Interaction of Boron Nitride Nanotubes with Aluminium: A Computational Study

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\textbf{ABSTRACT:} The interaction of boron nitride nanotubes (BNNTs) with Al has been investigated by means of quantum chemical calculations. Two model structures were used: a BNNT adsorbing a four atom Al\textsubscript{4} cluster, and a BNNT adsorbed on Al surfaces of different crystallographic orientations. The BNNTs were modeled as: (i) pristine, and (ii) having a boron (B-) or a nitrogen (N-) vacancy defect. The results indicated that the trends in binding energy for Al\textsubscript{4} clusters were, similar to those of the adsorption on Al surfaces, while the Al surface orientation has a limited effect. In all cases, the calculations reveal that Al binding to a BNNT was strongly enhanced at a defect site on the BNNT surface. This higher binding was accompanied by a significant distortion of the Al cluster or the Al lattice near the respective vacancy. In case of a B-vacancy, insertion of an Al atom into the defect of the BNNT lattice, was observed. The calculations suggest that in the Al/BNNT metal matrix composites, a defect-free BNNT experiences a weak binding interaction with the Al matrix and the commonly observed formation of AlN and AlB\textsubscript{2} was due to N- or B-vacancy defects within the BNNTs.

\textbf{1. INTRODUCTION}

Improving the strength and decreasing the weight of materials allows the design of novel ground-based vehicles, airplanes, and spacecrafts with increased payload capacity and improved fuel efficiency. With the introduction of nanofiberous materials, there is a promising lead in the development of new metal matrix composites (MMCs). In these composites the reinforcing material, usually a carbon fiber, is integrated into the metal matrix, enhancing the overall strength and/or stiffness of the MMC\textsuperscript{1}, known also as CMMCs (carbon fiber MMCs).

Nanotube–MMCs are an emerging class of new materials being developed to take advantage of the high tensile strength and low density of the nanotubes as a nanofiber reinforcing material. Today’s nanotube–MMCs exclusively use carbon nanotubes (CNTs), due to their relative ease of production and long history of research\textsuperscript{1-4}. A variety of metals are used as a metallic matrix in CNT-MMCs, including Al, Cu, Mg, Ni, Ti, Ag, Sn, and some alloys, such as W-Cu-CNT\textsuperscript{2}. The major challenges of CNT-MMCs are related to corrosion and formation of metallic carbides, due to poor CNT thermal stability\textsuperscript{4}. Experimentally, as shown by Bakshi et al.\textsuperscript{2}, the high reactivity of CNTs when integrated into metal alloys...
is seen through the ready formation of Al₄C₃, SiC, TiC, NbC, Fe₃C and other metal carbides that have
been commonly observed²⁻⁴. While the formation of interfacial phases between the CNT and the metal
can improve wetting of the nanotube with the matrix and increase the reinforcement capability², building
of a thick carbide layer degrades the overall mechanical performance of the composite³. As a result, a
reduction in strength and premature failure has been observed at higher CNT content (usually above 10
vol.-%)², which puts an upper limit to the CNT reinforcement capability.

By contrast, boron nitride nanotubes (BNNTs) possess superior chemical resistance and higher
thermal stability (up to 850°C in air)⁵, allowing them to survive most commonly-used MMC processing
techniques.⁶,⁷ BNNTs⁸⁻¹⁰ are a structural analog of CNTs, with the carbon atoms alternately being
substituted with boron and nitrogen atoms. Like CNTs, BNNTs are lightweight (1.37g/cm³) and exhibit
excellent elastic modulus (up to 1.3 TPa), strength (up to 33 GPa), toughness, and thermal conductivity.⁵
Thus, BNNTs are a potential alternative to CNTs in MMCs due to their higher chemical inertness and
enhanced thermal stability. The BNNT-MMCs are potentially superior to CNT-MMCs because the
BNNT structure is more durable, offering better mechanical flexibility¹¹ and strain to failure¹².

Of importance to this study is the development of advanced materials for aerospace applications.
Aluminum-based alloys are attractive for aerospace structural applications due to their light weight, high
strength, high thermal conductivity and strong corrosion resistance. Adding BNNTs to Al-MMCs is
expected to reinforce the mechanical strength of the composite, while further improving on its light
weight and corrosion resistance. The presence of boron in BNNTs provides enhanced adsorption against
neutron radiation, potentially improving the radiation shielding properties of BNNT/Al-MMC, which is
of importance for space applications. Since manufacturing and processing methods are expected to be
similar to that of aluminum alloys, replacement of aluminum with BNNT-MMCs is expected to be less
expensive and time consuming than other advanced material systems (e.g., carbon-fiber or ceramic
composites), which require different manufacturing techniques.

BNNT MMCs, have been integrated into an Al matrix⁶,⁷,¹³⁻¹⁷, where they are found to remain
stable even at elevated temperatures during processing. These investigations show an increase in tensile
strength by a minimum of 50%⁷,¹³,¹⁵ and a compressive strength increase of 300%¹⁷.

Studies on the mechanism of bonding of BNNTs to Al are not yet conclusive. In some cases, the
formation of AlN, AlB₂ and Al(BNO) phases have been reported⁶,¹⁵,¹⁷. In other cases, no such phases
were found⁷,¹³,¹⁴. Furthermore, Lahiri et al.⁶ showed that AlN and AlB₂ phases form only under
prolonged heat-treatment at 650°C, which is above the oxidation resistance of CNTs (400°C) and just
below the melting point of Al. The formation of these phases is likely to result from different synthesis
techniques and imperfect BNNTs, such as bamboo-like BNNT ⁷. Although initial studies have shown
that BNNT reinforced Al-MMC can reach a tensile strength of 300 MPa¹³ or even 420 MPa¹⁵ for a
sample containing 3 and 5 wt% BNNTs respectively, the quality of the synthesized BNNTs strongly
affects their ability to integrate with the Al matrix.

Computational studies can provide important information on the interaction between BNNT and
Al not only in terms of the mechanism and type of chemical bond formation, but also on the effect of the
nanotube diameter, chirality, presence of defects – knowledge that is difficult or at present impossible to
obtain experimentally. Employing density functional theory (DFT) calculations, the interaction of a
single metal atom with BNNTs has been successfully investigated in a wide variety of cases¹⁸⁻²². These
studies have been motivated by potential use of metal-doped BNNTs and BN nanosheets in applications
such as catalysis²³, nanoelectronics and spintronics²⁴⁻²⁸, gas sensing²⁹, and hydrogen storage³⁰.

Other studies have investigate the interaction of the BNNT with a small metal cluster. Quantum
chemical calculations, based on density functional theory (DFT), have shown²¹ an increased ability of
BNNTs doped with Alₙ (n = 6, 8, 10, 12, and 14) clusters to adsorb CO₂ gas. It has also been shown that
atomic doping can significantly alter the electronic and structural properties of BNNTs³².
The purpose of this study is to investigate in more systematic way the chemical binding between Al and BNNTs for the purpose of evaluating the applicability and the challenges of using BNNTs in a nanofiber metal composite as a perspective material for aerospace applications. Since the full environment of an adsorbed BNNT surrounded by Al matrix is too challenging to be simulated by first principle methods, this paper systematically considers two scenarios: the binding of small Al4 clusters to BNNTs, and the adsorption of BNNTs to Al metal surfaces. Here, BNNTs of pristine crystalline structure were studied, together with BNNTs that have B or N vacancies. The results suggest an explanation of the observed formation of AlN and AlB2 phases under certain conditions as reported in the literature6,15,17.

The presentation is organized as follows. Section 2 presents the computational method and the simulation models used in the investigation. Section 3 discusses the results as presented first for the adsorption of an Al4 cluster on a flat h-BN sheet (Section 3.1), then on a BNNT surface (Section 3.2), before the case of BNNT adsorption on Al surface is studied in Section 3.3, followed by a comparison between cluster adsorption and surface adsorption is presented in Section 3.4. The study concludes in Section 4.

2. METHOD AND MODELS

The interaction between Al and a single wall BNNT was studied in two distinctive models. The first model studied the adsorption of a four atom cluster (Al4) on BNNTs of various chiralities, as given in Table 1. As a reference to this model and to eliminate the effect of the BNNT curvature, adsorption of an Al4 cluster to a flat h-BN sheet was also studied. The second model examined the adsorption of a single wall (7, 7)-type BNNT on Al surfaces with Miller crystallographic indices of (100), (110), and (111). In all of the models, the h-BN sheet and BNNT were chosen to be either pristine (no defects), or containing a B- or N-vacancy defect, as shown in Figures 1(a) and (b), for the h-BN sheet.

