Theoretical Mapping of Interaction between Alkali Metal Atoms Adsorbed on Graphene-Like BC$_3$ Monolayer

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First-principles calculations using density functional theory and two methods in comparison, Quantum ESPRESSO and Siesta, are done on large supercells which describe different placements of two identical adsorbed alkali metal atoms (of either Na or K species) on the monolayer of boron carbide BC$_3$. The energy of single-atom adsorption over the center of C$_6$ ring, the center of C$_4$B$_2$ hexagon, and over a boron atom are preliminarily estimated, the effect of applying the Grimme D2 correction on the adsorption characteristics is evaluated, and the comparison of these results with available data is discussed. The interaction of two identical Na or K atoms adsorbed at close enough distances (less than $\approx 10\,\text{Å}$) is negligible if the adsorption occurs at the opposite sides of the BC$_3$ layer, but creates a steep repulsive potential at distances less than $\approx 8\,\text{Å}$ if both atoms are adsorbed on the same side of the monolayer. Relaxation patterns resulting from the two K atoms being trapped at adjacent adsorption sites in the lattice are explained. The results suggest that the density of adsorbed K atoms on BC$_3$ can be interestingly high.

1. Introduction

Boron carbide (BC$_3$) recently emerged as an interesting 2D material, in its structure and some properties close to graphene, with the difference that its single layer is semiconducting and not semimetallic. Certain expectations are related with using this material functionalized with metals, for so different purposes as alkali metal storage in batteries, enhanced sensibilization for gas sensing, and hydrogen storage. These lines of research brought about recent works of first-principles simulation, aimed at functionalization of this material with adsorbed alkali metal atoms. Zhao et al. probed different placements of Li, Na, and K atoms over different sites of BC$_3$, compared the corresponding adsorption energies, and traced the energy profiles across the barriers between adjacent adsorption sites. They used the VASP package on 3 $\times$ 3 supercells (of primitive cells with 2 formula units) and generalized gradient approximation for the exchange-correlation after the prescription of Perdew–Burke–Ernzerhof (GGA-PBE). Naqvi et al. used the same calculation method (on a smaller, 2 $\times$ 2 supercell) to probe the docking of the same alkali metals and moreover of the alkaline earth metals, with subsequent adsorption of CH$_4$, CO$_2$, and CO molecules at the metal sites. Bafekry et al. explored different placements and estimated corresponding adsorption energies for a long list of atoms and small molecules, in a series of calculations using OpenMX and Siesta methods with GGA-PBE, for 2 $\times$ 2 supercell. All these studies, anticipating the importance of accounting for dispersion interactions in the study of the systems in question, included semiempirical D2 correction after Grimme.

Whereas these studies permit to provide some consistent idea of how would the alkali metal atoms place themselves onto, and diffuse over, the BC$_3$ layer, we find it interesting to address a hitherto unexplored issue of interaction of adsorbed atoms at the surface. This may help to parametrize this interaction to adequately model the diffusion, and/or to estimate maximal density of atoms to be placed on the surface, which may be helpful for the aforementioned discussed issues, i.e., battery electrodes or gas sensors. In view to probe this interaction, we considered supercells of larger size that in the mentioned previous studies, and decorated with two (identical) alkali metal atoms. Specifically, we studied K–K and Na–Na interactions. Two calculation methods have been used in comparison: Siesta for principal large-size calculations and Quantum ESPRESSO for smaller-size benchmarks (including the Li adsorption as well, to this end). The calculation details are given in Section 2. We start with a short discussion of pristine BC$_3$ and the single-atom adsorption on it in Section 3, checking ourselves against the previous results, and come to novel results concerning interaction in Section 4. The conclusions are summarized in Section 5.

