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Influences of Si and C- Doping on the Al-27 and N-14 Quardrupole Coupling Constants in AlN Nanotubes: A DFT Study

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***Abstract*—**A computational study at the level density functional theory (DFT) was carried out to investigate the influences of Si and C-doping on the ^{14}N and ^{27}Al quadrupole coupling constant in the (10, 0) zigzag single – walled Aluminum-Nitride nanotube (AlNNT). To this aim, a 1.16nm, length of AlNNT consisting of 40 Al atoms and 40 N atoms were selected where the end atoms are capped by hydrogen atom. To follow the purpose, three Si atoms and three C atoms were doped instead of three Al atoms and three N atoms as a central ring in the surface of the Si and C-doped AlNNT. At first both of systems optimized at the level of BLYP method and 6-31G (d) basis set and after that, the NQR parameters were calculated at the level BLYP method and 6-311+G** basis set in two optimized forms. The calculate C_Q values for both optimized AlNNT systems, raw and Si and C-doped, reveal different electronic environments in the mentioned systems. It was also demonstrated that the end nuclei have the largest C_Q values in both considered AlNNT systems. All the calculations were carried out using Gaussian 98 package of program.

***Keywords*—**DFT, Quadrupole Coupling Constant, Si and C-Doping, Single-Walled AlN nanotubes.

I. Introduction

THE discovery of fullerenes[1], and carbon nanotubes [2], have been followed by a rapid development in the field of nanoscale materials. Among different materials, III-V semiconductors , and the Group–III nitrides, in particular, have attracted much attention [3]- [8], due to their unique properties and promising applications. For example, theoretical investigations have revealed that BN[3], AlN[5], GaN [6], nanotubes are semiconductors with the bond gap 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 [9].

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The electronegativity of N (eN=3.04) is considerably larger than that of Al (eAl=1.61) [10], which leads a charge transfer from Al to N so that the electronic charge density distribution along the AlN bond is strongly asymmetric. Therefore, Al atoms act as cations whereas N atoms act as anions in AlN nanotubes.In the same way, may AlN nanotubes suggest for optoelectronic applications [11].The sum of the valance electrons Al and N are equal to the sum of the valance electrons two carbon atoms. On the other hand, $(AlN)_n$ nanotubes are isovalent with C_{2n} nanotubes.Therefore, CNTs and AlNNTs are similar to each other. However, real AlNNTs have not been synthesized yet but the stability of tubular structure and having unique electronic properties were indicated by theoretical studies [12] , [13].

Nuclear quadrupole resonance, NQR, spectroscopy is well established as a versatile technique to study the details of the electronic and nuclear charge distribution about the nucleus of interest [14]. 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 [15].

For ^{27}Al and ^{14}N in order of spin angular momentum are 5/2and 1[16]. Experimentally, quadrupole coupling constants (C_Q) and asymmetry parameters (η_Q) are measured by NQR.

In this work we study the influences of Si and C- doping on the ^{27}Al and ^{14}N quadrupole coupling constants in the (10,0) zigzag single- walled AlNNT with tube length 1.16nm, the two ends of the tubes being capped by hydrogen atoms (see Fig. 1-4). To have a systematic interpretation of the purpose , two AlNNTs were considered in the NQR calculations, the first model is a raw AlNNT and the second model is a Si and C-doped AlNNT. In the Si and C-doped AlNNT the Si and C atoms have alternating position and there is a charge transfer from Si to C. Therefore, this form is an energetically stable form [17].All the structures were first optimized, and then the NQR calculations were performed. To the best of our knowledge, there are no available NQR data for the considered structures of AlNNTs in the literature. The calculated C_Q and η_Q parameters are presented in Tables I and II.