2.1. Simulation Method. All DFT calculations were done with the Vienna Ab initio Simulation Package (VASP)33 using a Perdew-Burke-Ernzerhof Generalized-Gradient Approximation (PBE-GGA) functional34 and a projector-augmented-wave (PAW) potential35. Unless noted, all structures were fully relaxed until the total energy converged to 1.0 x 10^-4 eV within the self-consistent loop, and forces of less than 0.01 eVÅ^-1 were reached. The k-space was sampled with a 1 x 1 x 1 Monkhorst Pack mesh36 and an energy cut-off of 400 eV was used for all calculations. Previous test calculations18, performed by some of the co-authors of this study conducted with single Al atoms on BNNTs have shown less than 0.01 eV changes in the binding energy upon an increase to 450 eV or a k-point mesh of 6 x 1 x 1. Van der Waals interactions were accounted for by means of the Grimme (D2) scheme37.

The reported binding energies, \( \Delta E \), for all simulated systems were defined as:

\[
\Delta E = E_{BN} + E_M - E_{sys}
\]  

where \( E_{BN} \) is the energy of the boron-nitride part of the system in isolated state. Depending on the model, this is either BNNT (pristine or with a defect) or an h-BN sheet (pristine or with N or B defect). The \( E_M \) term is the energy of the metal part, which can be an isolated and equilibrated Al4 cluster, or an Al slab with a free surface. The \( E_{sys} \) term is the total energy of the simulated system.

Electron transfer between atoms during the adsorption process was studied by employing the Bader charge analysis38 and calculating Bader charges associated with each atom before and after the adsorption. For example, Figure 1(a) shows the simulation model of an h-BN sheet with a B-vacancy. The values of the Bader charges show that away from the vacancy, B and N atoms acquired charges of 2.21 e and -
2.2. Computational Model for Interaction of a Al₄ Cluster with a BNNT. Before simulating the Al cluster adsorption to a BNNT, an isolated neutral Al₄ cluster of four Al atoms was optimized individually. In agreement with a recent study³⁹ on various Alₙ clusters that revealed a planar configuration for clusters of n < 6, the equilibrium cluster shape of the Al₄ cluster was found to be a planar rhombus with sides of length 2.58 Å, compared to 2.62 Å in ref. 39. While the model in ref. 39 is similar to this research, the slight difference in the estimated cluster size might be due to the energy minimization method used by Candido et al.³⁹, which employed a DFT-based molecular dynamics optimization starting from high temperature of 1000 K going down to approximately 0 K, instead of a gradient driven energy minimization.

The BNNT/Al₄ clusters were modelled in the same way as in a previous study on adsorption of a single Al atom¹⁸. Periodic boundary conditions were used, following the periodic supercell of the h-BN sheet (Figure 1), or the periodicity of the BNNT along its axis. An energy convergence study of the system dimensions showed that at a distance of 12.6 Å, the contribution from the periodic images of the Al₄ cluster and the BNNT was zero within the computational error (>0.01 eV). Consequently, the system dimensions for all cases studied (Table 1) were made equal to or greater than 12.6 Å. The only exception was due to computational limitations when adsorption on a (10, 5)-type BNNT was considered, due to the length of the lattice vector along the axis of the BNNT. This system was modelled with dimensions of 11.5 x 30 x 30 Å.

2.3. Computational Model for Studying BNNT Adsorbed on Al surfaces. The interaction of a BNNT with various Al metal surfaces was modelled by placing a (7, 7)-type single wall BNNT on flat Al surfaces (for an example, see Figure 2). The BNNT was modeled to be either pristine (no lattice defects), as shown in Figure 2a, or to contain a B- or N-vacancy (Figures 1(a) and 1(b)). Aluminum surfaces of (100), (110) and (111) crystallographic planes were modeled to investigate the influence of different facets on the BNNT adsorption.

The choice of the (7, 7)-type BNNT was dictated by two factors. First, the diameter, $D_{(m,n)}$, of a nanotube with chiral indices, $(m, n)³⁰$ is

$$D_{(m,n)} = \frac{\sqrt{3}r_0}{\pi} (m^2 + mn + n^2)^{1/2}. \quad (2)$$

Setting the B-N bond length equal to $r_0 = 1.4472$ Å, which was estimated for an equilibrated h-BN sheet, gives $D_{(7,7)} = 9.6738$ Å. This value was similar to the diameter of a typical synthesized single wall BNNT, estimated to be between 1 and 2 nm.¹⁰,⁴¹ In addition, of all nanotubes, the armchair $(m, m)$-type has the shortest periodicity along the tube axis, equal to $\sqrt{3}r_0$ (see Figure 2b), making it easier to choose a supercell dimension that was nearly commensurate with both the BNNT and Al lattice dimensions. Reducing the mismatch between the periodic length of the supercell and both constituents minimizes the misfit strain and stress in the system, which is an artifact of the use of periodic boundary conditions.

Prior to simulating the interaction of BNNTs with Al surfaces, the lattice constant, $a$, and atomic positions of a fully periodic Al single crystal structure were optimized, employing a 12 x 12 x 12 Monkhorst-Pack mesh³⁶. The optimized structure, which has a lattice constant $a= 4.0095$ Å, was cut along the respective directions to create the desired (100), (110) and (111) Al surfaces, leaving six atomic layers to define the thickness of the Al system in each case. During the adsorption simulations, the
bottom two layers of the Al slabs were frozen at their bulk (fully dense crystalline) interplanar distances, while the upper four layers were allowed to relax and smoothly transition from a bulk to a free surface state (Figure 2a).

To satisfy the periodic boundary conditions of the system, a suitable super cell was selected for each Al surface. The supercell in-plane (x-y)-dimensions for the modelled Al surface planes are displayed in Table 2.

In each case, the nanotube was placed on the Al surface with its axis lying along the x-direction (Figure 2b). The nanotube length, \( L \), can be expressed as, \( L = p \sqrt{3} r_0 \), where \( p \) is the number of repeating periodic segments along the tube axis. The value of \( p \) was chosen so that \( L \) is nearly commensurate with the periodicity of the Al lattice in the x-direction for each surface. The commensurability condition minimizes the strain in the BNNT induced by the lattice mismatch between the Al and the BNNT lattices. As a result, surfaces (100) and (110) accommodate BNNTs with \( p = 8 \) and \( L = 20.0530 \) Å, while surface (111) accommodates a BNNT with \( p = 9 \) and \( L = 22.5596 \) Å (Table 2). The difference between \( L \) and the size of the Al surface in the x-direction resulted in a misfit strain inflicted upon the BNNT being 0.54% for the (111) surface, and 0.03% for the (100) and (110) surfaces, employing the equilibrium bond distance determined from a \( h \)-BN sheet. For a relaxed (7, 7) BNNT, these values change to 0.44% and 0.12% due to the BNNT curvature.

Test calculations for the binding energy of an Al atom adsorbed to a flat \( h \)-BN sheet subject to strain of ±0.5% yielded a difference within the 0.01 eV range, which is an acceptable error within a DFT computation. Given the (7,7)-type BNNT diameter of ~9.7 Å, the BNNT periodic images in the y-direction have an outer wall-to-wall distance of 6.6, 7.3 and 10.0 Å for the Al (100), (110) and (111) surfaces. At these distances, test calculations reveal only very small attractive image forces (≤ 0.09 eV) for BNNTs on the (100) and (110), and the interaction was within the computational error for the (111) surface.

When a BNNT with a B- or N- vacancy defect was adsorbed to an Al surface, it became of a particular interest to isolate the binding energy contributed by the defect from the total binding energy. The defect binding energy is defined as an excess energy, \( \Delta E_{ex} \), through the equation

\[
\Delta E_{ex} = \Delta E - \Delta E_{pr}, \tag{3}
\]

where \( \Delta E \) is the total binding energy from Equation (1) of the BNNT with a defect, and \( \Delta E_{pr} \) is the binding energy of an equivalent pristine BNNT in the same position. Note that as defined, \( \Delta E_{ex} \) does not depend on the nanotube length, but only on the number of vacancies, which in the explored model was only one per system.

In a similar way, the charge transfer contribution from the defect site alone is defined as an excess charge, \( \Delta Q_{ex} \), through the equation

\[
\Delta Q_{ex} = \Delta Q - \Delta Q_{pr}, \tag{4}
\]

where \( \Delta Q \) is the total charge of the BNNT with a defect, and \( \Delta Q_{pr} \) is the total charge of an equivalent pristine BNNT adsorbed at the same position.

