forms an Al–N bond.

1. Introduction

Studies after the discovery of carbon nanotubes (CNTs) [1] demonstrated stable structures of alternative non-carbon based nanotubes, in which boron nitride nanotube (BNNT) is among the most important ones [2–4]. Subsequently, numerous studies have been devoted to characterize the various structural and electronic properties of BNNTs through experimental [5,6] and theoretical [7,8] methods. The stable tubular structure of BNNT was firstly recognized by calculations [9] and was then successfully synthesized [10]. In contrast with the CNTs, which are metallic or semiconductor depending on the tubular diameter and chirality, the BNNTs are always semiconductors independent of tubular diameter and chirality [11]. Furthermore, due to the slight negative charge of N atom and the slight positive charge of B atom, the polarity on the BNNTs is raised in contrast with the CNTs, which are non-polar. Hence, the BNNTs are proposed as potential materials for applications in electronic and mechanical devices.

The effects of impurities and doping on electronic and structural properties of BNNTs have been studied by earlier works [12]. In this work, the influence of aluminum doping (Al-doping) on electronic and structural properties of representative models of zigzag and armchair BNNTs (Figs. 1 and 2) is investigated based on density functional theory (DFT) calculations. Since BNNT contains two different elements, B and N, we study the case where an Al impurity replaces B, as well as the case where an Al impurity replaces N. The valence shells of B and Al atoms are iso-electronics; therefore, the effects of substitution of B atom by Al atom on the properties of BNNTs could be an interesting subject of study [13]. Moreover, since the BNNTs are viewed as semiconductors, they could be considered as n- or p-type doped. Substitution of N atom by Al atom could make the BNNTs a p-type semiconductor. In a recent study, Zhang et al. [14] indicated that Al-doped BN sheets are more proper for adsorption of carbon monoxide atoms than the pristine model. In a very recent study [15], we also investigated the properties of Al-doped BNNTs by calculations of geometrical and nuclear magnetic resonance (NMR) parameters. In another study, we have also shown that the effects of carbon doping on electronic and structural properties of BNNTs could be well investigated by calculations of quadrupole coupling constants (C_Q) at the sites of various ^{11}B and ^{14}N atoms [12]. In some cases, the NMR and C_Q parameters support each other; however, the C_Q parameters are more sensitive to the employed perturbations on the investigated structures. Therefore, due to the higher sensitivity of C_Q parameters to electronic sites of atoms, we have investigated the properties of Al-doped BNNTs by calculations of these parameters within the present work. To achieve this purpose, we have calculated electric field gradient (EFG) tensors in the geometrical optimized structures of the Al-doped BNNTs and converted them to C_Q parameters at the sites of ^{11}B, ^{14}N, and also ^{27}Al atoms. The C_Q parameters can be measured by the experimental technique of nuclear quadrupole resonance (NQR) spectroscopy.

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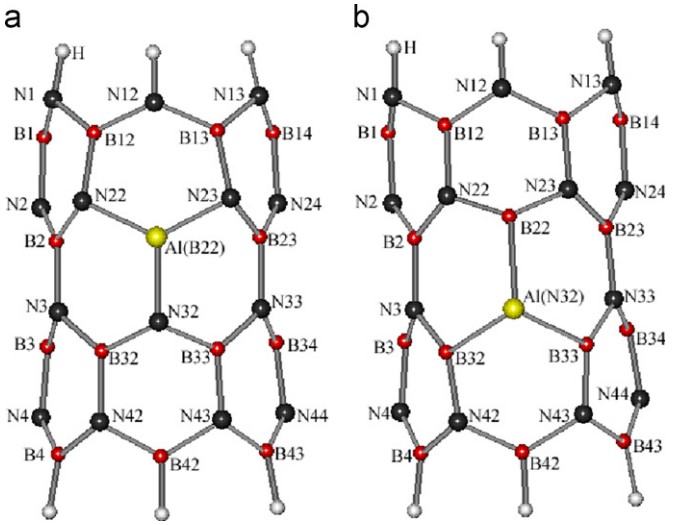

Fig. 1. 2D views of the Al-doped (6,0) zigzag BNNTs.

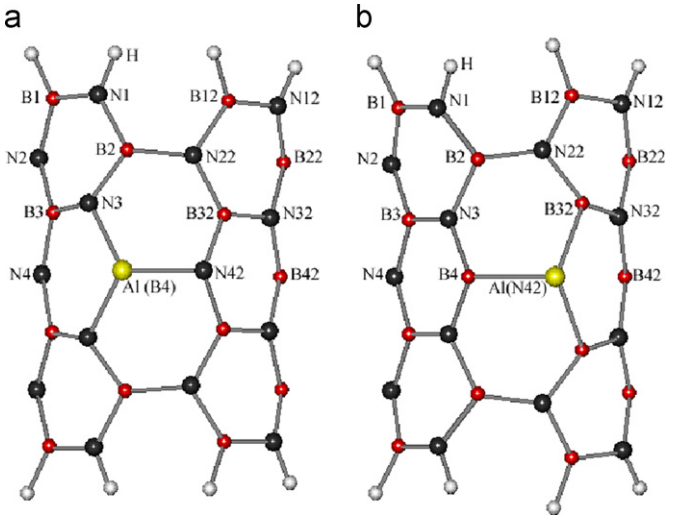

Fig. 2. 2D views of the Al-doped (4,4) armchair BNNTs.