II. Computational Aspects

DFT calculations were performed using Gaussian 98 suite of programs [18].Two models of (10, 0) zigzag single- walled AlNNTs with a length tube 1.16nm, were considered. In two models, the two ends of the both tubes being capped by hydrogen atoms for saturate the boundary dangling in order to stabilize the models, and to simulate the effect of a longer tube. Model one considers a raw AlNNT and model two a Si and C- doped AlNNT (see Figs. 1-4). Both systems were firstly optimized at the level of the BLYP method and 6-31G(d) standard basis set [19] , and then the NQR calculations were performed on the optimized model systems at the level of the BLYP method and 6-311+G** and 6-31G (d) standard basis sets.

Experimentally, quadrupole coupling constants (C_Q) and asymmetry parameters (η_Q) are measured by NQR. C_Q refers to the interaction energy of the nuclear electric quadrupole moment, (eQ), and the EFG tensors at the site of quadrupole nucleus.

Quantum chemical calculations yield principal components of the EFG tensor, q_{ii}, in atomic unit

1 au = 9.717365×10^{21} V m^{-2}, with $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$.

Equations (1) and (2) are used to directly relate the calculation EFG tensors with the measurable parameters C_Q and η_Q. The standard Q values reported by pyykkö [20]. Are employed in (1), Q (^{14}N) = $0.2044\times 10^{-29} m^2$ and

Q (^{27}Al) =$1.466 \times 10^{-29} m^2$.

Tables I and II exhibit the calculation NQR parameters for ^{14}N and ^{27}Al, respectively.