3. RESULTS

3.1. Al\(_4\) Cluster Adsorbed on a Flat \( h \)-BN Sheet. The adsorption of an Al\(_4\) cluster to a flat \( h \)-BN sheet was studied first. The adsorption was modelled to take place on a pristine \( h \)-BN sheet, as well as
one with containing a B- or an N-vacancy. A variety of independent different starting geometries was used for each simulated model.

3.1.1. A pristine h-BN sheet.

Figure 3 presents the structure of an Al$_4$ cluster adsorbed to a pristine h-BN sheet. The binding energy (Equation 1) for this case was estimated equal to 0.75 eV. The Bader analysis showed a charge on the Al$_4$ cluster of 0.30 e, signifying an electrostatic interaction with the h-BN sheet. The preferred sites of attraction were over four N atoms on the h-BN sheet. This configuration was marked in this study as P4. As a result of the adsorption, the Al-Al bonds of the Al$_4$ cluster were slightly elongated from their equilibrium length of 2.58 to 2.69 Å in the adsorbed state. The change in the bond length was a result of the cluster polarization; changes in the bond lengths of Al clusters with charge have been reported previously by Candido et al. 29 The increased Al-Al distance was larger than the distance between the N atoms of the BN sheet, equal to $\sqrt{3}r_0 = 2.4472$ Å, which resulted in a slight offset of three of the four Al atoms relative to the N atoms. The equilibrium distance between the mass center of the Al$_4$ cluster and the h-BN sheet were found to be equal to 2.78 Å.

3.1.2. An h-BN sheet with a B-vacancy.

Before discussing the adsorption of an Al$_4$ cluster on a h-BN sheet with a B-vacancy, the results for the adsorption of a single atom of Al on this sheet will be recalled from the previous study18 (Figure 4(a) and 4(b)). A comparison between Figure 4(a) with Figure 1(a) showed that when an Al atom was adsorbed at a B-vacancy, the N atoms neighboring the defective site became more negatively charged, changing from -1.63 e (Figure 1a) to -2.25 e (Figure 4a). In addition, the adsorbed Al atom acquired a positive charge of 2.34 e, indicating a charge transfer from the Al atom to the surrounding N atoms. As a result, the charge distribution of a pristine h-BN sheet was almost entirely recovered with the Al atom substituting the missing B atom. The side view of the sheet, given in Figure 4(b), shows that the Al atom is in-plane with the h-BN sheet, and the the local bond length, $r_0$, was increased from 1.45 Å (perfect h-BN) to 1.69 Å. The results suggest that in the h-BN sheet the Al atom formed a very similar bond with an N atom as with a B atom.

The situation for the adsorption of an Al$_4$ cluster, presented in Figure 5, is more complex. Three types of adsorbed configurations were identified in this case (Figures 5a, 5b, and 5c). In each of the three configuration types, one of the Al atoms substituted the missing B atom, bonding with the three neighboring N atoms on the BNNT. This atom is referred to as the B-substituting Al. Similarly to the single atom adsorption (Figures 4a and 4b), the B-substituting Al was adsorbed by the h-BN sheet, which left the remaining three Al atoms in an out-of-plane configuration. As a result, the B-substitution transformed the equilibrium planar shape of the Al$_4$ cluster (shown in Figure 3) into a deformed tetrahedron with one tip at the site of the missing B atom.

In Figure 5(a) two of the Al atoms were in positions over two of the nearest N atoms, with the fourth Al positioned over the B-substituting Al atom. This configuration is marked as B2, indicating adsorption at a B-vacancy with two overlapped N atoms. Another configuration is shown in Figure 5(b) where all three Al atoms overlapped with N atoms on the h-BN sheet. Accordingly, this adsorption configuration is marked as B3. In the B3 configuration, the Al tetrahedron became elongated with two of its angles being close to 120º rather than 60º as in an equilateral tetrahedron. The elongation allowed the three Al atoms to fit better to the three neighbouring N atoms. There are two possible orientations of the elongated Al$_4$ tetrahedron. While Figure 5(b) shows the case where the B-substituting Al is at the tip with 60º angle, Figure 5(c) shows the case where the B-substituting Al atom is at the 120º tip. To distinguish between these two orientations, the B3 configuration is subdivided into B3-60 and B3-120 sub-configurations, respectively indicating the angle between the Al atoms at the substitution site. Each of the three identified
adsorption configurations were found to be stable, with binding energies equal to: 10.83 eV, 10.29 eV, and 10.39 eV for the B2, B3-60, and B3-120 configurations, respectively.

Bader analysis showed a strong redistribution of the electron charges between the Al atoms (as indicated in Figure 5). Since the total charge of an isolated BNNT or an Al4 cluster has to be zero, the total charge transfer, \( \Delta Q \), during adsorption can be calculated as the total charge of either the BNNT or the Al4 cluster after adsorption. The calculation showed a charge transfer of around \( \Delta Q = -2.5 \) e from the Al4 cluster to the \( h \)-BN sheet, which was close to the charge transfer, \( \Delta Q = -2.34 \) e, found during single atom adsorption (Figure 4a). The difference was that in the case of a cluster adsorption, the charge transfer was distributed among all of the four Al atoms with the B-substituting Al atom donating most of the charge. As in the single atom adsorption scenario, this charge transfer helped to almost fully restore the redistribution of charges around the vacancy site to those in a pristine \( h \)-BN (i.e., close to \( \pm 2.21 \) e).

3.1.3. An \( h \)-BN sheet with an N-vacancy.

As in the B-vacancy case, the results for the adsorption of a single Al atom at an N-vacancy will be recalled first from ref. 18, and are presented here in Figures 4(c) and 4(d). Due to an electronegativity difference between the Al and B atoms, there was a partial electron transfer from the Al to the B atoms. Unlike in the B-vacancy scenario, this electron transfer did not compensate the charge redistribution that existed around the vacancy site before adsorption, but contributed to it as follows: comparing Figure 1(b) – before adsorption, with Figure 4(c) – after adsorption, one can see that the charges on the B atoms around the vacancy site have decreased from 1.48 e (compared to 2.21 e in a pristine \( h \)-BN sheet) to 0.88 e, and 1.26 e for different B atoms. Also, by contrast with the B-vacancy adsorption, the Al atom remained out of the plane of the \( h \)-BN sheet (Figure 4d) and was asymmetrically positioned, being closer to one of the B atoms, at 2.11 Å, and at 2.31 Å from the other two B atoms. The extent of charge transfer was also greater to the closer B atom. The results indicated the formation of a different type of Al-B bonding, compared to the B-N bonding. In terms of both charge distribution and bond lengths, the binding tended to be more localized on one of the three nearest B atoms, rather than being equally shared as in the Al-N3 type of structure. This is more characteristic of a covalent bond formation, as found in the AlB3 crystalline compound42.

The case of an Al4 cluster adsorbed on the \( h \)-BN sheet with an N-vacancy is presented in Figure 6. Similarly to adsorption on the sheet with a B-vacancy, there were three possible adsorption configurations found, which, following the nomenclature defined above, were indicated as N2, N3-60, and N3-120 (Figures 6a, 6b, and 6c). The letter N represents a N-vacancy adsorption. In all of the three configurations, one of the Al atoms from the cluster substituted the missing N atom. There was one notable geometrical difference from the B-adsorption: only the N2 configuration transformed the Al4 cluster into a tetrahedral shape (Figure 6a). In both of the N3 configurations, the Al4 cluster retained its planar shape as in its isolated state, but it became a more elongated rhombohedron, with two angles approximately 60° and two approximately 120°. Depending on the angle at the Al closest to the vacancy site, two types of N3 configurations were identified and indicated as N3-60 and N3-120 types, as shown in Figures 6(b), and 6(c), respectively. The attraction between N and Al in both of the N3-configurations caused the Al4 cluster to become inclined with one tip towards the vacancy.

As in the single atom adsorption, the structure of the system was governed by the interaction of the N-substituting Al atom with its surrounding neighbors. The difference being that, in the case of a cluster, all four Al atoms participated in the charge transfer, with the largest contribution coming from the N-substituting Al, equal to 1.36 - 1.38 e, compared to the 0.28 - 0.48 e for the rest of the Al atoms (Figure 6). The total charge transfer, \( \Delta Q \), in the range of -2.5 to -2.6 e, was substantially higher than for the case of a single atom adsorption, but was close to \( \Delta Q = -2.5 \) e for a cluster adsorption at a B-vacancy site. The binding energy of the cluster during N-vacancy adsorption was found to be more than 4 times lower compared to the B-vacancy adsorption, but was still more than 8 times stronger than in the pristine
adsorption. The strongest binding was found for the N2 configuration with $\Delta E = 3.51$ eV (Figure 6a), which was the only N-configuration where the Al$_4$ cluster took a tetrahedral shape. The other two configurations, N3-60 and N3-120 (Figures 6b and 6c) that retained the planar cluster shape, showed slightly lower binding energies of 3.37 eV and 3.45 eV, respectively.

