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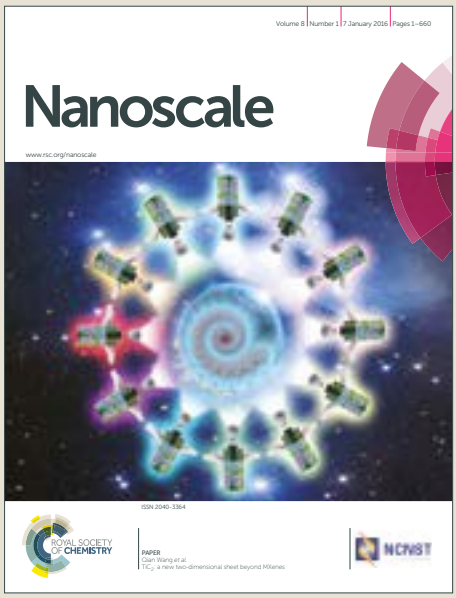

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ARTICLE

Borophene Layers on Al(111) Surface – The Finding of a Borophene Layer with hexagonal Double Chain and B_9 Nonagons from *Ab initio* Calculations

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We have studied the stability of several borophene layers on Al(111) surface and found a structure called 9R from *ab initio* calculations. This layer competes with χ_3 and β_{12} borophene layers and is made up of boron nonagons that form a network of hexagonal boron double chain. Remarkably it has no B_6 hexagon unlike other borophene layers. All the three layers lie significantly lower in energy than the honeycomb layer recently reported on Al(111) surface [Science Bulletin 2018, **63**, 282]. We discuss the structural stability and electronic structure of different borophene layers in the light of the role of the filling factor *f* of boron atoms in boron hexagons in a honeycomb layer as well as charge transfer from the Al substrate to the borophene layer as obtained from the Bader charge analysis. The electron localization function shows that the 9R layer has two-center bonding within the nonagon rings and three-center bonding between the rings. Calculations of the phonon spectra show that a free 9R layer is dynamically stable raising the hope of its isolation. The electronic structure shows that in all cases the borophene layer is metallic.

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Introduction

Boron is one of the most fascinating elements in the periodic table that forms atomically thin two dimensional nanostructures with many *polymorphs* of its so called borophene layer[1] in analogy with graphene[2] which is a *unique* atomically thin layer of its neighboring element carbon. As boron is deficient of one electron compared with carbon, its graphene-like honeycomb (H) structure is not stable. However, boron atoms can be added at the centers of the boron hexagons (B_6) in this structure which provide the required electrons and stability of the atomically thin layers. Thus a so-called alpha (α) boron layer is electronically equivalent to graphene with 2/3rd of the hexagons having a boron atom at the center such that each empty hexagon is surrounded by six hexagons having a boron atom at the center. This is known to be the most stable *unsupported* layer of boron.[3] By varying the number of filling boron atoms and their distribution, one can obtain different borophene layers.[3,4] When a borophene layer is realized in experiments on a substrate, the relative stability of different borophene layers can vary depending on the substrate[5,6] due to the possibility of charge transfer and nature of interactions between the borophene layer and the substrate. Here report the finding of a borophene layer without B_6 hexagons on Al(111) surface using *ab initio* calculations.

So far the most studied system is that of a borophene layer on Ag(111) surface in which case triangular (T), χ_3, β_{12} (see Ref. 3 for nomenclature) as well as α layers have been synthesized.[1,7] These different structures can arise due to different deposition methods and may also depend on the chemical potential of B atoms in the precursor solution.[4] Therefore, exploration of different competing structures of borophene on a substrate is very important. We have studied the stability of different borophene layers on Al(111) surface and found for the first time a borophene layer called 9R which has nonagon rings as its building blocks. This layer has a hexagonal network of boron double chain and remarkably no B_6 hexagon. Energetically it competes with χ_3 and β_{12} borophene layers that have been well studied on Ag(111) surface.[8] Recently Kim *et al*.[9] have also found from calculations that a 9R type layer structure is formed on Ag(111) surface with the assistance of Mg atoms. But our work shows a simple way to form 9R borophene layer by using Al substrate. Aluminum is an interesting case as there is AlB_2 phase in bulk where H-type layers of boron exist. Also the lattice constants of bulk Al and Ag are similar (4.05 Å and 4.09 Å, respectively) which suggest that the lattice mismatch for the borophene layer on Al(111) surface can be expected to be small and it gives opportunity to study the effects arising from different charge transfers on Al (111) and Ag(111) surfaces. Very recently an H-layer of borophene has been reported[10] using molecular been epitaxy (MBE) on Al(111). Therefore it is very desirable to study the stability of different borophene layers on

