Fe-DOPED HEXAGONAL BORON NITRID NANOTUBES: A FIRST-PRINCIPAL STUDY OF ELECTRONIC AND VIBRATIONAL PROPERTIES

Bouamra FAIZA

LPCMIA, Physics Department, Saad Dahlab University, Blida1, Route de Soumaa, BP 270, Blida 09000, Algeria, bouamra_faiza@univ-blida.dz

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Abstract

This theoretical study continues our previous work on the properties of Fe-doped hexagonal boron nitride (h-BN) [1]. In the first part of our research, the structural and thermoelectric properties were examined following Fe atoms incorporation. The present investigation aims to confirm the stability of the newly obtained materials and to explore their potential as a dopant for oxide nanomaterials sensitive layers in order to minimize their operating temperature in the field of harmful gas detection, as well as their suitability for biomedical applications through the optimization of vibrational (IR and Raman) properties. The calculations were performed at the level of Self-Consistent Field Linear Combination Atomic Orbitals (SCF-LCAO-DFT) approach with the Becke, 3-parameters, Lee-Yang-Parr (B3LYP) functional, implemented in the CRYSTAL17 code. The h-BN nanotubes were generated from a two-dimensional hexagonal BN sheet, The resulting nanotubes exhibit semiconducting behavior, and the analysis of the IR and Raman spectra revealed the active vibrational modes of (9,0) boron nitride nanotubes. These results are supported by the vibrational mode analysis of both the primitive and (2×1×1) supercells.

Keywords: BNNT, DFT, Raman, IR, CRYSTAL CODE

1. INTRODUCTION

Hexagonal boron nitride (h-BN) is a layered material structurally analogous to graphite [2], consisting of alternating boron and nitrogen atoms arranged in a two-dimensional hexagonal lattice. Because of its strong in-plane covalent bonds and weak interlayer van der Waals interactions [3], h-BN exhibits exceptional thermal stability, chemical inertness, high electrical resistivity, and excellent mechanical strength [4,5]. These properties make it an attractive material for applications in high-temperature electronics nanodevices, Lithium batteries and Hydrogen storage, sensors, and protective coatings [6,7].

When rolled into cylindrical forms, h-BN layers give rise to boron nitride nanotubes (BNNTs), which combine the robustness of carbon nanotubes with wide-bandgap semiconducting behavior. Their structural perfection, high thermal conductivity, and resistance to oxidation make BNNTs a suitable platform for exploring doping effects and defect engineering. In particular, transition-metal doping has been shown to significantly alter the electronic and vibrational characteristics of BNNTs, enabling property tuning for catalytic, optical, and sensing applications [7]. Among the various transition metals, iron (Fe) stands out due to its variable oxidation states and strong interaction with nitrogen atoms, which can profoundly influence the charge distribution and local vibrational dynamics of h-BN systems [8,9]. Substitutional doping of Fe into the boron sites is therefore of considerable interest, as it can induce modifications in the phonon spectrum and electronic density of states, offering a means to tailor the spectroscopic responses of BNNTs [9].

From a theoretical standpoint, the investigation of doped BNNTs provides essential insight into the relationship between structural distortion, electronic redistribution, and vibrational activity. Density Functional Theory (DFT), particularly in its hybrid functional form B3LYP, offers a reliable framework for predicting structural, electronic, and spectroscopic properties with a balanced treatment of exchange–correlation effects. At the level of DFT-B3LYP calculations we can calculate IR and Raman vibrational modes, it becomes possible to identify characteristic phonon modes associated with dopant incorporation and to assess how Fe atoms modify the dynamic behavior of the BNNT lattice.

The analysis of the Raman spectra of (0, n)-BNNTs (n = 6–19) reveals three characteristic frequency regions: Low-frequency region (< 500 cm^{-1}): two main Raman bands are observed, corresponding to the radial breathing mode (RBM) and the elliptical deformation mode (EDM). The RBM is particularly important for identifying specific nanotubes and their chirality, as its frequency inversely depends on the tube diameter, Intermediate-frequency region: several peaks appear that are almost independent of the nanotube size and High-frequency region: a few Raman-active bands with E_{1g}, E_{2g} (≈ 1356 cm^{-1}) and A_1g (≈ 1365 cm^{-1}) symmetries are found close in frequency. These results are consistent with previous studies and indicate that the A_{1g} and E_{2g} bands are significantly enhanced under resonant excitation.