3.1.4. Summary for Al$_4$ cluster adsorption on an h-BN sheet.

A summary of the results for adsorption of an Al$_4$ cluster on a flat h-BN sheet is given in Table 3. The weakest binding was found to be with the pristine h-BN sheet, arising from an induced electrostatic quadrupole interaction between the 4-atom cluster and the h-BN sheet. The strongest binding was found at a B-vacancy site, where one of the Al atoms from the cluster substituted for the missing B atom, forming a strong Al-N bond with the surrounding N atoms. The adsorption at the N-vacancy site was of intermediate strength. In both types of vacancies, the B2 and N2 tetrahedral cluster configurations showed the strongest binding. Although the binding energy of the Al$_4$ cluster was very different for the B- and N-vacancy systems, the charge transfer between the cluster and the supercell of the h-BN sheet was approximately the same, ranging from 2.5 - 2.6 e from the cluster to the lattice. Thus, an equal amount of charge transfer participated in different types of bond formation at the two vacancy types. The question about the type of binding will be discussed in more detail at the end of this study after presenting all of the simulation results.

The total charge transfer was found to be relatively insensitive to the configuration of the Al$_4$ cluster on the h-BN sheet, varying between 2.52 and 2.59 e. A notable difference was observed only in the charge distribution between the four Al atoms, as shown in Table 3. In all cases, the substituting Al atom contributed the most charge, which was higher for the B-vacancy (1.58 - 1.64 e), compared to the N-vacancy (1.36 - 1.38 e). The Al atoms positioned above N atoms shared an almost equal amount of charge - around 0.30 - 0.35 e, and around 0.45 e for the B- and N-vacancy adsorptions, respectively. The Al atom which was farthest away from any N-atom had the smallest charge contribution, around 0.2 - 0.3 e in both cases.

3.2. Al$_4$ Cluster Adsorbed to a BNNT Surface. Compared to the adsorption to a flat h-BN sheet, adsorption of an Al$_4$ cluster on a BNNT introduces the effect of the curved BNNT surface. In addition, the direction of the curvature relative to the h-BN sheet introduces the effect of chirality.

3.2.1. A pristine BNNT.

The case of binding on a pristine BNNT will be considered first. Figure 7 shows the configurations of an Al$_4$ cluster adsorbed on a zig-zag (12, 0)-type BNNT, and on an armchair (5, 5)-type BNNT. Both configurations were very similar in geometry to those observed for the P4 adsorption on the h-BN sheet shown in Figure 3. Notably, the nanotube chirality defined the orientation of the adsorbed cluster, following the pattern on the h-BN sheet (see Figure 3). While on the zig-zag BNNT the cluster was symmetrically positioned with respect to the nanotube axis (Figure 7a), on the armchair BNNT the cluster was tilted at 30$^\circ$ to the BNNT axis, following the chiral angle (Figure 7b).

After studying a variety of BNNTs, the role of curvature and chirality on the binding energy was revealed in Figures 8(a) and 8(b). A general trend, seen in Figure 8(a), was that $\Delta E$ for the armchair (m, m)-type BNNTs of $D > 10$ Å followed a $1/D^2$ dependence, as predicted by the theory of linear elasticity$^{43,44}$. Consequently, a deviation from the $1/D^2$ dependence would indicate the presence of non-linear effects in the binding energy. Such non-linear effects of higher order$^{45}$ were found for $D < 10$ Å, where the nanotube diameter became comparable to the side length (~ 3 Å, Figure 7) of the Al$_4$ cluster. For the single Al atom adsorption, reported previously$^{18}$, the $1/D^2$ dependence was followed over the entire range of nanotube diameters, which indirectly suggested that the non-linear effects seen in the cluster adsorption were indeed a result of the finite cluster size. The data for the zig-zag (m, 0)-type
BNNTs was very scattered in this study compared to the data for the armchair \((m, m)\)-type BNNTs, and did not show a clear trend. A better notion of the chiral angle dependence of \(\Delta E\) could be obtained from Figure 8(b) where the results for BNNTs of comparable radii, between 10.5 and 11.6 Å, were presented. In contrast to the single atom adsorption energy\(^{18}\), for which the binding energy was reported to be independent of the BNNT chirality\(^{18}\), the results for the Al\(_4\) cluster showed a clear decrease of \(\Delta E\) with increase of the chiral angle. This decrease, approximately 20\% for an increase of the chiral angle from 0\(^\circ\) to 30\(^\circ\), indicated that the zig-zag type BNNTs more strongly adsorb the Al\(_4\) cluster than the armchair type BNNTs.

Another interesting curvature effect was found for the charge transfer, \(\Delta Q\), between the Al\(_4\) cluster and the BNNT. Figure 9(a) shows a sudden stepwise increase of \(\Delta Q\) at around \(1/D^2 \approx 0.01 \text{ Å}^{-2}\) \((D \approx 10 \text{ Å})\). Figure 9(b) shows that at the same value of \(1/D^2 \approx 0.01 \text{ Å}^{-2}\), there was a crossover of the rate of decrease of the adsorption distance, \(d\), with decrease of \(D\). Such a crossover in the behavior of either \(\Delta Q\) and \(d\) was not found for a single Al atom adsorption, given as a reference in both Figures 9(a) and 9(b). Notably, the crossover happened when \(d_{Al_4} \approx D\). This result could be interpreted as a size effect related to the cluster size relative to the nanotube diameter. When the cluster size was much smaller than \(D\) \((1/D^2 \to 0\), all of the cluster atoms interacted equally with the BNNT, as in the limiting case of a planar \(h\)-BN. When the cluster size became comparable to \(D\), some of the cluster atoms became closer to the BNNT surface than others, which lead to the redistribution of cluster charges. This charge redistribution resulted in increased cluster polarization and an increase of the overall charge transfer, \(\Delta Q\). When \(D\) reached a certain small enough value \((D \approx 10 \text{ Å})\), only one or two of the cluster atoms could interact effectively with the BNNT, and the adsorption distance became comparable to that of a single atom adsorption. In other words, the discontinuity of \(\Delta Q\) at \(D \approx 10 \text{ Å}\) can be interpreted as a transition from a collective cluster adsorption to a more localized single atom adsorption as the tube diameter became too small for all of the cluster atoms to interact equally with the BNNT.

3.2.2. A BNNT with a B-vacancy.

Adsorption at a vacant site on a BNNT was generally similar to the situation for adsorption on an \(h\)-BN sheet with a vacancy. Introducing a vacancy defect site on the BNNT substantially increased the adsorption energy of the Al\(_4\) cluster and the strongest adsorption was experienced at a B-vacancy. The same types of configurations (B2, B3-60, and B3-120) as had been found for Al\(_4\) adsorption on an \(h\)-BN sheet were identified for Al\(_4\) adsorption on both armchair, and zig-zag BNNTs. A few examples are shown in Figure 10. Figure 10(a) gives top and side views of the B2 configuration that appeared on a chiral \((5, 5)\) BNNT. Examples of B3-60 on a chiral \((7, 7)\) BNNT, and of B3-120 on a zig-zag \((12, 0)\) BNNT are shown in Figures 10(b) and 10(c), respectively. No substantial difference in the Bader charge redistribution was found between different cluster configurations on the BNNT, nor were the charges significantly different from those found for the planar \(h\)-BN adsorption configurations (Figures 5a - 5c).

A summary of the results for adsorption on the B-vacancy is given in Table 4. As in the pristine adsorption case (Figure 8a), there was a general trend of decrease of the binding energy with increase of the nanotube diameter, approaching the values for planar \(h\)-BN adsorption, which are given at the bottom in Table 4 for reference. This trend was followed for all of three configurations (B2, B3-60, and B3-120). In contrast, the charge transfer, while varying slightly \((-0.1 \text{ e})\) between the different configurations, did not show a consistent diameter dependence. The precision of the data was not good enough to reveal any unambiguous dependence on the nanotube chirality in that case.