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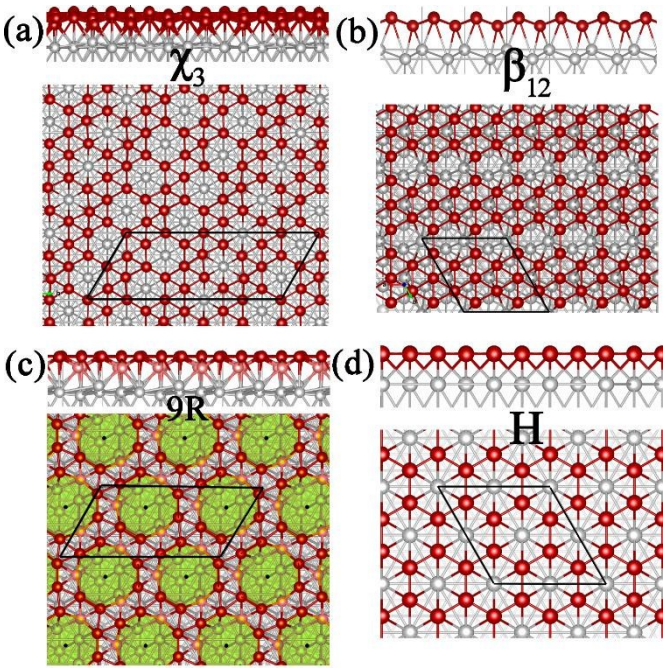

Figure 1. Side and top views of the optimized atomic structures of (a) χ_3, (b) β_{12}, (c) (9R), and (d) H borophene layers on Al(111) substrate. Grey and wine-red balls represent Al and B atoms, respectively. For the side view, only the surface layer of Al(111) slab is taken along with the borophene layer. In (c), the pale pink balls represent buckled B atoms which lie closer to the Al(111) surface while the remaining B atoms form three dimers with the shortest bond length. The unit cell used in our calculations is shown by the black lines. The nonagons are filled with green color in (c) in order to highlight the hexagonal double chain of boron. It can be seen that there is no B_6 hexagon in it. In (a) there is a zig-zag double chain while in (b) infinite chains of filled and empty hexagons alternate. Buckling can be seen in χ_3 and β_{12} borophene layers also.

Al(111) surface. We find that 9R layer is among the low lying borophene structures on Al(111) surface and interestingly a free 9R layer is dynamically stable giving hope for the possibility of its isolation.

The atomic structures of borophene layers have been generally modelled by starting with an H layer (no B atoms at the centers of hexagons) or a T layer (all hexagons in H layer have a B atom at the center).[3,4,11-14] Different borophene layers are obtained by filling (emptying) B_6 hexagons in H (T) layer in different numbers and in different fashion. The filling factor, *f*, representing the ratio of the filled B_6 hexagons to the total number of hexagons in the unit cell, plays an important role in the stability of the borophene layer. For H (T) layer, *f* attains the value 0 (1). The α layer is obtained with $f = 2/3$. In this structure, there are eight boron atoms in the unit cell. Among these, six B atoms form the H layer while the remaining two B atoms are at the centers of two hexagons and give away six electrons so that the B atoms in the H layer mimic carbon atoms. Since we are interested in borophene layer on a metal substrate which can be expected to donate some electrons to the H layer, the optimum value of *f* in such cases can be expected to be less than 2/3. Earlier theoretical studies explored different borophene layers[6] on Ag, Au, Ni, and Cu.[15] Recently the formation of H layer has been reported[10] on Al(111) substrate rather than the most stable isolated α boron layer. However, we find that the H layer lies significantly higher in energy than the 9R layer with nonagons that we report here and in which strikingly there are no B_6 hexagons. We have explored many structures including α, β_{12}, χ_3, H, T, Kagome (K) and a few other possibilities. In the χ_3 structure which competes with the 9R structure and lies lowest in energy, hexagons are formed between infinite zig-zag double chains. β_{12} layer also competes with the χ_3 layer and it is the second best on Al(111) surface. It has alternate rows of filled and empty hexagons. On the other hand in the 9R layer we have a *hexagonal network of boron double chain but no boron hexagon*.

The new form of borophene layer we have obtained on Al(111) surface, comprises of B_9 nonagons such that the interaction between them leads to the formation of a hexagonal double chain network of boron. This is in contrast to many other forms of borophene that have a 2D network of B_6 hexagons with a fraction of them having a B atom at the center. It is to be noted that isolated 9-member ring of boron forms a wheel-shaped structure when a transition metal atom such as Ir[16], Ru[17], Fe[18], and Zn[19] is doped at the center of the nonagon, as theoretical and experimental studies show. Also it has been shown[20] that such disk-shaped clusters have strong stability when there are 12 delocalized valence electrons such as for B_9^- and there is a large HOMO-LUMO gap. In the present study, instead of doping at the center, we have connected B_9 rings in a layer. We compare the results of the energetics, stability, and bonding in different borophene layers on Al(111) surface and hope that our new finding will open up new directions in the study of the family of 2D structures of boron.

Computational Methods

We have used projector augmented wave pseudopotential method[21] and generalized gradient approximation[22] for the exchange-correlation functional as implemented in Vienna Ab initio simulation package[23] (VASP). We modelled different polymorphs of borophene layer on Al(111) surface to understand their structural stability and electronic properties. The ions were relaxed until the absolute value of force on each ion became less than 0.01 eV/Å while the energy was converged with a tolerance of 10^{-5} eV. We first performed calculations on bulk FCC Al and the optimized lattice constant (4.04 Å) is in very good agreement with the experimental value (4.0495 Å). The Al(111) surface is modelled by taking a seven-layer slab with thickness of 14.025 Å and keeping the lattice parameters in the plane of the slab to be the same as in bulk. However, for boron layers on Al(111) surface we considered different supercells to allow for changes in the structure. These included 2×2, 2×4, 2×4, 2×5, 2×2, 3×3, and 2×2 supercells, respectively, for H, K, 9R, χ_3, β_{12}, α, and T borophene layers and correspondingly the Brillouin zone has been sampled by a dense **k**-points mesh of 17x17x1, 17x9x1, 17x9x1, 17x7x1, 17x17x1, 11x11x1, and 17x17x1. We allowed relaxation of all ions for pure Al(111) surface as well as