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

$$\eta_Q = |\,(q_{xx} - q_{yy}) / q_{zz}\,| \quad (2)$$

$$(|q_{zz}| > |q_{yy}| > |q_{xx}|;\ 0 < \eta_Q < 1)$$

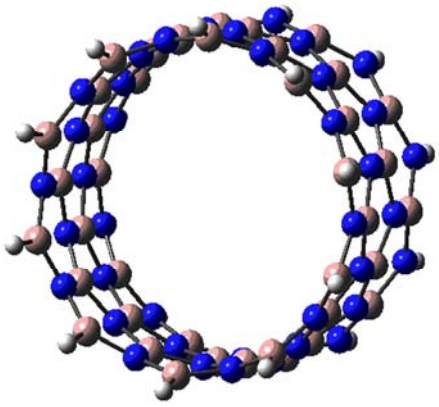

Fig. 1 The (10, 0) zigzag single- walled AlNNT in 3D view

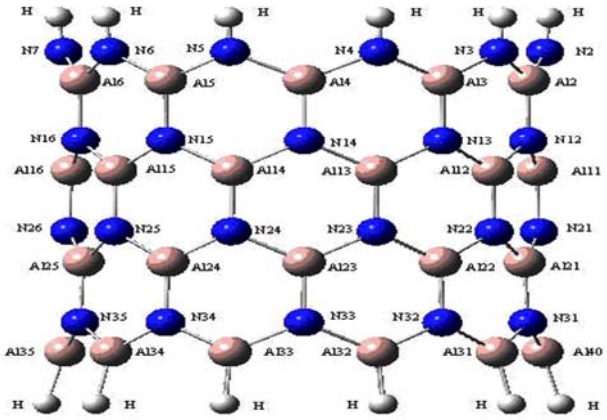

Fig. 2 The raw AlNNT in 2D view, the front side

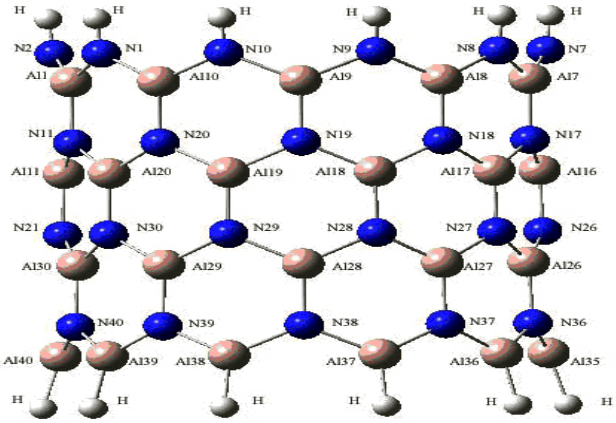

Fig. 3 The raw AlNNT in 2D view, the back side

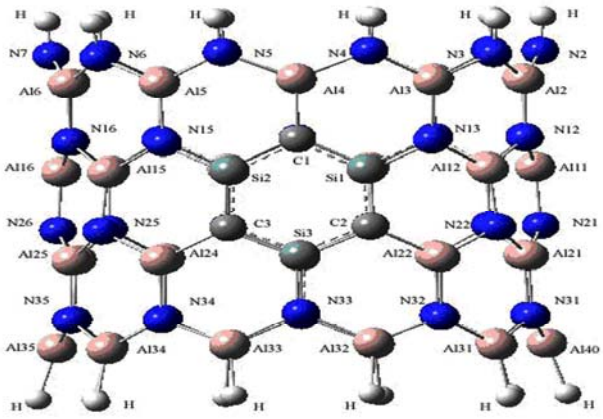

Fig. 4 The Si and C-doped AlNNT in 2D view; the front side. The back side is the same as in 3

III. Results and Discussion

A DFT study was carried out to investigate the influences of Si and C-doping on the quadrupole coupling constant of the ^{27}Al and ^{14}N nuclei in the H-capped (10, 0) zigzag single – walled AlN nanotube (AlNNT). To this aim, a 1.16nm, length of AlNNT consists of 40 Al atoms and 40 N atoms were selected where the end atoms are capped by hydrogen atom. To follow the purpose, three Si atoms and three C atoms were doped instead of three Al atoms and three N atoms as a central ring in the surface of the Si and C- doped AlNNT. Firstly, the two model systems were optimized, and then the NQR (C_Q) and (η_Q) calculations were carried out on the optimized structures. With the use of the 6-31G(d) and 6-311+G** basis sets we found out that in the raw model and Si and C-doped model the difference between NQR parameters almost is equal. Therefore, we are using only the results taken from the 6-311+G** basis set for shortening the text (see Tables I and II). The following text will discuss the calculated results of C_Q (^{27}Al) and C_Q (^{14}N) in the two model systems separately.