2. Computational aspects

All DFT calculations are performed using the Gaussian 98 package [16]. Two representative models of (6,0) zigzag and (4,4) armchair single-walled BNNTs are considered within this study (Figs. 1 and 2). The ends of nanotubes are saturated by hydrogen atoms. Each model has two forms of Al-doping, doping of B by Al and doping of N by Al, individually, resulting in four forms of Al-doped BNNTs; $B_{23}AlN_{24}H_{12}$ (Fig. 1a), $B_{24}N_{23}AlH_{12}$ (Fig. 1b), $B_{27}AlN_{28}H_{16}$ (Fig. 2a), and $B_{28}N_{27}AlH_{16}$ (Fig. 2b). At first, the structures are allowed to relax by all atomic geometry optimization at the level of BLYP exchange-functional and 6–31 G* standard basis set. The details of optimized structures can be found in an earlier study [15]. Afterwards, the EFG tensors are calculated in the optimized structures at the same level of theory. The validity of the employed level of theory for the electronic structure study of nanotubes has been examined earlier [17].

Quantum chemical calculations yield EFG tensors in the principal axis system (PAS) in the order $|q_{zz}| > |q_{yy}| > |q_{xx}|$; therefore, directly relating to the experiments, the quadrupole coupling constants (C_Q) are evaluated by Eq. (1). C_Q refers to the interaction energy of the nuclear electric quadrupole moment (eQ) and the EFG tensors at the site of quadrupole nucleus, which is directly measured by NQR spectroscopy [18]. The C_Q parameters are calculated for ^{11}B, ^{14}N, and ^{27}Al atoms where the standard Q values reported by Pyykkö [19] are employed in Eq. (1), $Q(^{11}B)=40.59$ mb, $Q(^{14}N)=20.44$ mb, and $Q(^{27}Al)=146.6$ mb. The calculated NQR parameters are exhibited in Tables 2 and 3 for the zigzag and armchair BNNTs, respectively.

$$C_Q(\mathrm{MHz}) = e^2 Q q_{zz} h^{-1} \quad (1)$$

3. Results and discussion

3.1. Zigzag models of Al-doped BNNT

As shown in Fig. 1a, a boron atom (B22) of the zigzag model is doped by an aluminum atom (Al), which results in the $B_{23}AlN_{24}H_{12}$ model. In our recent study [20], it was shown that due to the similarity of electronic properties, the atoms of the pristine BNNTs could be divided into some layers based on the equivalent calculated NQR parameters in each layer. However, doping of the BNNTs by other atoms corrupts this characteristic feature of the pristine BNNTs. Comparing the calculated NQR parameters of ^{11}B atoms in this form of the Al-doped model (Table 2) with those of the pristine model that were obtained previously [20], Table 1 reveals that the EFG tensors at the sites of ^{11}B atoms do not undergo significant changes because they are not directly corelated to the Al-doped atom. The largest magnitudes of changes belong to ^{2}B and ^{23}B in which the values of their C_Q are reduced by a magnitude of 0.22 MHz in the Al-doped model. The changes belonging to the NQR parameters of ^{14}N atoms are more significant. Three N atoms, ^{22}N, ^{23}N, and ^{32}N, are directly connected to the Al atom. Comparison of the results of Table 2 with those of Table 1 indicates that the values of $C_Q(^{14}N)$ for ^{12}N12, ^{22}N, and ^{23}N, which belong to the Al-membered ring, undergo significant changes. The C_Q value of ^{12}N, placed at the end of nanotube, is increased by a magnitude of 0.52 MHz in comparison that of the pristine model (Table 1). However, the C_Q values of ^{22}N and ^{23}N are reduced by a magnitude of 0.22 MHz. C_Q of ^{32}N undergoes the most significant change among other ^{14}N atoms in this form of the Al-doped zigzag nanotube, which is increased by a magnitude of 1.24 MHz from pristine to the Al-doped model. The changes of other $C_Q(^{14}N)$ values are almost negligible.

As shown in Fig. 1b, a nitrogen atom (^{32}N) of the zigzag model of BNNT is doped by an Al atom, resulting in $B_{24}N_{23}AlH_{12}$. In this form, three B atoms, ^{22}B, ^{32}B, and ^{33}B, are directly connected to the Al atom. The most significant change of the value of $C_Q(^{11}B)$ belongs to ^{22}B, which is increased by a magnitude of 1.32 MHz from pristine to the Al-doped model; furthermore, those of ^{32}B and ^{33}B are also increased by a magnitude of 0.45 MHz. The next degree of changes is for ^{42}B in which its C_Q is reduced by a magnitude of 0.18 MHz. Comparing situations ^{42}B and ^{12}N, where both atoms are located at the ends of the nanotube, it is revealed that the C_Q value of N is increased whereas that of B is reduced. It is known that the valence shells of these two atoms are different, where N has an excess of two unpaired electrons whereas B has lack of electrons. These differences may cause different behaviors of these atoms in similar situations. Changes of C_Q values for other ^{11}B atoms are not notable.

3.2. Armchair models of Al-doped BNNT

The calculated NQR parameters for the armchair Al-doped BNNT (Fig. 2) are listed in Table 3. As illustrated in Fig. 2a, a boron atom (^{4}B) is replaced by an aluminum atom (Al). Since there is