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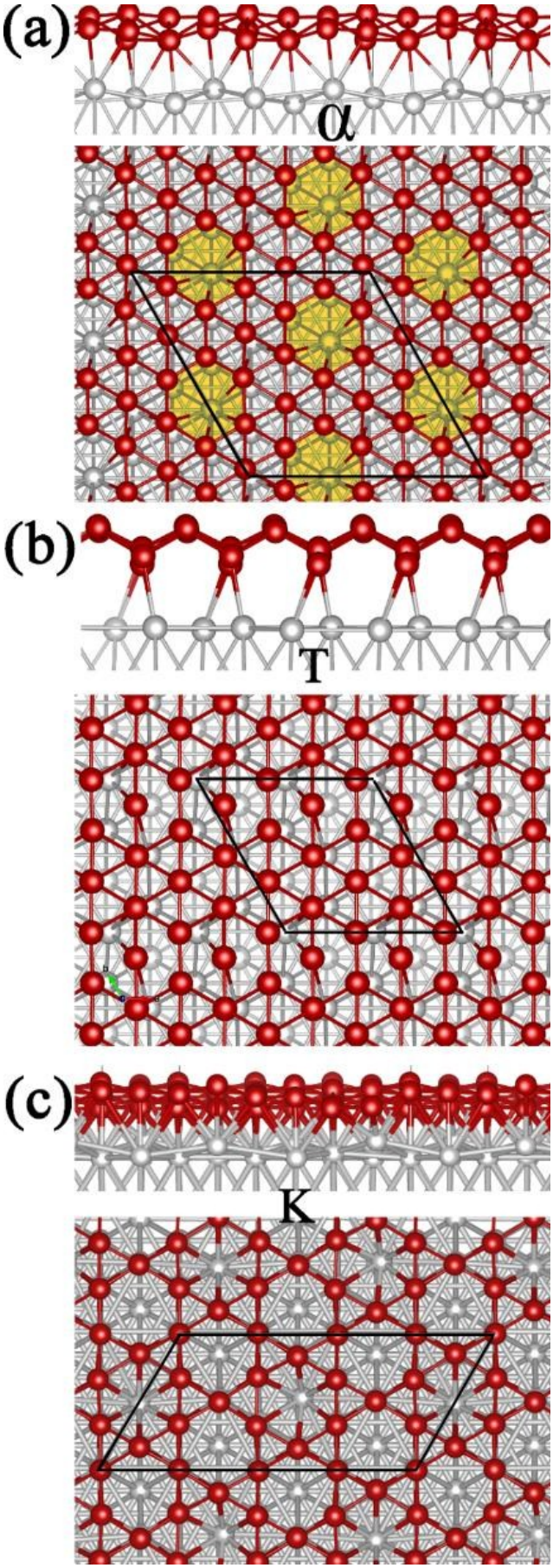

Figure 2. Side and top (only top Al layer and borophene layer shown) views of the optimized atomic structures of (a) α, (b) T, and (c) K borophene layers on Al(111) substrate. Black lines show the unit cell considered in our calculations. Note that if we remove a triangle of nearest neighbor boron atoms in the unit cell of the T layer in (b), we obtain the 9R structure. The empty hexagons are filled with yellow color in (a) in order to highlight the double chains of α boron layer. It can be seen that in (a) empty hexagons have six hexagons with a boron atom at the center around them.

