Density Functional Calculations of ^{27}Al, ^{11}B, and ^{14}N and NQR Parameters in the (6, 0) BN-AlN Nanotube Junction

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Abstract—Density functional theory (DFT) calculations were performed to calculate aluminum-27, boron-11, and nitrogen-14 quadrupole coupling constant (CQ) in the representative considered model of (6, 0) boron nitride-aluminum nitride nanotube junction (BN-AlNNT) for the first time. To this aim, 1.3 nm length of BN-AlN consisting of 18 Al, 18 B, and 36 N atoms was selected where the end atoms capped by hydrogen atoms. The calculated CQ values for optimized BN-AlNNT system reveal different electrostatic environment in the mentioned system. The calculations were performed using the Gaussian 98 package of program.

Keywords—Nanotube Junction, Density functional, Nuclear Quadrupole Resonance.

I. INTRODUCTION

THE discovery of carbon fullerenes by Kroto, Smalley and Curl [1] in 1985 and later on carbon nanotubes by Iijima[2] served as a turning point in the exploration of this unknown territory. Perhaps equally important was the discovery of inorganic nanotubes and fullerene-like structures[3] in 1992, establishing a new paradigm in the nanomaterials and leading to the birth of a new field of inorganic materials. Carbon nanotubes are metallic, semimetallic, or semiconducting; depending on their chirality [4].This raises the possibility of forming nanoelectronic devices by joining tubes of differing chirality. However, theoretical investigations have revealed that BN, AlN, GaN [5,6] nanotubes are semiconductors with the bandgap larger than 2 eV for most tubes depending on their diameter rather than their chirality, quite different from the cases of single-walled carbon nanotubes [7]. The tubular form of boron nitride was first noted by shore and co-workers [8, 9] who observed a turbostatic tubular structure with a diameter on

the order of 1 micrometer, and 50 to 100 micrometer in length. More recently, BN nanotubes made of BN honeycomb layers have been produced in pure form by several groups using a varity of methods [10-12]. Electron energy loss spectra (EELS) measurements [13] indicate that the B to N ratio in the all these BN nanotubes and, polyhedral nanoparticles is close to 1:1. Experiments indicate that BN materials represent improvements in hydrogen storage capacity com pared with C analogues [14]. The first theoretical study of AlN nanotubes by Zhang and Zhang proposed smooth and uniform diameter AlN nanotubes [15], Infinite armchair and zigzag AlN nanotubes [16], AlN fullerene cages [17] and open ended armchair and zigzag AlN nanotubes [18] have been theoretically studied. In contrast to BN nanotubes and bulk AlN crystal, AlN nanotubes are metallic in character. However, finite AlN nanotubes predicts a large bandgap. Hybrid BN and AlN composite, [19], alloy and nanolaminates have been known for some times as wide gap semiconducting materials. These studies indicate that a combination of BN and AlN nanotubes could be possible to synthesize as (3-5)-(3-5) heterojuncions as well. Actually, coaxial cubic aluminum nitride-boron nitride Composite nanotubes have already been synthesized by a two stage route [20]. Recently, Piquini et al. by theoretical investigation studied the energetic, and structural properties of a hybrid zigzag (10, 0) BN-AlN nanotube [21].

Nuclear quadrupole resonance (NQR) spectroscopy is an insightful technique to study the physical properties of matters in solid –phase [22] The NQR measurable parameters are Quadrupole Coupling Constant (CQ) and asymmetry parameter (ηQ) which both are also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors. Nuclei with spin angular momentum, I, greater than one-half, $I > 1/2$, have the nuclear electric quadrupole moment, eQ, which interacts with the electric field gradient, EFG, tensor originated at the site of quadrupole nuclei. For Al-27, B-11and N-14 spin angular momentums in order of are 2.5, 1.5 and 1.therefore Al-27, B-11 and N-14 are very sensitive to the electronic density at the sites of nuclei and feel changes by any perturbation. Electrostatic properties for

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isolated zigzag (6, 0) AlNNT [23] and isolated zigzag (6, 0) BNNT [24] were reported.