3.2.3. A BNNT with an N-vacancy.

Examples of adsorption at an N-vacancy site are shown in Figure 11 for the zigzag \((12, 0)\) BNNT. As for the B-vacancy, all three adsorption configurations observed for the \(h\)-BN sheet with an N-vacancy
were found: N2, N3-60, and N3-120 (Figures 11a, 11b, and 11c, respectively). The results are summarized in Table 5. Compared to the B-vacancy adsorption results, the data for both binding energy and charge transfer showed much larger scattering, obscuring any systematic trend dependence on the nanotube diameter for different adsorption configuration types. The binding energies fluctuated between 3 and 4 eV, bracketing the $h$-BN sheet values of 3.51 eV, without showing a systematic dependence on the nanotube diameter. This might indicate that curvature effects did not have a dominant role on the binding energy in this case. An exception was the notably larger binding energy, between 5.8 and 6.5 eV, found for the $(8, 0)$ BNNT. This anomaly has been reproduced with several independent simulations and was also noted to a lesser extent in the case of single atom adsorption. The much greater adsorption energy observed for these systems may be due to the very small nanotube diameter, where curvature effects became significant. Overall, it should be noted that the binding to an N-vacancy site was 2 to 4 times weaker than to a B-vacancy site, but was still 3 to 4 times stronger than the adsorption to a pristine BNNT, which was around 1 eV.

3.3. BNNT Adsorption on Al Surfaces. An armchair $(7, 7)$-type BNNT was used to study tube adsorption on three types of Al surfaces: $(100)$, $(110)$ and $(111)$. As in the Al$_4$ cluster adsorption study, the BNNT was simulated with either no lattice defects, a B-vacancy defect, or a N-vacancy defect.

3.3.1. Electron density plots.

Similar to the adsorption of an Al$_4$ cluster, introducing a vacancy defect into the BNNT created a strong binding point with the Al atoms. This binding was clearly revealed through the electron density plots shown in Figure 12. In the pristine BNNT case (Figure 12a), the electron density of the B and N atoms along the nanotube length did not show any noticeable disturbance, while the electron density of the Al atoms indicated a slight attraction to the BNNT when compared to the equivalent atoms at the bottom free Al surface. The Al surface plane remained structurally undisturbed in this case. By contrast, the presence of a B-vacancy (Figure 12b) caused one of the Al atoms to leave the metal surface to substitute for the missing B atom in the BNNT lattice. The zoomed-in view of the electron density shows that the Al atom has bound to the three N atoms at the defect site, pointing to strong bonding of the BNNT to the Al surface. In the case of an N-vacancy (Figure 12c), there was no extraction of an Al atom from the surface. The distortion in the electron density was smaller than what has found for the B-vacancy case, but it still showed a point of attraction on the BNNT towards the metal surface.

3.3.2. A pristine BNNT.

An example configuration of a pristine BNNT adsorbed on a $(100)$ Al surface, already introduced in the “Methodology and Models” section to explain the system setup, is shown in Figure 2. After geometry optimization, the adsorption distance, $d$, between the top layer of Al atoms and the BNNT surface (Figure 2a) was estimated, along with the system energy, $E_{\text{sys}}$, which was used to calculate the binding energy, $\Delta E$, from Equation (1). The resulting values of $d$ and $\Delta E$ per nanotube length, $L$, are listed in Table 6 for each surface type. In addition, to reveal the charge distribution on both the Al surface and the BNNT, Bader charges are shown in Figure 2(b) for all atoms in the top Al layer and for the B and N atoms at the bottom of the BNNT. The Al atoms located beneath the nanotube showed a slightly larger charge ($0.07 - 0.11$ e) compared to the atoms away from the nanotube ($0.03 - 0.05$ e). A corresponding increase in the Bader charges of the N atoms, from $-2.21$ e in the isolated state to $-2.24$ e in the adsorbed state, was also observed. To quantify this, the last column in Table 6 lists the charge transfer per unit nanotube length, $\Delta Q/L$. The value of $\Delta Q$ was calculated as the total charge of the BNNT in the adsorbed state, assuming an overall neutral charge in the isolated state. The binding of the nanotube to the Al surface was, therefore, due to both an electrostatic attraction and a van der Waals attraction. The charge distribution on the Al surface and the BNNT was determined by the geometrical arrangement.
of the atoms on the Al surface relative to the BNNT lattice. This arrangement was found different for each Al surface, being also dependent on the BNNT axis orientation on the surface.

The results in Table 6 show that some quantities were more sensitive to the type of the surface plane, whereas others are sensitive to the BNNT orientation on the surface. For example, the adsorption distance, $d$ (Figure 2a) was found to fluctuate around $3.10 \pm 0.02 \text{ Å}$ for the (001) surface, and around $2.88 \pm 0.01 \text{ Å}$ for the (110) surface, regardless of whether the BNNT was orientated in the [001] or [110] direction. The data for the (111) surface in the [110] direction gives an intermediate value of $d = 3.03 \text{ Å}$. The binding energy, $\Delta E/L$, on the other hand, was found to be more sensitive to the BNNT orientation than to the surface plane. For the [001] direction, on both (001) and (110) planes, $\Delta E/L$ was around $0.21 \pm 0.01 \text{ eV/Å}$. For the [110] direction on the same planes, however, this value was notably lower at around $0.17 \pm 0.005 \text{ eV/Å}$. For a nanotube oriented along the [110] direction on the (111) plane, $\Delta E/L = 0.22 \text{ eV/Å}$, which was at 0.05 eV/Å higher than for the same orientation on the (001) and (110) planes. A similar behavior, dominated by the nanotube orientation, was also found for the charge transfer, $\Delta Q/L$, which was estimated to be around $0.022 \pm 0.001 \text{ e/Å}$ for the [001] direction, and around $0.019 \pm 0.002 \text{ e/Å}$ for the [110] direction on either the (001) or (110) surfaces, while the value for the (111)/[110] adsorption case was found somewhat higher at around $0.0275 \text{ e/Å}$.

### 3.3.3. A BNNT with a B-vacancy.

The atomic configurations at a B-vacancy site during adsorption are shown in Figure 13 for all three of the studied Al surfaces. As the side and front views show, in all three surface planes one of the Al atoms was extracted from the surface and was attached to the BNNT lattice, substituting for the missing B atom. In the process, the substituted Al atom acquired a charge of $1.86$, $1.69$, and $2.12 \text{ e}$ on the (100), (110), and (111) surfaces, respectively. Some of the nearby atoms in the Al lattice also acquired smaller charges, between $-0.12 \text{ e}$ and $+0.62 \text{ e}$, which indicated a significant local charge redistribution in the Al lattice close to the vacancy site. It is notable that in the case of the (110) surface, the adsorption has caused a pronounced local strain in the Al lattice under the BNNT vacancy site. Overlaying a rectangular frame over the top view of the Al lattice in Figure 13(vi) helped to highlight these atomic displacements toward the vacancy site along the tube axis. The strain was estimated to be as high as 6% in the direction along the nanotube axis.

### 3.3.4. A BNNT with an N-vacancy.

The atomic configurations at an N-vacancy during adsorption are shown in Figure 14 for all three of the studied Al surfaces. Compared to the BNNT with a B-vacancy, the side and front views in Figure 14 show a weaker attraction between the atoms from the Al surface and the BNNT. Nonetheless, there was evidence that an Al atom from the surface was being attracted to the vacancy created by the missing N atom. On the (100) and (110) facets, this Al atom can be identified as the one with the highest induced charge, which was found to be equal to $0.73 \text{ e}$, and $0.68 \text{ e}$ on the (100) and (110) surfaces, respectively. The effect was most pronounced in the case of the (111) surface (Figures 14vii and 14viii), where the relevant Al atom acquired a charge of $1.32 \text{ e}$ and was almost removed from the surface plane. As was found for the case of the BNNT with a B-vacancy, the interaction of the (110) surface and a BNNT with a N-vacancy also produced significant strain on the Al surface around the vacancy site.

### 3.4. Comparison between Cluster Adsorption and Surface Adsorption.

The results presented in Sections 3.2 and 3.3 showed a number of similarities between the two simulated models: the adsorption of an Al4-cluster on a BNNT, and the adsorption of a BNNT on an aluminum surface. There were also some differences. In both models, the binding between the Al and the h-BN sheet was found to be qualitatively and quantitatively very different in the case of binding at a pristine BNNT, at a B-vacancy site, or at an N-vacancy site. For both cases of a cluster or surface adsorption, the results suggested three
distinctively different types of bond formation between the Al and the nanotube, depending on the local structure of the B-N lattice.