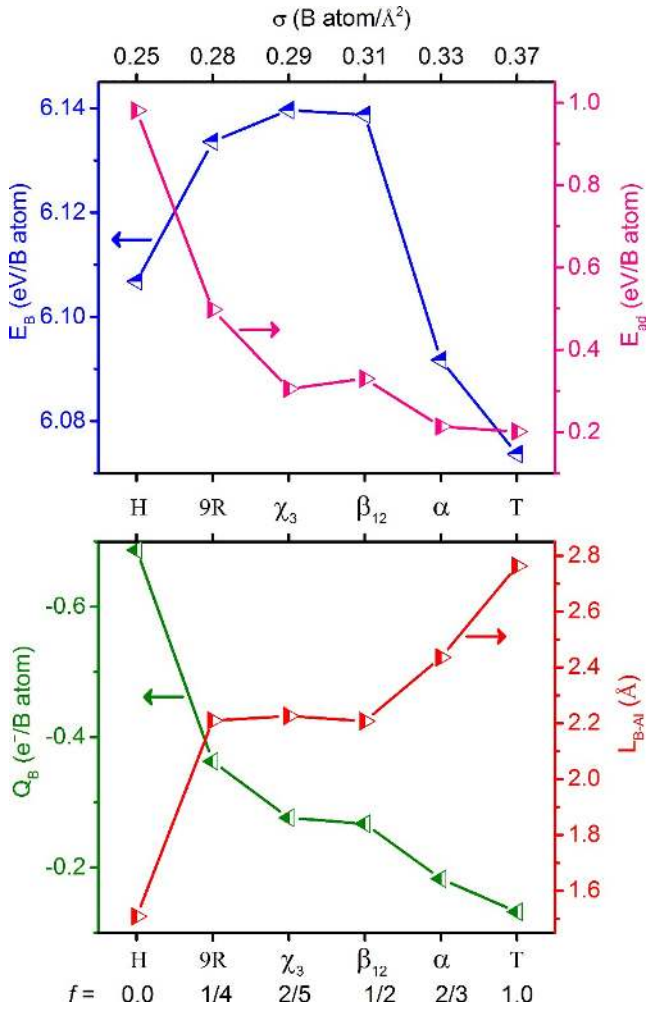

Figure 3. (Top) Cohesive energy (E_B) and adsorption energy (E_{ad}) per B atom and (bottom) average distance ($L_{B\text{-}Al}$) between the borophene layer and the substrate and the average charge transfer per B atom (Q_B) from the substrate. The layers are ordered with increasing value of *f*. The average number of B atoms (σ) per unit area is given at the top of the panels.

in the case of adsorption of borophene layers without applying any constraint and symmetry. We studied the dynamical stability of the isolated 9R borophene layer by calculating the phonon dispersion relations using the phonopy code.[24] For this purpose very tight convergence criteria in energy (10^{-8} eV) and force (0.0001 eV/Å) were used.

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Results and discussion

Several borophene layers such as H, K, α, χ_3, β_{12}, and T were modelled on Al(111) surface and the optimized atomic structures of all these layers are shown in Figures 1 and 2 in the increasing order of their energy. In order to compare the relative stability of the layers, we calculated the cohesive energy per boron atom (E_B) on Al(111) surface using the formula $E_B = [E(Al)+NE(B)-E(B_L+Al)]/N$ where $E(B_L+Al)$, E(Al), E(B) and N are the total energies of the borophene layer deposited on the Al substrate, bare Al substrate, atomic energy of boron atom and the total number of boron atoms in the considered unit cell in the combined system. Initial calculations showed that on Al(111) surface, χ_3 layer is energetically the best configuration and that the β_{12} layer is the next stable structure when compared with other borophene layers. The energy difference between these two structures are very small which show that these phases can coexist on Al surface. Similarly on Ag (111) surface, it is shown from *ab initio* calculations that three different structures of borpphene may coexist.[25] Note that the β_{12} layer has been found to be the most reactive layer among α, β_{12} and T layers.[26] Interestingly the adsorption energy per B atom (E_{ad}) defined as $E_{ad} = [E(B_L+Al)-E(B_L)-E(Al)]/N$ where $E(B_L)$ is the total energy of the free borophene layer with the same structure as on Al(111) surface, is the highest for β_{12} layer among these three as it can be seen from Figure 3.

The stability of the layers has been understood from the f value which is 2/3 for the most stable unsupported borophene layer (α). For the χ_3 and β_{12} layers, the f values are, respectively, 2/5 and 1/2 and these are less than the value for α layer as expected. Therefore, these χ_3 and β_{12} layers become more stable as some charge is transferred from Al substrate to the boron layer (see Figure 3). For the free α layer, the bonding states are fully occupied and any charge transfer would be accommodated in the anti-bonding states that would make it less stable. On the other hand, the K layer with f value of 1/4 (Figure 2d) has charge transfer from the Al substrate but it lies 0.303 eV per B atom higher in energy compared with the χ_3 layer. The relative energies of the layers are given in Table 1. *Our results show that H layer is energetically more favorable than α layer, but it does not have the lowest energy.* In the present work we introduce the term surface atomic density (σ) of boron atoms as the 9R borophene layer does not have any B_6 hexagon. This has been calculated from $\sigma = N/A$ where A is the surface area of the substrate within the considered unit cell. This is also given in Figure 3 for all the cases. It can be noted that the optimal value of σ to achieve the highest stability of the borophene layer on Al(111) surface is around 0.3 B/Å^2.

In order to find other possible structures of the borophene layer, we modified the K layer and obtained a structure with B_9 nonagons (9R) as shown in Figure 1(c). Interestingly χ_3, β_{12}, and 9R structures compete closely in energy as it can be seen in Table 1. A striking feature of the 9R layer is that the atomic structure has no B_6 hexagon while all other borophene layers have B_6 hexagons without and with a B atom at the center. χ_3 and β_{12} layers are known and have been studied on Ag(111) substrate.[8] Here we discuss in detail the 9R new borophene layer on Al(111). It has closed packed arrangement of B_9 rings which are not planar (see Figure 1(c)). There are three B_2 dimers with shortest B-B distance of 1.665 Å and they are interconnected by three boron atoms which are 0.849 Å buckled towards the substrate and with which they bind strongly. The B-B bond length between the dimer atoms and the buckled B atoms is 1.727 Å. The dimers and the buckled atoms are shown in red-wine and pale-pink balls, respectively, in Figure 1. Among the buckled atoms, two are in the bridging position to the underlying Al atoms and one is at the top site of the Al atoms. The bond distance between the substrate Al atoms and the B atoms located at the top and bridging site are 2.145 Å and 2.249 Å, respectively. However, the average bond length between the dimer atoms and the substrate Al atoms is significantly longer (2.468 Å). Thus, these dimer B atoms do not bind strongly with the substrate. The shortest B-B bonds, associated with B_2 dimers, have strong two-center (2c) bonding. The nonagon rings are bonded with each other by forming a hexagonal network of boron double chain. Note that boron double chains are important constituents of borophene layers and can be also seen in α and χ_3 layers (Figures 1 and 2) which are stable on Ag (111) surface[13,27,28] but the way double chains occur is different in each case. The B-B bond lengths in the inter-nonagon region lie in the range of 1.721 Å to 1.760 Å. The average angle between the boron atoms in the 9R layer is 125.5° and these lie in the range of 122.8° to 131.4° suggesting sp^2 type of bonding. Interestingly for the boron atoms on top of Al atoms the bonding has locally sp^3 like character as these boron atoms have significant charge transfer from the Al surface and mimic carbon. These results also suggest the occurrence of some covalent-bond characteristic between the borophene layer and the substrate.