This paper discusses and provides a better understanding of the deformation caused by the presence of Fe ions in the matrix of h-BN nanotubes and the effect on the spectroscopic Raman and IR properties, based on the theoretical (ab-initio) calculations of the total energy of the optimized structures.

In the next section, a brief representation of the first-principle SCF-LCAO-DFT-B3LYP method implemented in CRYSTAL17 software and details about the basis set used for each element of the unit cell and the other conditions of calculations as Monkhorst k points in the reciprocal space, accuracy of integrations. Furthermore, we represent the way of obtaining SWBN and the effect of the substitution of Fe ions with B on the atomic structure will be discussed. in the Sec. III, we analyze the structural, electronic, and vibrational properties of (9,0) and (10,0) BNNTs in their pristine and Fe-doped configurations. The results provide the IR and Raman spectra of (9,0) BNNT, offering new insights into the phonon-mode evolution and the potential functionalization of BN nanotubes.

2. COMPUTATIONAL DETAILS

As mentioned in the previous section, calculations were carried out within the framework of Density Functional Theory (DFT) using the CRYSTAL17 program package [11]. The B3LYP hybrid exchange–correlation functional [9,10], which combines Becke's three-parameters exchange functional with the Lee–Yang–Parr correlation functional, was employed to provide a good, optimized structures and accurate description of the electronic structure and vibrational properties of the studied systems. This hybrid functional has been demonstrated to yield reliable results for boron nitride–based nanostructures, particularly in predicting their spectroscopic behavior.

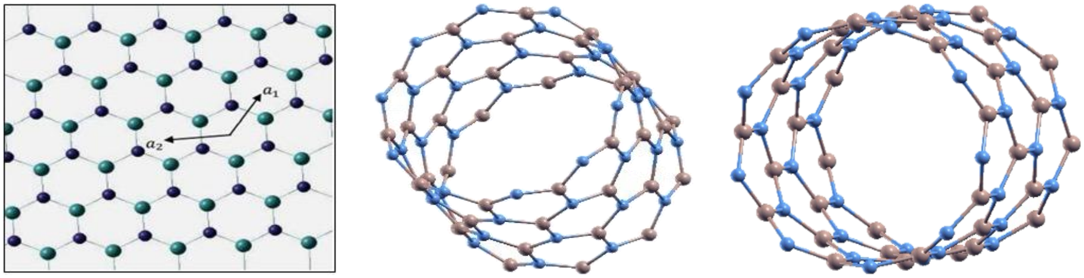


Figure1 (a) BN hexagonal (γ=120°) sheet, structures of non-doped: (b) BNNT (2x1x1)p (10,0) and (c) BNNT (2x1x1)p (9,0). Blue and purple circles represent, respectively, B and N atoms.

The hexagonal boron nitride nanotubes (h-BNNTs) were generated by rolling a two-dimensional BN hexagonal sheet, using SLAB model, along the (9,0) and (10,0) chiral vectors see **Figure1**.

To simulate Fe doping, boron atoms were substituted by one and two Fe atoms, respectively, per supercell, resulting in 1Fe and 2Fe **Figure 2**.

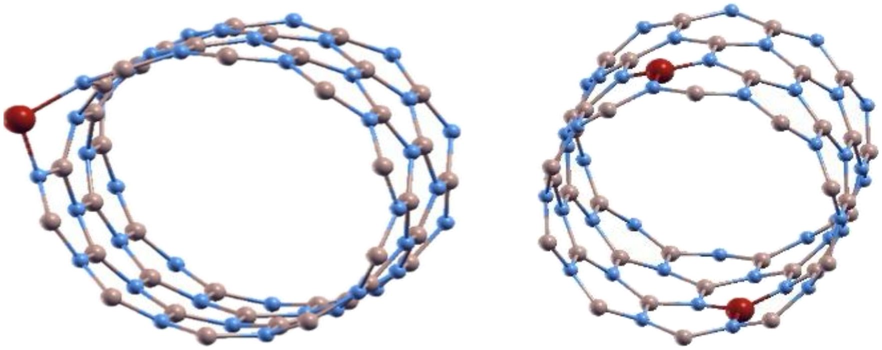


Figure 2 optimized structures of BNNT/1Fe and BNNT/2Fe (10,0).

All structures were optimized using a (2×1×1)*p* supercell, ensuring negligible interaction between periodic images. The self-consistent field (SCF) convergence threshold was set to 10^{-8} a.u. on energy, and the total energy gradient was minimized below 10^{-4} a.u. during structural relaxation.