### 3.4.1. A pristine BNNT.

A pristine BNNT showed a relatively weak binding with aluminum in all cases. The weak binding arose primarily from the charge redistribution which occurred between nearby aluminum atoms and the BNNT, producing multipolar (quadrupole and higher order) electrostatic interactions. A small net charge transfer from the Al to the BNNT of $\Delta Q = 0.30 \, \text{e}$ in the case of an Al$_4$ cluster (Table 3), and of around $\Delta Q/L = 0.020 \pm 0.003 \, \text{e/Å}$ in the case of surface adsorption has also been found (Table 6). The binding energies were estimated to be $\Delta E = 0.75 \, \text{eV}$ for the Al$_4$ cluster adsorption (Table 3), and around $\Delta E/L = 0.20 \pm 0.03 \, \text{eV/Å}$ for the Al surface adsorption (Table 6). The adsorption distance for a cluster was estimated (Figure 3) to be 2.78 Å, which was close to the average adsorption distance of $d = 3.00 \pm 0.12 \, \text{Å}$ found for the three Al surfaces (Table 6).

### 3.4.2. A BNNT with a B-vacancy.

In the case of adsorption at a B-vacancy, the simulation results suggested the formation of an Al-N chemical bond, as found in AlN compounds. The estimates for the Al-N bond lengths between the substitute Al atom and the three surrounding N atoms are summarized in Table 7 for all of the studied adsorption scenarios, together with the results for a single Al atom adsorption reported previously$^{18}$.

In the case of the Al$_4$ cluster adsorption, one of the bond lengths was always shorter, and equal to $d_{\text{Al-N}} = 1.78 - 1.79 \, \text{Å}$, compared to the other two, which varied between 1.85 and 1.88 Å (Figure 5, Table 7). As seen from Figure 5, the bond length affected the charge at the respective N atom, being less negative ($-2.24 \, \text{e}$) for the shorter bond, and more negative (between $-2.29$ and $-2.33 \, \text{e}$) for the longer bond.

The situation was found similar in the case of surface adsorption (Figure 13, Table 7). The three bond lengths were again split into two groups (Figures 13iii, 13vi, and 13ix), but this time, two of the bonds had the shorter length of 1.81 – 1.83 Å, while the longer bond varied between 1.88 and 1.99 Å. The shorter bond lengths compared well with those of an isolated Al$_2$N$_2$ and Al$_2$N$_2$ cluster$^{47}$, reported to be in the range of 1.79 – 1.82 Å. The longer bond correlates well with the Al-N distance in wurtzite AlN, estimated$^{48}$ at 1.917 Å. The N atoms at the shorter bonds again had gained less negative charges, between $-2.23$ and $-2.25 \, \text{e}$, compared to the charge at the longer bond varying between $-2.29$ and $-2.35 \, \text{e}$, depending on the surface type. These values should be compared to the N-charge of the undisturbed B-N lattice, equal to $-2.21 \, \text{e}$, suggesting that Al substituting B showed closer charge distribution to the original B-N bond for the shorter Al-N bond.

The charge transfer during cluster adsorption, varying between 2.49 and 2.56 e (Table 7), was higher than in the case of a single atom adsorption (of 2.34 e)$^{18}$, but lower than the excess charge transfer, $\Delta Q_{\text{ex}}$ (Equation 4), for the surface adsorption, which varies between 2.88 and 3.13 e (Table 7), depending on the configuration. The high charge transfer in all of these adsorption scenarios was consistent with ab initio calculations$^{48}$ on wurtzite AlN. Those calculations showed that the high difference in electronegativity between Al and N, calculated at 1.82, leads to significant charge transfer, consistent with the predominantly ionic character of the AlN bond. The binding energy, $\Delta E$, for cluster adsorption, varying between 10.29 and 10.83 eV, was around the value for a single atom adsorption of 10.44 eV (Table 7). The excess binding energy, $\Delta E_{\text{ex}}$ (Equation 3, Table 7) of the BNNT/Al surface adsorption, estimated between 6 and 9 eV, was lower, but of the same order of magnitude as of the Al$_1$ and Al$_4$ cluster binding. These results, taken together, suggested a similar type of Al-N bond formation occurring during adsorption at a B-vacancy site in all of these scenarios.

### 3.4.3. A BNNT with an N-vacancy.
The computational results for adsorption of Al clusters or surfaces on an N-vacancy in a BNNT are summarized in Table 8. In these cases, as already discussed, one of the Al atoms was found to move slightly towards the vacant site. As in the B-vacancy binding, the strength of the Al-B bond was dependent on the distance between the Al and B atoms. In the cluster adsorption case, the bond length varied between 2.1 and 2.2 Å (Figure 6, Table 8), which was very close to a single Al atom adsorption bond length found to be between 2.1 and 2.3 Å (Figure 4d). The calculated Bader charges at the B atoms surrounding the N-vacancy for the cluster adsorption were between 0.55 and 0.99 e (Figure 6), which were lower than in the case of a single atom adsorption (0.88 and 1.26 e in Figure 4c).

In the case of surface adsorption, the Al-B bond length occupied two distinct ranges of values (Figures 14iii, 14vi, and 14ix). The shorter one, estimated to be between 2.16 and 2.30 Å, was in the same range as that of cluster adsorption. That bond length was close to the Al-B distance in AlB₂ (aluminium diboride), which is equal to 2.383 Å, suggesting a chemical bonding similar to the predominantly covalent bond in the AlB₂ phase. The calculated Bader charges at the respective B atoms were calculated between 0.63 and 1.00 e (Figure 14), which was in the same range as for the cluster adsorption, suggesting that the shorter Al-B bond was of a similar type as the cluster adsorption binding. By contrast, the longer Al-B bond distance varied between 2.89 and 3.42 Å, depending on the type of surface and the nanotube orientation, as summarized in Table 8. The corresponding B atoms showed higher Bader charges between 1.3 and 1.4 e (Figures 14 i-vi). These values were close to the charge of the B atom before adsorption, estimated to be 1.48 e (Figure 1b), suggesting a very weak or no bond formation in those cases.

The charge transfer that occurs during cluster adsorption at an N-vacancy site, varying between 2.52 and 2.59 e (Table 8), was in the same range as in the case of adsorption at a B-vacancy (Table 7). By contrast, the single atom adsorption at an N-vacancy showed much lower charge transfer of 0.97 e (Table 8). The excess charge transfer, ∆Qex (Equation 4), during surface adsorption varied between ∆Qex = 1.04 to 1.95 e, depending on the configuration (Table 8). These values were lower than those observed for a B-vacancy surface adsorption (∆Qex = 2.88 to 3.13 e, Table 7).

The excess binding energy during surface adsorption, listed in Table 8, was also substantially lower (∆Eex = 0.31 to 1.76 eV) than in the case of a cluster adsorption (∆Eex = 3.37 to 3.51 eV). A similar trend of a weaker surface than cluster binding was also found for the B-vacancy adsorption (Table 7). These results suggested that Al bonding at an N-vacancy site was more localized, but weaker than at a B-vacancy site.

4. CONCLUSION

The presented work studied the interaction of a BNNT with Al in the form of small four-atom clusters, and with Al surfaces of different orientations, to obtain an understanding of the interactions between the metal and the BNNT. Particular attention was given to the influence of defects within the BNNT, in the form of B- and N-vacancies.

The cluster study, in which a four-atom cluster was adsorbed to a BNNT, examined the dependence of the adsorption on the BNNT diameter and chirality. This dependence was most clearly pronounced in the case of adsorption to a pristine (no lattice defects) BNNT. The binding energy followed a general linear elastic 1/D² behavior. The binding energy was also found to decrease by approximately 20% with an increase of the chiral angle from 0° to 30°, indicating stronger interactions with the zig-zag type BNNTs compared to the armchair BNNTs. The binding was due to electrostatic interaction between the induced charge redistribution on the nanotube and the Al₄ cluster, accompanied by a net charge transfer to the BNNT, which additionally polarized the cluster. A transition was found
from a collective cluster adsorption to a more localized single atom adsorption as the tube diameter becomes too small for all of the cluster atoms to interact equally with the BNNT.

The presence of a vacancy on the nanotube strongly increased adsorption due to the formation of an Al-N bond at the vacancy site in the case of a B-vacancy, and of an Al-B bond in the case of an N-vacancy. The Al-N bond appeared to be very similar in electron density distribution to the B-N bond of a pristine BNNT, with Al replacing B. The Al-B bond, formed at an N-vacancy site, was found to be similar to the predominantly covalent bond in the AlB2 phase.

Several stable adsorption configurations of the Al4 cluster were identified. During adsorption at a B-vacancy site, the Al4 cluster was transformed from its initial square planar form into a tetrahedral geometry with one tip at the vacancy site, where the Al atom substituted for the missing B atom. The tetrahedron could be either equilateral or strongly elongated, with the equilateral shape having the highest binding strength. During adsorption at an N-vacancy site, the Al4 cluster could take either the form of a tetrahedron, or remain planar, but transforming from a square shape to a $60^\circ$ - rhombus. Again, the tetrahedron form showed the lowest energy and thus the highest binding strength.