Another important finding is that in our calculations the H layer is not the most stable form of borophene on Al substrate (refer Figure 3). This is in contrast to the recent studies.[10] Our results show that the H layer lies 0.033 eV per B atom higher in energy than the lowest energy structure χ_3. It is important to note that the energy difference between various polymorphs is

Table 1. Cohesive energy per B atom (E_B), relative energy (ΔE) with respect to the χ_3 layer, and the filling factor f for all the borophene layers we have studied. In the case of the 9R layer, the value of f is symbolic as there are no B_6 hexagons. Also in the cases of χ_3 and K layers, there are no hexagons with a B atom at the center. The values of f for 9R and K layers are the same but the cohesive energy is significantly lower for the K layer suggesting the importance of the structure.

Layer X	E_B eV/B atom	$\Delta E = E_B(\chi_3) - E_B(X)$ eV/B atom	f	Lattice parameters (Å)	
				a	b
χ_3	6.140	0.000	0.40	5.71	14.28
β_{12}	6.139	0.001	0.50	5.71	5.71
9R	6.134	0.006	0.25	5.71	11.42
H	6.107	0.033	0.00	5.71	5.71
α	6.092	0.048	0.67	8.57	8.57
T	6.074	0.066	1.00	5.71	5.71
K	5.837	0.303	0.25	5.71	11.42

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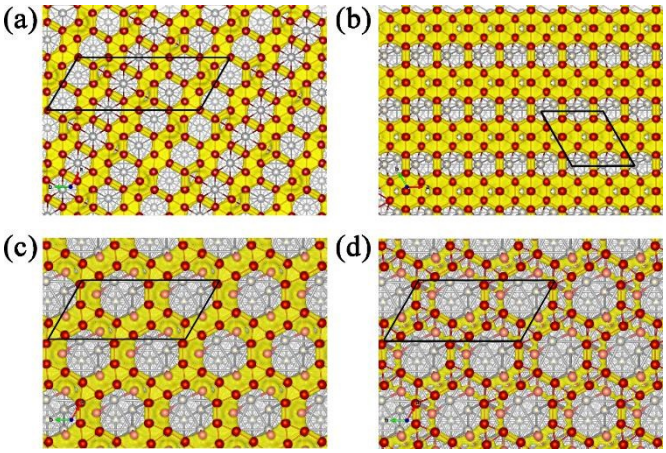

Figure 4. Plot of the charge density for (a) χ_3, (b) β_{12}, and (c and d) 9R borophene layers on Al(111) surface. For (a), (b), and (c), the isosurface value is 0.115 $e^-/Å^3$ and for (d) the value is 0.125 $e^-/Å^3$. Black line shows the unit cell considered in our calculations.

small and in some cases it is of the order of room temperature or less. Thus, the physical and chemical parameters controlled in experiments may affect the structure of the borophene layer on Al substrate. As example, by varying the thickness of the borophene layer, we can obtain different structures as shown for Pb surface.[29] The adsorption energy also contributes to the stability of the layers. We find that the value of E_{ad} is the lowest for the T layer and also very similar value for the α layer. The latter is very stable in pristine form. Also there is larger separation between the α layer and the Al surface compared with χ_3. Similarly the T layer has the weakest interaction with the surface and largest separation between the borophene layer and the surface. We find that the value of E_{ad} increases when *f* decreases and it is the highest for the H layer which is highly unstable in isolated form because there are no π electrons available in contrast to graphene. After the H layer, the next strongly interacting layers are the 9R, β_{12}, and χ_3 layers. This interaction increases the stability of these layers over the α-layer which is the most stable free borophene layer.

Further we have performed the bond length analysis for the χ_3 layer and it shows that in this structure, zig-zag double chains of boron atoms act as backbone and such chains are bonded with each other by the short bonds of length 1.599 Å – 1.655 Å (mean value 1.625 Å). The B-B bond lengths in double chains vary in the range of 1.651 Å to 1.812 Å with the mean value of 1.724 Å. Some boron atoms in the χ_3 layer are buckled by up to 0.969 Å as it can be seen in Figure 1. The average distance between the boron atoms and the substrate Al atoms ($L_{B\text{-}Al}$) is obtained by calculating the difference between the average z coordinates of B atoms and that of Al atom in the top layer of the substrate, using the formula,

$$L_{B\text{-}Al} = \frac{\sum_{z=1}^{N} B_z}{N} - \frac{\sum_{z=1}^{N_{Al}} Al_z}{N_{Al}} \quad (1)$$

where B_z and Al_z are the *z*-coordinates of B and top layer Al atoms, respectively, while N_{Al} is the total number of atoms in the top Al layer in the considered unit cell. The value of $L_{B\text{-}Al}$ is 2.226 Å for the χ_3 layer whereas for the 9R layer it is 2.209 Å. In order to compare this parameter for all the modelled layers, we have plotted the values in Figure 3. It is clear that the value of $L_{B\text{-}Al}$ decreases with decreasing *f* and it is the least for the H layer. These results suggest that the filling of boron atoms in the honeycomb network reduces its interaction with the Al substrate.