In the present theoretical investigation we studied the electrostatic properties of a zigzag (6,0) BN-AlN Nanotube junction. To this aim, the EFG tensors at the sites of various Al-27, B-11 and N-14 nuclei in zigzag (6,0) single walled BN-AlN Nanotube junction(see Fig. 1) are calculated (Table I and II), to indicate how much the electronic properties of this model respect to isolated zigzag (6, 0) AlNNT and isolated zigzag (6, 0) BNNT has changed. To the best of our knowledge, there are no available NQR data for the considered structures of zigzag (6, 0) BN-AlN Nanotube junction.

II. COMPUTATIONAL METHODS

DFT calculations were performed using Gaussian 98 suite of programs [25]. One model with length tube 1.3 nm and 72 atoms, 36 in the AlN and 36 in the BN nanoptubes, is used to simulate the (6, 0) BN-AlN Nanotube heterojunction. In this model two ends of the being capped by hydrogen atoms for saturate the boundary dangling in order to stabilize the model, and to simulate the effect of a longer tube. system was firstly optimized at the level of the B3LYP method and 6-31G(d) standard basis set, and then the NQR calculations were performed on the optimized model system at the level of the B3LYP method and the 6-31G** standard basis. Relating directly to the experiments, eq. (1) is employed to convert the calculated EFG tensors at the sites of 27Al, 11Band 14N nuclei to the measurable NQR parameter, quadrupole coupling constant (CQ) (Tables I and II). The CQ refers to the interaction energy between the eQ and the EFG tensors at the site of quadrupole nucleus. The standard Q values reported by Pyykkö, are employed in eq. 1; Q (Al-27) =1.466 ×10-29m2, Q (B-11) =0.4059×10-29m2 And Q (N-14) = 0.2044× 10-29 m2 respectively.

$$CQ(MHz) = e2Qqzzh-1 \qquad (1)$$
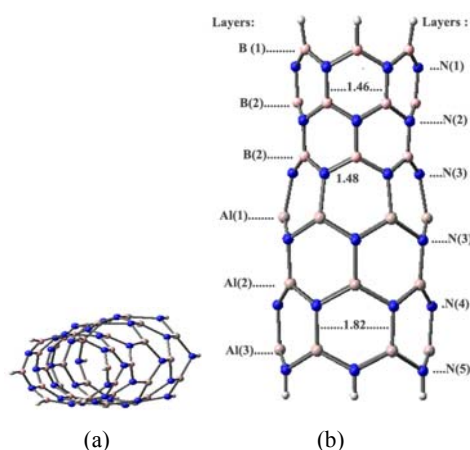

(a)   (b)

Fig. 1 (a) 3D and (b) 2D views of the considered H-capped (6,0) SW-BN/AlN

III. RESULTS AND DISCUSSION

The accuracy of the employed methodology has been checked through calculations (NQR parameters) for isolated (6, 0)AlN and (6, 0)BN nanotubes. A good agreement with previous theoretical results has been obtained .The optimized structure of the studied BN/AlN (6,0) heterojunction with length tube 1.3 nm and 72 atoms (18 Al,18B, and 36 N atoms) is shown in Fig. 1. In this structure two ends of tube being capped by hydrogen atoms. Diameters of the isolated AlN and BN nanotubes, significant structural rearrangements are observed at the nanotube junctions. The zigzag configurations of both discrete tubes give rise to the different junction configurations, depending on the tubes terminating layers. Firstly, this model was optimized and then the CQ calculation was carried out on the optimized structure (Tables I and II). In the following text, the evaluated CQ parameter at the sites of Al-27, B-11and N-14 for the considered mode of (6, 0) BN/AlN is discussed, respectively.