In the case of BNNT adsorption to an Al surface, the interactions between a (7, 7) BNNT with three types of Al surface planes, (100), (110), and (111), were modelled. In general, it was found that the binding energy varied in the range of 10% from plane to plane and being also dependent on the BNNT orientation with respect to the crystallographic axis of the plane. In the case of pristine BNNT adsorption, the interaction with the metal surface occurred through induced multipolar electrostatic interactions of van der Waals type, with a small charge transfer per nanotube length ($< 0.03$ e/Å) from the nanotube to the metal surface.

As in the case of cluster adsorption, the presence of a vacancy in the BNNT strongly increased the local binding by creating a chemical bond between the metal surface and the BNNT. In both types of vacancies, one Al atom from the metal surface substituted the missing B or N atom at the vacancy site. The B-vacancy adsorption, leading to the formation of an Al-N bond, was approximately twice as strong as the N-vacancy adsorption, where a weaker Al-B bond was formed. In both types of vacancies, the binding energy of the chemical bond was more than an order of magnitude higher than the van der Waals electrostatic binding with a pristine BNNT.

In a broader context, the results from this study showed that AlN and AlB2 compounds are likely to form predominantly at a defect site on the B-N lattice. These findings offer an explanation for the reported formation of AlN, AlB2 or Al(BNO) phases in previous studies, although others have not observed such phases. The presented calculations showed that the formation of these phases is strongly dependent on the purity and the crystallinity of BNNTs, among other factors such as temperature, pressure and time of treatment. The simulation results are important in the context that most BNNTs are not synthesized without defects, and that the prolonged treatment required for the formation of Al based MMCs enhances the presence of interface phases like AlN and AlB2.

ACKNOWLEDGEMENTS

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REFERENCES:

TABLES:

**Table 1.** System cell dimensions for the adsorption of an \( \text{Al}_4 \) cluster on an \( h \)-BN sheet and on a BNNT for all modelled systems.

<table>
<thead>
<tr>
<th></th>
<th>( x ) [Å]</th>
<th>( y ) [Å]</th>
<th>( z ) [Å]</th>
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<tr>
<td><strong>h-BN sheet</strong></td>
<td>15.3</td>
<td>15.3</td>
<td>15.5</td>
</tr>
<tr>
<td><strong>BNNT type</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Armchair (n, n), ( n = 5, 7, 8, 10 )</td>
<td>12.6</td>
<td>30</td>
<td>30</td>
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<tr>
<td>Zigzag (n, 0), ( n = 8, 9, 12, 17 )</td>
<td>13.0</td>
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<td>30</td>
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<tr>
<td>Chiral (9, 6)</td>
<td>19.0</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Chiral (10, 5)</td>
<td>11.5</td>
<td>30</td>
<td>30</td>
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</tbody>
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*The \( x \)- and \( y \)-axis form a 120° angle in this case (see Figure 1).*

**Table 2.** \( \text{Al} \) supercell in-plane (x-y) dimensions for the model of a BNNT adsorbed on \( \text{Al} \) surface, including the number of the nanotube segments, \( p \), along the nanotube length oriented in the \( x \)-direction.

<table>
<thead>
<tr>
<th>Surface plane</th>
<th>Surface supercell</th>
<th>( x ) [Å]</th>
<th>( y ) [Å]</th>
<th>( p )</th>
<th>( L ) [Å]</th>
</tr>
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<tr>
<td>(100)</td>
<td>5[001] x 4[010]</td>
<td>20.0475</td>
<td>16.0380</td>
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<td>5[001] x 3[110]</td>
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<tr>
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<td>22.6812</td>
<td>22.6812</td>
<td>9</td>
<td>22.5596</td>
</tr>
</tbody>
</table>

*The \( x \)- and \( y \)-axis make 120° angle in this case.*

**Table 3.** Binding energy, \( \Delta E \), and charge transfer, \( \Delta Q \), for \( \text{Al} \) cluster adsorption on a plane \( h \)-BN sheet.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>P4</th>
<th>B2</th>
<th>B3-60</th>
<th>B3-120</th>
<th>N2</th>
<th>N3-60</th>
<th>N3-120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy, ( \Delta E ) (eV)</td>
<td>0.75</td>
<td>10.83</td>
<td>10.29</td>
<td>10.39</td>
<td>3.51</td>
<td>3.37</td>
<td>3.45</td>
</tr>
<tr>
<td>Charge transfer, ( \Delta Q ) (e)</td>
<td>0.30</td>
<td>2.56</td>
<td>2.52</td>
<td>2.49</td>
<td>2.52</td>
<td>2.59</td>
<td>2.59</td>
</tr>
<tr>
<td>Charge at each Al in decreasing order (e)</td>
<td>0.14</td>
<td>1.58</td>
<td>1.64</td>
<td>1.64</td>
<td>1.38</td>
<td>1.37</td>
<td>1.36</td>
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<td></td>
<td>0.14</td>
<td>0.36</td>
<td>0.33</td>
<td>0.36</td>
<td>0.43</td>
<td>0.45</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0.34</td>
<td>0.28</td>
<td>0.29</td>
<td>0.43</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>-0.01</td>
<td>0.28</td>
<td>0.27</td>
<td>0.20</td>
<td>0.28</td>
<td>0.33</td>
<td>0.31</td>
</tr>
<tr>
<td>Al(_4) cluster shape*</td>
<td>Square</td>
<td>Tetrahedron</td>
<td>Extended tetrahedron</td>
<td>Tetrahedron</td>
<td>60°-rhombus</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The shapes are only an approximation to the closest regular geometry.*
Table 4. Binding energy, $\Delta E$, and charge transfer, $\Delta Q$, for Al$_4$ cluster adsorption at a B-vacancy site on various BNNTs of ($m$, $n$) indices. Index ($\infty$, $\infty$) indicates an $h$-BN sheet, given for comparison.

<table>
<thead>
<tr>
<th>Nanotube indices</th>
<th>Chiral angle [%]</th>
<th>Diameter (Å)</th>
<th>Al$_4$ cluster</th>
<th>Al$_1$ single atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B2</td>
<td>B3-60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta E$ (eV)</td>
<td>$\Delta Q$ (e)</td>
</tr>
<tr>
<td>Zig-zag</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8, 0)</td>
<td>0</td>
<td>6.4</td>
<td>11.88</td>
<td>2.57</td>
</tr>
<tr>
<td>(9, 0)</td>
<td>0</td>
<td>7.2</td>
<td>11.23</td>
<td>2.57</td>
</tr>
<tr>
<td>(12, 0)</td>
<td>0</td>
<td>9.6</td>
<td>11.21</td>
<td>2.56</td>
</tr>
<tr>
<td>(17, 0)</td>
<td>0</td>
<td>13.6</td>
<td>9.61</td>
<td>2.54</td>
</tr>
<tr>
<td>Chiral</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10, 5)</td>
<td>19.11</td>
<td>10.6</td>
<td>11.01</td>
<td>2.55</td>
</tr>
<tr>
<td>(9, 6)</td>
<td>23.41</td>
<td>10.5</td>
<td>11.32</td>
<td>2.55</td>
</tr>
<tr>
<td>Armchair</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5, 5)</td>
<td>30</td>
<td>6.9</td>
<td>11.30</td>
<td>2.55</td>
</tr>
<tr>
<td>(7, 7)</td>
<td>30</td>
<td>9.7</td>
<td>11.26</td>
<td>2.44</td>
</tr>
<tr>
<td>(8, 8)</td>
<td>30</td>
<td>11.1</td>
<td>11.24</td>
<td>2.55</td>
</tr>
<tr>
<td>(10, 10)</td>
<td>30</td>
<td>13.9</td>
<td>11.06</td>
<td>2.54</td>
</tr>
<tr>
<td>Plane h-BN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>($\infty$, $\infty$)</td>
<td>-</td>
<td>$\infty$</td>
<td>10.83</td>
<td>2.56</td>
</tr>
</tbody>
</table>

*Single atom adsorption$^{18}$
Table 5. Binding energy, $\Delta E$, and charge transfer, $\Delta Q$, for Al$_4$ cluster adsorption at an N-vacancy site on various BNNTs of $(m, n)$ indices. Index $(\infty, \infty)$ indicates an $h$-BN sheet, given for comparison.