Further we calculated the Bader charge considering all electrons and the average Bader charge on B atoms (Q_B) for all the borophene layers is shown in Figure 3. Q_B has been calculated by taking an average of the excess charge on boron atoms by using the formula,

$$Q_B = \frac{\sum_{i=1}^{n}(B_i - 3)}{n} \quad (2)$$

where B_i and *n* are the total charge on interacting B atoms and the total number of B atoms that have excess number of electrons, respectively. It is important to note that the B atoms such as those at the center of hexagons having less than three electrons (positively charged) are not considered for calculating Q_B value, because these B atoms act as source of electrons to stabilize the borophene layer. The charge transfer from the substrate is maximum (~0.7 e per B atom) for the H layer as none of its hexagonal holes are filled with additional B atoms. This B layer does not have buckling as also reported in Ref. [10]. The Q_B value decreases for all other layers and it is the least for the T layer which has all its hexagonal holes filled. Thus, the *f* value has significant effect on charge transfer and interaction with the metal substrate. In the case of the 9R structure where there are no B_6 hexagons, the dimers do not have much charge transfer from the substrate, but the buckled B atoms have significant excess charge. Among these the bridging and top site B atoms have B_i values of 4.21 e and 3.62 e, respectively. Thus, the Q_B value for this case is calculated to be 1.01 e per B atom suggesting that these buckled B atoms mimic carbon.

As the χ_3, β_{12}, and 9R layers lie close in energy and are the low lying borophene structures on Al(111) surface, we have studied the bonding nature in these layers. Figure 4 shows the charge density for these cases. One can see that for the isosurface value of 0.115 e/Å^3, the charge density in the χ_3 layer is located around the bonds connecting the zig-zag double chains and also in the double chains representing two-center and multi-center bonds, respectively. When the isosurface value is increased to 0.125 e/Å^3, similar features are found to continue. In the case of the β_{12} layer, there are strong two-center bonds connecting the hexagons and delocalized charge in the chains with hexagons. For the 9R layer, the isosurface with 0.125 e/Å^3 value (Figure 4(d)) shows that the charge is located only around the nonagons which show strong covalent bonding within the B_9 ring. The bond distance analysis supports this observation. When the value of the isosurface is reduced to 0.115 e/Å^3 (Figure 4(c)), delocalized charge density can be seen on the entire hexagonal network formed by the boron double chain. In order to provide more details about the bonding nature in this structure, we calculated the electron localization

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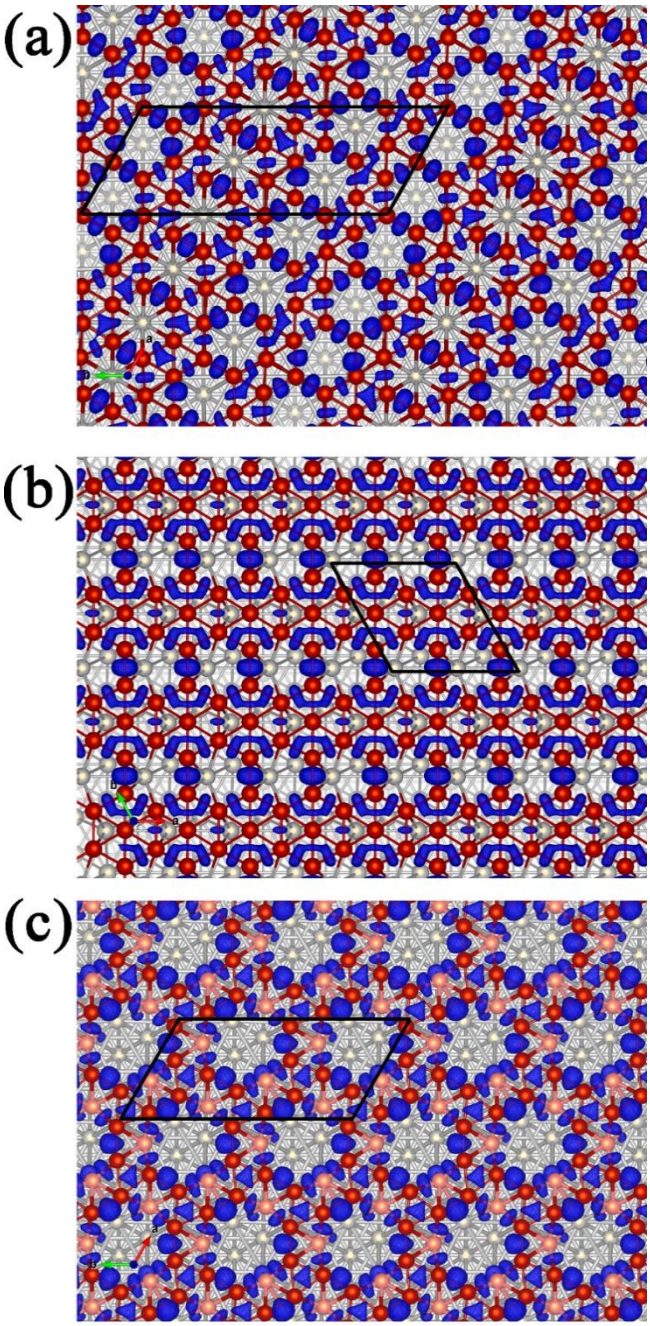