A. The ^{27}Al Quadrupole Coupling Constants

Table I exhibits the calculated NQR parameters at the sites of ^{27}Al nuclei in both model systems of raw and Si and C-doped AlNNTs. A quick look at the results reveals that in the row system 40 Al atoms of the considered model can be divided into four equivalent layers with similar electrostatics properties in the length tube, Al1-10, Al11-20, Al21-30 and Al31-40. Furthermore, the EFG tensors at the sites of the ^{27}Al nuclei in the raw system do not feel equivalent electrostatic environments as can be seen by their decreasing of C_Q values from the Al-end to N-end of the nanotube. This is because electronegativity of N (eN=3.04) is considerably larger than that of Al (eAl=1.61). This yields an asymmetric charge distribution along the nanotube. Therefore, the Al atoms on each end have the largest C_Q values, which decrease along the tube to the opposite end. Furthermore, table I exhibits that Si and C-doped in the tube changes the electrostatic environment of the AlNNT, as can easily be seen by the C_Q (^{27}Al) and η_Q (^{27}Al) of various Al nuclei in the two model systems. There are 40 Al atoms in the raw AlNNT system, and in the Si and C-doped system, three Al atoms are replaced by Si atoms. In the first layer, from Al-1 to Al-10, which have similar electrostatic environments in the raw system all mentioned nuclei feel a similar electrostatic environment (see Table I).However, in the Si and C-doped system it is noteworthy that the couples of Al-2/Al-6, Al-3/Al-5,Al-1/Al-7 and Al-8/Al-10 in symmetric positions have similar electrostatic environments, but different from the parameters of nuclei in other positions. On the other hand, the ^{27}Al EFG tensors at their sites feel similar electrostatic environments. However, the calculated C_Q parameters of Al-1, Al-7, Al-8, Al-9 and Al-10 are same in the two systems, for Al-4 is directly chemically bound to C-1, and it's C_Q (^{27}Al) is increased by 0.5MHz, rather than the raw system, the average Al-N bond length is about (1.83 ^{0}A), and Al-C bond length (1.90 ^{0}A), and for Si-C is (1.78 ^{0}A). whereas Al-3and Al-5, which are the neighborhood of N-13 and N-15, which are directly chemically bound to Si-1and Si-2, are changed, and their C_Q (^{27}Al) are reduced by 0.5MHz. In the second layer, from Al-11 to Al-20, which have similar electrostatic environments, in the raw system. However, Al-13and Al-14 are replaced in order of by Si-1and Si-2, respectively, in the Si and C-doped system. The C_Q (^{27}Al) values of this series do not show any significant changes. In the third layer, from Al-21 to Al-30, those have similar electrostatic environments in the raw system. In the Si and C-doped system, Al-23 is replaced by Si-3 then Al-22 and Al-24 which are placed in the two neighbour sides of Si-3 and are directly bound to C-2 and C-3 , respectively, have similar NQR parameters but different from those in the raw system ,their C_Q (^{27}Al) are increased by 0.7MHz. However, the C_Q (^{27}Al) values of Al-21, Al-25, Al-26, Al-27, Al-28, Al-29 and Al-30 remained almost unchanged in the two model system. In the forth layer, from Al-31 to Al-40, are located in the Al-end of the nanotube, which have similar electrostatic environments in the raw system. In the Si and C-doped system, Al-32and Al-33, which are in the neighbourhood of N-33, which is directly chemically bound to Si-3, are changed. And their C_Q (^{27}Al) is reduced by 0.2MHz, rather than the raw system. The couples of Al-31/Al-34, Al-35/Al-40, Al-36/Al-39 and Al-37/Al-38 in symmetric positions have similar electrostatic environments. Al-H bond length is (1.59 ^{0}A). The change of η_Q (^{27}Al) almost agrees with the changes of C_Q (^{27}Al) for various Al nuclei in the considered AlNNT model system.

B. The ^{14}N Quadrupole Coupling Constants

Table II exhibits the calculated NQR parameters at the sites of ^{14}N nuclei in both model systems of raw and Si and C-doped AlNNTs. A quick look at the results reveals that parallel with Al atoms, the 40 N atoms of the considered model of AlNNT can be divided into four equivalent layers with similar electrostatic properties in the length tube, N1-10, N11-20, N21-30 and N31-40. Furthermore, C_Q (^{14}N) changes amount are lower than C_Q (^{27}Al) and the N atoms on each end have the largest C_Q values, of the AlNNT, which means that the nuclei at the ends of the AlNNT are more active than those located in the other positions of the nanotube. There are four layers of N nuclei in the raw AlNNT, whereas this similarity is perturbed by Si and C-doping. In the first layer, from N-1 to N-10, are located in the N-end of the nanotube. Which have similar electrostatic environments, in the raw system, however, N-4 and N-5 which are in the neighbourhood of Al-4, which is directly chemically bound to C-1 in the Si and C-doped system. The C_Q (^{14}N) values of this series do not show any significant changes. Al-N bond lengths for this layer are same, and it is (1.82 ^{0}A), and for N-H bond length is (1.04 ^{0}A). In the second layer, from N-11 to N-20, Where N-14 is replaced by C-1 in the Si and C-doped system. Although the mentioned nuclei have similar electrostatic environments in the raw system, they lose this similarity in the Si and C-doped

system and are divided into three sets of nucleus. The first set is consists N-13 and N-15 that they in order of make chemically bound to Si-1 and Si-2, respectively, Si-N bond length is (1.74 ^{0}A), and there is a charge transfer from Si to N, and bond length for Al3-N13, Al12-N13, Al5-N15 and Al15-N15 is (1.84 ^{0}A), in this section, and as a result their NQR parameters are significantly influenced by these bonds. C_Q (^{14}N) of N-13 and N-15 is increased by 0.65MHz. The second set is consists N-12 and N-16, C_Q (^{14}N) values for this nucleus is increased.