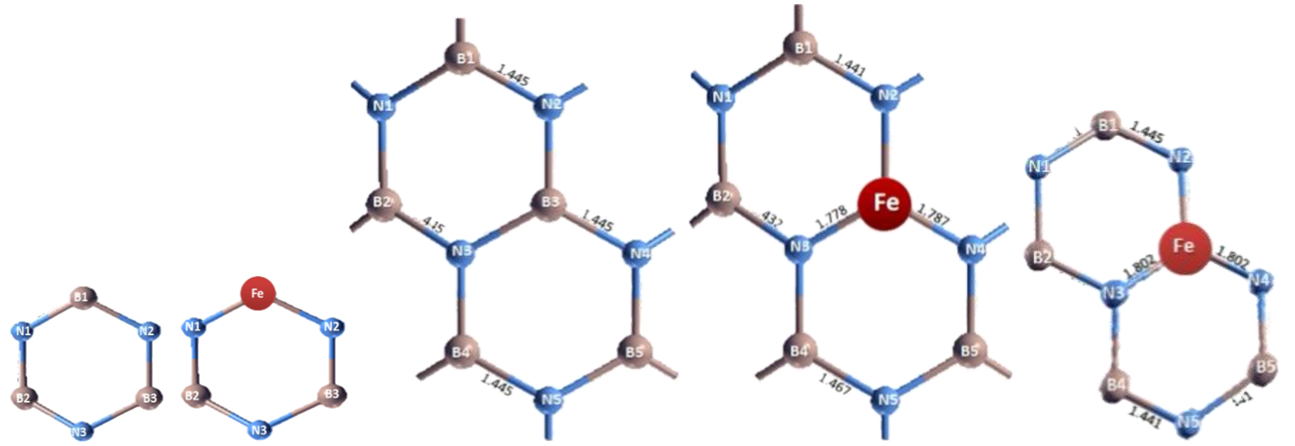
The reciprocal space was sampled using an appropriate Monkhorst–Pack k-point mesh to guarantee convergence of total energy and electronic density. The atomic basis sets for B, N, and Fe atoms were taken from the CRYSTAL17 library**,** with polarization functions included to properly describe the Fe–N and Fe–B bonding interactions. The optimized geometries were then used for vibrational frequency calculations to obtain **infrared (IR)** and **Raman spectra**, which were analyzed to identify active phonon modes and to investigate the influence of Fe doping on the vibrational characteristics of h-BN nanotubes.

3. RESULTS AND DISCUSSION

3.1. Structural optimization and stability

The optimized geometries of pristine and Fe/BN nanotubes were obtained after full relaxation of atomic positions and lattice parameters at the B3LYP level. In the undoped (9,0) and (10,0) BNNTs, the B–N bond lengths were found to be approximately 1.45 Å, consistent with previously reported values for hexagonal boron nitride. After Fe substitution at the boron site, a local distortion of the lattice occurred due to the larger atomic radius and different electronegativity of the Fe atom compared to boron.

For the 1Fe configuration, the Fe–N bond length increased to around 1.86 Å, while the neighboring B–N bonds were slightly elongated, indicating a moderate structural relaxation in the vicinity of the dopant site. In the 2Fe configuration, a stronger distortion was observed because of the magnetic coupling and charge redistribution between the two Fe atoms, see **Figure 3**. Despite these local deformations, the optimized structures remained dynamically stable, confirming that Fe incorporation into the BN lattice is energetically favorable and does not break the nanotube's cylindrical symmetry.



(a) (b)

Figure3 the interatomic optimized bounds for non-doped and doped BNNT with: (a) 1Fe and (b) 2Fe, respectively

It is important to note that significant variations in the interatomic distances between neighboring cells ~ 0.3 Å were observed. These results indicate that the charge distribution is modified, as shown in **Table 1**. The oxidation state was calculated using the relation $\Delta x = Q_i - Q_f$, where Q_i and Q_f, represent the initial and final charges of the neighboring atoms, respectively, as obtained from Mulliken population analysis.

Table1 oxidation state of neighboring atoms of Fe for: (a) non doped BNNT, (b) BNNT/1Fe and (c) BNNT/2Fe.