Figure 5. Plot of the electron localization function for (a) χ_3, (b) β_{12}, and (c) 9R borophene layers on Al(111) surface. In all the cases the isosurface value is 0.79 $e^-/Å^3$.

function (ELF) and it is shown in Figure 5. One can see that there is strong two-center bonding in the B_2 dimers and three-center bonding in the triangles formed by the bonding between the buckled nonagons. The buckled boron atoms are bonded with the dimers through two-center bonds which is evident from the value of ELF between them. Thus, the nonagons have two-center bonding within the rings and three-center bonding between the rings. Figure 5(a) shows the ELF plot for the χ_3 layer. One can see strong two-center bonding in bonds connecting the zig-zag boron double chains while within the chains there is two as well as multicenter bonding. A similar

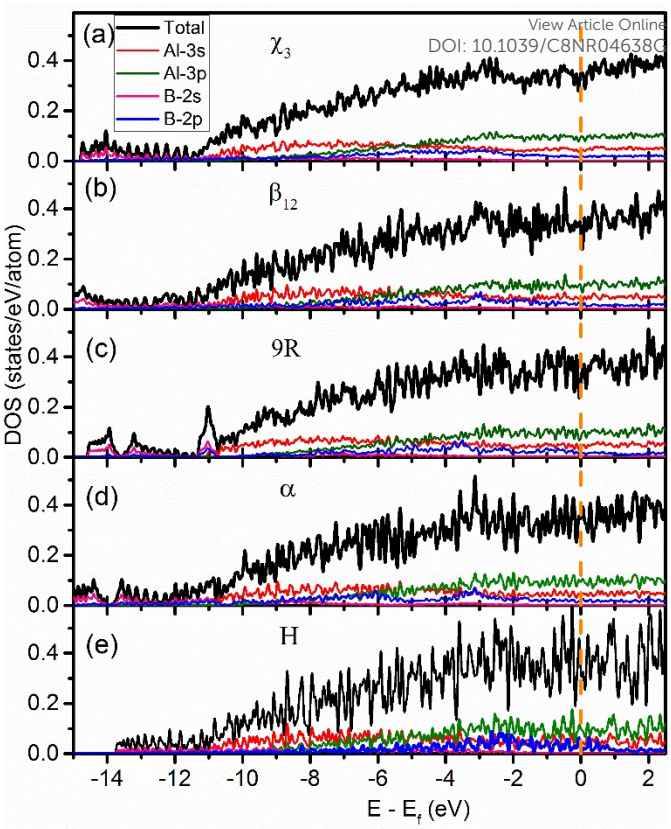

Figure 6. Total and partial densities of states for (a) χ_3, (b) β_{12}, (c) 9R, (d) α, and (e) H borophene layers on Al(111). The Fermi energy has been taken to be the reference of energy in all the cases and it is shown by the broken line. The partial density of states arising from the 2*p* orbitals of boron shows metallic behaviour of the borophene layers.

behavior is obtained for β_{12} layer as shown in Figure 5(b). There is two-center bonding in bonds connecting rows of hexagons each with a B atom at the center while two-center as well as multi-center bonding within these filled hexagons.

Figure 6 shows the total and partial densities of states (DOSs) for χ_3, β_{12}, 9R, α, and H borophene layers on Al(111) surface. The total and partial DOSs per atom have been obtained by dividing the calculated total and partial DOS for the unit cell by the total number of atoms in the unit cell. The total and partial DOSs show broadly similar behaviour in all the cases except for the 9R case where there is a significant peak at around -11 eV. Furthermore, in all cases the borophene layer shows metallic character with significant number of states near the Fermi energy (E_F). Note that a semiconducting direct band gap borophene layer has been obtained on Cu substrate.[30] The partial DOSs show that the 2*p* orbitals of boron and 3*s* and 3*p* orbitals of Al have the dominant contribution near the E_F.

An interesting question is if an isolated 9R layer would be stable. To understand this we removed the Al substrate and optimized the free 9R borophene layer. After optimization the layer becomes flat and it is shown in Fig. 7(a) and (b). One can find a 1x1 rhombus unit cell with side of 5.877 Å. We calculated the electronic structure and studied the dynamical stability of

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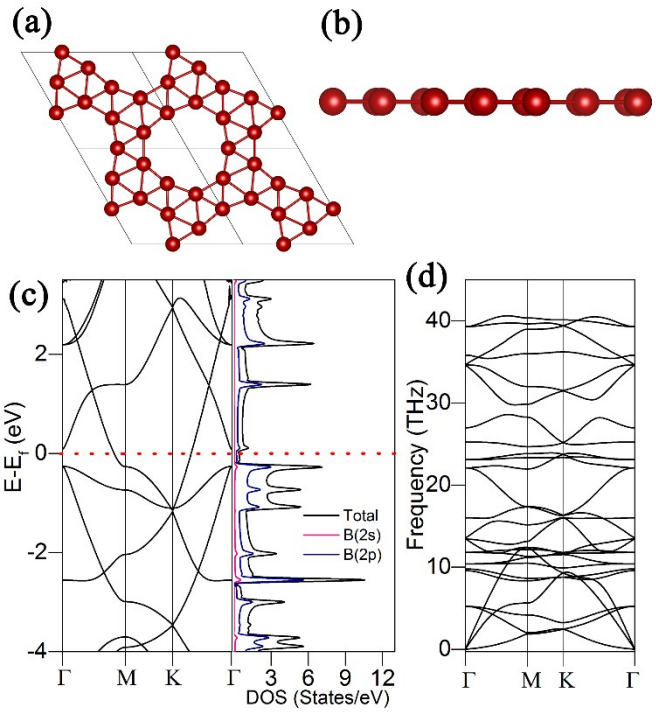