TABLE I
THE ^{27}AL NQR PARAMETERS A

Nucleus	C_Q (MHz).	η_Q
Al-1	30.7 , 30.7	0.03 , 0.02
Al-2	30.7 , 30.8	0.03 , 0.06
Al-3	30.7 , 30.2	0.03 , 0.13
Al-4	30.7 , 31.2	0.03 , 0.07
Al-5	30.7 , 30.2	0.03 , 0.13
Al-6	30.7 , 30.8	0.03 , 0.06
Al-7	30.7 , 30.7	0.03 , 0.02
Al-8	30.7 , 30.7	0.03 , 0.03
Al-9	30.7 , 30.7	0.03 ,0.03
Al-10	30.7, 30.7	0.03 , 0.03
Al11	31.7 , 31.7	0.01 , 0.03
Al-12	31.7 , 31.7	0.01 , 0.04
Al-13	31.7 , --	0.01 , --
Al-14	31.7 , --	0.01 , --
Al-15	31.7 , 31.7	0.01 , 0.04
Al-16	31.7 , 31.7	0.01 , 0.03
Al-17	31.7 , 31.7	0.01 , 0.01
Al-18	31.7, 31,6	0.01 , 0.01
Al-19	31.7 , 31,6	0.01 , 0.01
Al-20	31.7 , 31.7	0.01 , 0.01
Al-21	31.8 , 31.7	0.001 , 0.01
Al-22	31.8 , 32.5	0.001, 0.16
Al-23	31.8 , --	0.002 , --
Al-24	31.8 , 32.5	0.001 , 0.16
Al-25	31.8 , 31.7	0.001 , 0.01
Al-26	31.8 , 31.8	0.001 , 0.02
Al-27	31.8 , 31.8	0.001, 0.03
Al-28	31.8 , 31.8	0.002 , 0.01
Al-29	31.8 , 31.8	0.001, 0.003
Al-30	31.8 , 31.8	0.001 , 0.002
Al-31	36.6 , 36.7	0.11 , 0.11
Al-32	36.6 , 36.4	0.11 , 0.20
Al-33	36.6 , 36.4	0.11, 0.20
Al-34	36.6 , 36.7	0.11 ,0.11
Al-35	36.6 , 36.6	0.11 , 0.11
Al-36	36.6 , 36.6	0.11 , 0.11
Al-37	36.6 , 36.6	0.11 , 0.11
Al-38	36.6 , 36.6	0.11 , 0.11
Al-39	36.6 , 36.6	0.11 , 0.11
Al-40	36.6 , 36.6	0.11 , 0.11

[a] In each raw ,the first number is for raw AlNNT,the second one is for Si and C-doped AlNNT