(a)	**Atoms**	**N**	**N**	**B**	**B**
	$Q_i\|e-\|$	7	7	5	5
	$Q_f\|e-\|$	8.042	8.042	3.958	3.958
	$\Delta x(\|e-\|)$	-1.042	-1.042	1.042	1.042

(b)	**Atoms**	**N**	**N**	**B**	**B**	**Fe**
	Q_i |e-|	7	7	5	5	26
	Q_f |e-|	8.258	8.258	3.958	3.958	24.393
	Δx (|e-|)	-1.258	-1.258	1.042	1.042	1.607

(c)	**Atoms**	**N**	**N**	**N**	**N**	**Fe**	**Fe**	**B**	**B**	**B**
	Q_i |e-|	7	7	7	7	26	26	5	5	5
	Q_f|e-|	8.222	8.222	8.384	8.033	24.433	24.433	3.905	3.966	3.926
	Δx (|e-|)	-1.222	-1.222	-1.384	-1.033	1.567	1.567	1.095	1.034	1.074

As results, the Mulliken population analysis revealed a net charge transfer from Fe to the neighboring nitrogen atoms, confirming the ionic character of the Fe–N bonding. This redistribution of charge also affects the local electronic density, influencing the vibrational response of the doped systems.

3.2. Vibrational and spectroscopic properties

The optical characteristics of nanotubes are closely related to their absorption, photoluminescence, Raman and infrared (IR) spectra. The quality of nanotubes including, their chirality, size, and possible structural defects, can be reliably determined using these optical techniques [10]. In this section, we present the IR and Raman spectroscopic results obtained for BNNT (9,0) non doped structures, calculated using the CRYSTAL17 program. Calculations of vibrational IR and Raman of doped structures are very hard and not yet converged. **Figure 4** represents IR and Raman spectra of the primitive BNNT cell.

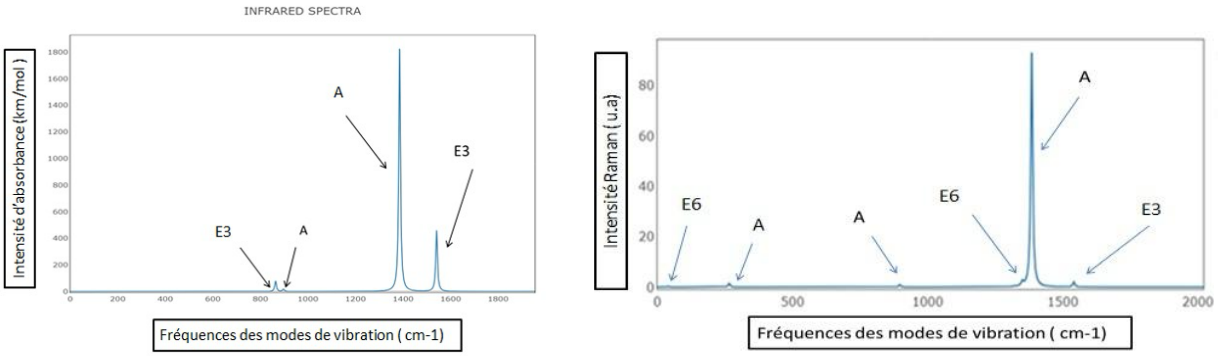


Figure4 IR and Raman spectra of BNNT primitive cell

The vibrational analysis provides insight into how size influences the phonon dynamics and spectroscopic behavior of h-BN nanotubes. For pristine (9,0) BNNTs, the Raman-active modes are dominated by in-plane B–N stretching vibrations around 1370–1380 cm^{-1}, corresponding to the well-known $\mathbf{E_{2g}}$ mode of hexagonal BN. several new peaks appear in both the IR and Raman spectra for (9,0) BNNT.

4. CONCLUSION

In this work, the effect of presence of Fe atoms in the matrix of BNNT on structural cell was studied to demonstrate that there are an observable effect on charge distribution for neighboring atoms of Fe sites, this were systematically investigated using first-principles calculations within the DFT–B3LYP framework, as implemented in the CRYSTAL17 code. The substitution of boron atoms by Fe atoms induces noticeable local lattice distortions and charge redistribution within the BN network. The structural optimization confirmed the stability of both 1Fe and 2Fe configurations, with moderate elongation of Fe–N bonds compared to B–N bonds. These changes suggest that Fe incorporation can effectively tailor the electronic properties of BN nanotubes for electronic and sensing applications.

Furthermore, vibrational spectra of BNNT unit cell without Fe atoms are represented to verify the choice of optimization conditions used to release our theoretical calculation. Comparing different modes of vibrational properties

Overall, this study demonstrates that Fe-doped h-BN nanotubes exhibit tunable electronic and vibrational properties, which can be leveraged for the design of nanoscale devices, sensors, and optoelectronic components. The results would provide theoretical guidance for future experimental work aimed at validating and exploiting the spectroscopic features of transition-metal-doped BN nanostructures.

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