A. The Al-27 and B-11 Quadrupole Coupling Constants

Table I exhibits the calculated CQ parameter at the sites of Al-27 and B-11 nucleus in the model system of (6, 0) BN/AlN. A quick look at the results reveals that in this model 18 Al and 18 B atoms can be divided into six equivalent layers with similar electrostatics parameters in the length tube. Almost no difference is observed in the evaluated CQ parameter at the sites of nuclei in each layer, therefore, the average of values are reported in Table I for Al-27 and B-11 nuclei. Furthermore, the EFG tensors at the sites of the Al-27 and B-11 nuclei in this model don't feel equivalent electrostatic environments. However, as can be seen CQ values for B nucleus decreasing form B-end to middle of the length of the tube. These values for Al nucleus decreasing from middle to other end. There are four kinds of chemical bondings in this model including Al-N, B-N, Al-H and B-H ones in different positions of nanotube. These bonds have different lengths (see Fig.1).The B-H and N-H bondings are located at the ends of nanotube and those B and N nuclei contributing to these bondings in layers 1 and 12 have the largest magnitudes of CQ among other nuclei. Since the larger CQ refers to the higher electron density at the sites of nuclei. B-1 layer is placed at the end of the tube and forms B-end of the BN/AlN nanotube. Therefore, because of the important roles of ending atoms in growing and synthesizing processes of nanotubes, distinguished properties are expected for this layer. Al-4 layer also have important roles in growing and synthesizing processes of nanotubes. In contrast with isolated AlN and BN nanotubes in this hetero junction model CQ values for Al-27 and B-11 are significantly decreased.

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TABLE I
THE B-11 AND AL-27 C_Q PARAMETERS IN THE BN-ALN NANOTUBE JUNCTION[A]

Layers	B-11 C_Q(MHz)	Al-27 C_Q(MHz)
Layer 1	3.53	-
Layer 2	2.76	-
Layer 3	2.67	-
Layer 4	-	22.74
Layer 5	-	22.71
Layer 6	-	22.00

[a]See Fig. 1 for details

TABLE II
THE N-14 C_Q PARAMETER IN THE BN-ALN NANOTUBE JUNCTION[A]

Layers	N-14 C_Q(MHz)
Layer 1	0.96
Layer 2	0.96
Layer 3	1.63
Layer 4	0.28
Layer 5	0.56
Layer 6	2.11

[a]See Fig. 1 for details

B. The N-14 Quadrupole Coupling Constants

Table II exhibits the calculated CQ parameter at the sites of N-14 nuclei in the (6, 0)(BN⊕AlN) nanotube. A quick look at at the results reveals that parallel with Al atoms, the 40 nitrogen atoms of the considered model of the BN/AlN nanotubes can be divided into six equivalent layers with similar electrostatics parameters in the length of the tube. Almost no difference is observed in the evaluated CQ parameter at the sites of N-14nuclei in each layer, therefore, the average of values are reported in Table II. In contrast with isolated AlN and BN nanotubes in this heterojunction model CQ values for N-14 are significantly decreased. In the BN/AlN nanotube, the CQ values for the N-3 and N-6 layers respect with other layers are significantly increased. In contrast with isolated AlN and BN nanotubes in this heterojunction model CQ values for Al-27 and B-11 are significantly decreased.

IV. CONCLUSION

By the calculated EFG tensors at the sites of various Al-27, B-11and N-14 nuclei in the model of (6, 0) zigzag (BN⊕AlN) heterojunction and converting them to measurable CQ parameters some trends are remarkably concluded. First, the calculated EFG tensors reveal that various Al, B and N nuclei in the length of BN/AlN are divided into some layers with equivalent electrostatic properties in each layer. In addition, the magnitude of CQ is the largest for both B and N nuclei located at the ends; however, this magnitude is the variable for those nuclei located at the middle of nanotube. Second, the optimization process yielded average Al-N bond length of 1.82 Ao and for B-N bond length was from 1.46 to 1.48 Ao. Third, in contrast with isolated AlN and BN nanotubes in the (BN⊕AlN) heterojunction model CQ values for Al-27 and B-11 are significantly decreased.

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