<table>
<thead>
<tr>
<th>Nanotube indices</th>
<th>Chiral angle [°]</th>
<th>Diameter (Å)</th>
<th>Al$_4$ cluster</th>
<th>Al$_4$ single atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N2</td>
<td>N3-60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta E$ (eV)</td>
<td>$\Delta Q$ (e)</td>
</tr>
<tr>
<td>Zig-zag</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8, 0)</td>
<td>0</td>
<td>6.4</td>
<td>6.03</td>
<td>2.64</td>
</tr>
<tr>
<td>(9, 0)</td>
<td>0</td>
<td>7.2</td>
<td>3.21</td>
<td>1.70</td>
</tr>
<tr>
<td>(12, 0)</td>
<td>0</td>
<td>9.6</td>
<td>3.29</td>
<td>2.46</td>
</tr>
<tr>
<td>(17, 0)</td>
<td>0</td>
<td>13.6</td>
<td>3.34</td>
<td>2.63</td>
</tr>
<tr>
<td>Chiral</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10, 5)</td>
<td>19.11</td>
<td>10.6</td>
<td>2.93</td>
<td>2.31</td>
</tr>
<tr>
<td>(9, 6)</td>
<td>23.41</td>
<td>10.5</td>
<td>3.39</td>
<td>2.55</td>
</tr>
<tr>
<td>Armchair</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5, 5)</td>
<td>30</td>
<td>6.9</td>
<td>3.59</td>
<td>2.45</td>
</tr>
<tr>
<td>(7, 7)</td>
<td>30</td>
<td>9.7</td>
<td>3.47</td>
<td>2.38</td>
</tr>
<tr>
<td>(8, 8)</td>
<td>30</td>
<td>11.1</td>
<td>3.45</td>
<td>2.53</td>
</tr>
<tr>
<td>(10, 10)</td>
<td>30</td>
<td>13.9</td>
<td>3.43</td>
<td>2.55</td>
</tr>
<tr>
<td>Plane $h$-BN</td>
<td></td>
<td></td>
<td>3.51</td>
<td>2.52</td>
</tr>
</tbody>
</table>

*Single atom adsorption$^{18}$

Table 6. Adsorption distance, $d$, binding energy per unit length, $\Delta E/L$, and charge transfer, $\Delta Q/L$, for adsorption of a pristine (7, 7) BNNT on Al surfaces.

<table>
<thead>
<tr>
<th>Surface type/BNNT direction</th>
<th>$d$ (Å)</th>
<th>$\Delta E/L$ (eV/Å)</th>
<th>$\Delta Q/L$ (e/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (001)/[001]</td>
<td>3.09</td>
<td>0.197</td>
<td>0.0213</td>
</tr>
<tr>
<td>Al (010)/[001]</td>
<td>2.88</td>
<td>0.216</td>
<td>0.0224</td>
</tr>
<tr>
<td>Al (001)/[110]</td>
<td>3.12</td>
<td>0.166</td>
<td>0.0170</td>
</tr>
<tr>
<td>Al (101)/[110]</td>
<td>2.89</td>
<td>0.170</td>
<td>0.0199</td>
</tr>
<tr>
<td>Al (111)/[110]</td>
<td>3.03</td>
<td>0.222</td>
<td>0.0275</td>
</tr>
</tbody>
</table>
Table 7. Al-N bond lengths, binding energy, $\Delta E$, and charge transfer, $\Delta Q$, for adsorption at a B-vacancy site.

<table>
<thead>
<tr>
<th>System</th>
<th>Configuration</th>
<th>Al-N bond length (Å)</th>
<th>$\Delta E$ (eV)</th>
<th>$\Delta Q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_1$ / h-BN*</td>
<td>B2</td>
<td>1.79 - 1.88</td>
<td>10.83</td>
<td>2.56</td>
</tr>
<tr>
<td>Al$_1$ / h-BN</td>
<td>B3-60</td>
<td>1.78 - 1.85</td>
<td>10.29</td>
<td>2.52</td>
</tr>
<tr>
<td>Al$_1$ / h-BN</td>
<td>B3-120</td>
<td>1.79 - 1.86</td>
<td>10.39</td>
<td>2.49</td>
</tr>
</tbody>
</table>

Table 8. Al-B bond lengths, binding energy, $\Delta E$, and charge transfer, $\Delta Q$, for adsorption at an N-vacancy site.

<table>
<thead>
<tr>
<th>System</th>
<th>Configuration</th>
<th>Al-B bond length (Å)</th>
<th>$\Delta E$ (eV)</th>
<th>$\Delta Q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_1$ / h-BN*</td>
<td>N2</td>
<td>2.09 - 2.19</td>
<td>3.51</td>
<td>2.52</td>
</tr>
<tr>
<td>Al$_1$ / h-BN</td>
<td>N3-60</td>
<td>2.10 - 2.19</td>
<td>3.37</td>
<td>2.59</td>
</tr>
<tr>
<td>Al$_1$ / h-BN</td>
<td>N3-120</td>
<td>2.11 - 2.21</td>
<td>3.45</td>
<td>2.59</td>
</tr>
</tbody>
</table>

*Single atom adsorption$^{18}$; **Bond length and energy of bond dissociation$^{47}$; ***F. Litimein et al$^{48}$. 
Figure 1. Relaxed $\textit{h}$-BN sheet with (a) B-vacancy, and (b) N-vacancy defects. For clarity, only some of the atoms around the vacancy site and from a pristine region are shown together. Here and in all other figures Bader charges are given as multiples of the electron charge and shown in the color of the atom they apply to. Distances in Å are given in black.
Figure 2. Configuration for a (7, 7) BNNT adsorbed on (100) Al surface: (a) side view; (b) top view. Al atoms that do not belong to the top surface layer are dimmed.

Figure 3. Adsorption of an Al₄ cluster to a pristine h-BN sheet in top (left), and in side (right) views.
Figure 4. Adsorption of a single Al atom to a h-BN sheet at a B-vacancy in (a) top view, and (b) side view, and at a N-vacancy in (a) top view, and (b) side view.
Figure 5. Adsorption of an Al₄ cluster to a h-BN sheet with a B-vacancy, showing the three possible adsorption configurations (a) B2, (b) B3-60, and (c) B3-120 in top (left), and in side (right) views.
Figure 6. Adsorption of an Al$_4$ cluster to a $h$-BN sheet with a N-vacancy, showing the three possible adsorption configurations (a) N2, (b) N3-60, and (c) N3-120 in top (left), and in side (right) views.
Figure 7. Adsorption of an Al₄ cluster to: (a) a zig-zag (12, 0) BNNT, and (b) to a chiral (5, 5) BNNT are shown in top (left) and in side (right) views.
Figure 8. Dependence of the Al\textsubscript{4} cluster binding energy, $\Delta E$, on (a) the BNNT diameter, $D$, and (b) on the chiral angle, $\phi$, given for zig-zag and armchair BNNTs. The data for single atom Al\textsubscript{1} adsorption\textsuperscript{18} is given for comparison. The lines are least square fits to the respective data points.
Figure 9. Dependence of (a) the total electron charge transfer, $\Delta Q$, and (b) the adsorption distance, $d$, of an Al$_4$ cluster or a single atom Al to a pristine BNNT of indices $\langle m, n \rangle$ as given versus the tube diameter, $D$. The lines are least square fits to the data points.
Figure 10. Examples of an Al₄ cluster adsorbed at a B-vacancy site on a various BNNTs, showing the three possible adsorption configurations (a) B2 on a (5, 5) BNNT, (b) B3-60 on a (7, 7) BNNT, and (c) B3-120 on a (12, 0) BNNT in top views (left), and in side views (right).
Figure 11. Examples of an Al$_4$ cluster adsorbed at an N-vacancy site on a (12, 0) BNNT, showing the three possible adsorption configurations (a) N2, (b) N3-60, and (c) N3-120 in top views (left), and in side views (right).
Figure 12. Electron density plotted as an isosurface for the adsorption of a (7, 7) BNNT on Al: (a) a pristine BNNT on (110) Al sheet - isosurface level shown at 0.074 e/Å³; (b) and (c) a BNNT with a B-vacancy and an N-vacancy, respectively, on a (001) Al sheet - isosurface level shown at 0.056 e/Å³. The ivory and blue spheres indicate B and N atoms, respectively. Aluminum atoms are shown in pink.
Figure 13. Atomic configurations at a B-vacancy site on a (7, 7) BNNT after adsorption on the (100), (110), and (111) Al surfaces in front, side, and top view, as indicated.
Figure 14. Close snapshots of the atomic configurations at an N-vacancy site on a (7, 7) BNNT after adsorption on the (100), (110), and (111) Al surfaces in front, side, and top view, as indicated.