Figure 7. (a) Optimized atomic structure of isolated 9R borophene layer which becomes flat as shown in (b). In (a) we have shown four unit cells. (c) Electronic energy band structure for the isolated 9R borophene layer and the associated density of states (DOS) curves (per unit cell) with contributions from 2*s* and 2*p* orbitals of boron. (d) The calculated phonon spectrum. The symbols are symmetry points in a hexagonal Brillouin zone.

the isolated 9R borophene layer by calculating the phonon dispersion relations using the phonopy code.[23] These results of the band structure and phonon dispersion spectrum are shown in Figure 7(c) and (d), respectively. It is found that the 9R layer is metallic and non-magnetic. All the frequencies are real which confirm the dynamical stability of the 9R structure in isolated form. The band structure shows three Dirac cone-like features. Two of them are lying at -3.46 eV, -1.162 eV below the Fermi energy and the third one is at 2.94 eV above the Fermi energy. There is a low dispersion band with the bottom at -1.105 eV at the K point which is 0.057 eV above the second Dirac cone. These observations are in agreement with a previous report[9] on 9R type structure. These results give hope that it may become possible to isolate a 9R borophene layer.

Conclusions

In summary, we have studied the stability of different borophene layers on Al(111) surface from *ab initio* calculations and reported the finding of a new borophene layer structure called 9R. It is made up of nonagons with three strongly bonded B_2 dimers and three connecting B atoms in between the dimers. The B_2 dimers do not interact strongly with the substrate but the connecting B atoms are nearer to the Al(111) surface and interact strongly with polar covalent bonding character mimicking carbon. Interactions between the buckled nonagons lead to the formation of a hexagonal network of boron double chain but strikingly there is no B_6 hexagon which is the basic building block of other known borophene layers. We have shown that this novel structure competes with χ_3 and β_{12} borophene layers. The χ_3 layer has the lowest energy while β_{12} and 9R layers lie only 1 meV and 6 meV per B atom higher in energy. All these three layers lie significantly lower in energy than the H layer which has been reported recently in literature. Similar to Ag substrate, we believe that it may be possible to produce these polymorphs on Al(111) substrate. Our results on different borophene layers with the boron filling factor *f* of B_6 hexagons ranging from 0 to 1 show that this filling factor *f* plays an important role in the stability of the supported borophene layers. Also the stability depends on the charge transfer from the substrate to the borophene layer as well as the interaction with the substrate. The analysis of the bonding character and electronic properties suggests that in the 9R layer the intra B-B bonds in nonagons have two-center bonds while the inter-nonagon B-B bonds are three-center bonds. The electronic density of states shows that the borophene layer is metallic. We have further studied the stability of a free 9R borophene layer by calculating phonon spectra and found it to be dynamically stable so that there could be a possibility to isolate it. Our results give hope that it may be possible to form different templates of borophene layer and that our finding will stimulate further exploration of novel layered structures of versatile element boron.

Conflicts of interest

There are no conflicts to declare.

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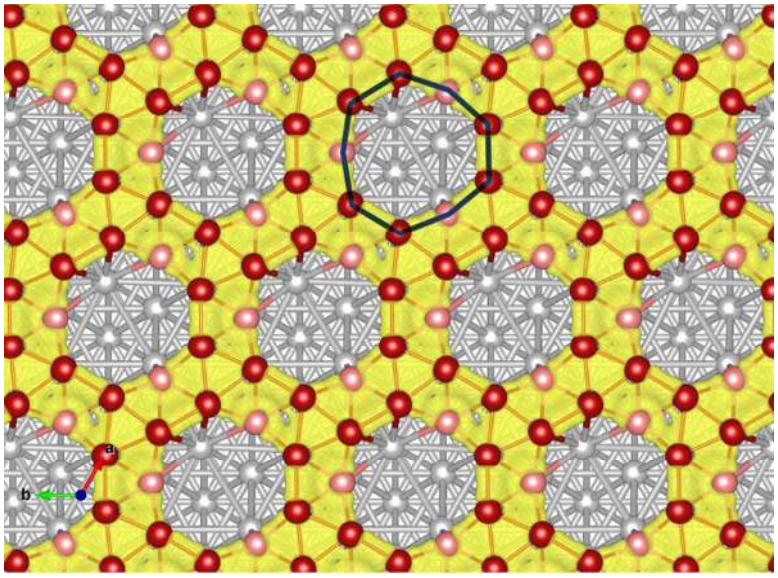

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Caption: A modulated borophene layer made of B_9 nonagons (wine and pink balls, one shown in black line) and hexagonal double chain on (111) surface of Al (grey balls).

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