TABLE II
THE ^{14}N NQR PARAMETERS

Nucleus	C_Q (MHz).	η_Q
N-1	2.45 , 2.44	0.66 , 0.65
N-2	2.45 , 2.44	0.66 , 0.67
N-3	2.45 , 2.46	0.66 , 0.65
N-4	2.45 , 2.43	0.66 , 0.59
N-5	2.45 , 2.43	0.66 , 0.59
N-6	2.45 , 2.46	0.66 , 0.65
N-7	2.45 , 2.44	0.66 , 0.67
N-8	2.45 , 2.44	0.66 , 0.65
N-9	2.45 , 2.44	0.66 , 0.64
N-10	2.45 , 2.44	0.66 , 0.64
N-11	0.36 , 0.37	0.22 , 0.23
N-12	0.35 , 0.47	0.22 , 0.05
N-13	0.35 , 1.00	0.20 ,0.94
N-14	0.35 , ---	0.20 , ---
N-15	0.35 , 1.00	0.21 , 0.94
N-16	0.35 , 0.47	0.21 , 0.05
N-17	0.35 , 0.37	0.22 , 0.23
N-`18	0.35 , 0.35	0.20 , 0.21
N-19	0.35 , 0.34	0.20 , 0.22
N-20	0.35 , 0.35	0.21 , 0.21
N-21	0.30 , 0.29	0.74 , 0.65
N-22	0.30 , 0.34	0.75 , 0.37
N-23	0.30 , ----	0.74 , ----
N-24	0.30 , ----	0.77 , ----
N-25	0.30 , 0.34	0.74 , 0.37
N-26	0.30 , 0.29	0.74 , 0.65
N-27	0.30 , 0.30	0.75 , 0.77
N-28	0.30 , 0.29	0.74 , 0.83
N-29	0.30 , 0.29	0.76 , 0.83
N-30	0.30 , 0.3	0.74 , 0.78
N-31	0.51 , 0.58	0.99 , 0.98
N-32	0.51 , 0.67	0.99 , 1.00
N-33	0.51 , 0.86	0.99 , 0.1
N-34	0.51 , 0.67	0.99 , 0.6
N-35	0.51 , 0.58	0.98 , 0.98
N-36	0.51 , 0.52	0.99 , 0.95
N-37	0.51 , 0.49	0.99 , 0.99
N-38	0.51 , 0.49	0.99 , 0.97
N-39	0.51 , 0.49	0.99 , 0.99
N-40	0.51 , 0.53	0.98 , 0.95

[a] In each raw ,the first number is for raw AlNNT,the second one is for Si and C-doped AlNNT.

By 0.12MHz. The third set is consists N-11, N-17, N-18, N-19 and N-20, C_Q (^{14}N) values of this series are almost constant. In the third layer, from N-21 to N-30, where N-23 and N-24 are replaced in order of by C-2 and C-3, in the Si

and C-doped system. The couples N-21/N-26, N-22/N-25, N-27/N-30, and N-28/N-29 which are in symmetric positions in the Si and C-doped system, C_Q (^{14}N) values of this series do not show any significant changes. In the forth layer, from N-31 to N-40, where N-33 is chemically bound to Si-3 in the Si and C-doped system and its C_Q (^{14}N) increases by 0.35MHz. The C_Q (^{14}N) values for the couples N-32/N-34 and N-31/N-35 which are in symmetric positions also in order of increased by 0.16MHz, and 0.07MHz, but for remain other nucleus almost unchanged in the two model systems. In agreement with the changes of C_Q (^{14}N), the values of η_Q (^{14}N) are also changed in the considered systems

IV. Concluding Remarks

We performed a DFT study to evaluate NQR parameters (C_Q and η_Q) to investigate the influences of Si and C–doping, by calculations of EFG tensors at the sites of ^{27}Al and ^{14}N nuclei in the two (10,0) AlNNT model systems including raw and Si and C-doped systems. The calculated parameters for the two systems show significant differences for some nuclei, whereas for some other nuclei no difference is observed. From the calculated results, some trends are concluded. First, in the raw system of AlNNT, the electrostatic environment at the sites of various nuclei can be divided into four equivalent layers. Second, in the raw system of AlNNT, the NQR parameters at the sites of Al and N nuclei in ending layers are significantly different from those of other layers. For this system, the values of C_Q (^{27}Al) are increased from the N-end to the Al-end nuclei, however, all of four N layers have almost the value differences of C_Q (^{14}N), but in order of aren't increased from Al-end to N-end. Third, the C_Q (^{27}Al) values and C_Q (^{14}N) values of those Al and N nuclei which are directly chemically bound to the C and Si atom have increased in the Si and C-doped system. Forth, the influences of Si and C-doping on the C_Q parameters for those nuclei in the neighbourhood are significant, and with increasing the distance of doping decrease, and finally for the far ones they are inert.

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