2. Calculation Methods and Technical Details

We used two first-principles DFT methods in comparison, the plane-wave pseudopotential Quantum ESPRESSO (QE) and numerical orbitals pseudopotential Siesta. Exchange-correlation was treated within the GGA, using the PBE parameterization. Siesta is generally expected to be more efficient than plane-wave methods in treating large open low-coordinated systems, but, at the same time, potentially sensitive to the “quality” of fixed basis functions adopted. After some tests, we found it sufficient to use double-zeta basis functions for all atoms,
including notably 3p as a valence state for potassium. For sodium, the choice of the valence configuration for the construction of pseudopotential, namely, the attribution of Na 2p states (situated in a free atom at $\pm 30$ eV) either to valence states or to the core was not so obvious, as an accurate treatment of such semicore states may be essential for correct grasping of fine total-energy trends. Both cases have been tested. The pseudopotentials used were norm-conserving, generated according to the Trouiller–Martins scheme\cite{15} for the following free-atom configurations (the cutoff radii in Bohr being indicated in parentheses for each l-channel): K 4s$^1$ (3.14) 3p$^6$ (1.83) 3d$^1$ (3.14) 4f$^0$ (2.54), Na 3s$^1$ (2.30) 2p$^6$ (2.30) 3d$^0$ (2.30) 4f$^0$ (2.30), and Na 3s$^2$ (2.83) 3p$^6$ (2.83) 3d$^0$ (3.13) 4f$^0$ (3.13), B 2s$^2$ (1.74) 2p$^1$ (1.74) 3d$^0$ (1.74) 4f$^0$ (1.74), C 2s$^2$ (1.54) 2p$^2$ (1.54) 3d$^0$ (1.54) 4f$^0$ (1.54). The PAO.EnergyShift parameter in Siesta was set to 0.015 Ry, that resulted in the maximal extension of basis functions of 5 Å.

In QE calculations, the kinetic energy and the charge density cutoffs were set to 50 Ry and 400 Ry, respectively. The convergence threshold for self-consistency in energy was set to $10^{-7}$ Ry. Ultrasoft pseudopotentials have been used with QE.

A 8 × 8 × 1 undisplaced k mesh was used in electronic structure calculations for pristine BC$_3$, with appropriate reduction in larger supercells. The supercell “thickness” in the slab geometry (i.e., the separation between periodically repeated BC$_3$ monolayers) was set at 30 Å, sufficient to exclude spurious interaction of adatoms with substrate across the vacuum layer, and to provide a reference “no interaction” energy of monolayer plus isolated atom when the latter was removed to the maximal distance (15 Å).

### 3. Pristine BC$_3$ and Adsorption of Alkali Metals on it

Planar Boron carbide, described in the study by Tanaka et al.,\cite{31} is characterized by a honeycomb planar lattice like that of graphene, in which one carbon atom out of four (equivalently, two atoms within a $2 \times 2$ graphene supercell) is substituted by boron. In principle, one can imagine different relative placements of B atoms on the honeycomb lattice, corresponding to para-, ortho-, and meta-isomers (referred to as types A, B, and C in the study by Zaporotskova and Boroznin\cite{16}). However, the para-isomer is singled out by its more regular and symmetric arrangement in which every carbon atom has exactly one boron neighbor, and there are no B–B bonds. This isomer retains the hexagonal (super)structure, which makes a pattern of C$_6$ (perfect) hexagons with the C–C bond lengths $d_{\text{C-C}} \approx 1.4$ Å and C$_2$B$_2$ (distorted) hexagons around the perfect ones, with the C–B bond lengths $d_{\text{C-B}} \approx 1.6$ Å. The lattice parameter of this hexagonal unit cell which hosts two formula units is $a = \sqrt{3}(d_{\text{C-C}} + d_{\text{C-B}})$. Differently from perfect infinite graphene which has a zero gap, BC$_3$ has the band gap of 0.65 eV (in a single sheet). A summary of previous data concerning pristine BC$_3$, along with our present results, is shown in Table 1.

The works aimed at the study of alkali metal adsorption on BC$_3$ from first principles are not numerous. Understandably, the possible adsorption sites probed in previous works (notably Zhao et al.\cite{5} are over the center of one or another hexagon, over the C–C or C–B bonds, or over the one or the other atom species. Zhao et al. argued (with respect to Li, Na, and K on BC$_3$, which we could confirm, see the following text), that only three of these sites, over the both hexagons and atop a boron atom, emerge as local energy minima for adsorption.

There seems to be a consensus among the calculations done that the hollow site over the center of the C$_6$ hexagon, referred to as HC in the following, is the preferential one, closely followed by the hollow site over the center of the C$_2$B$_2$ hexagon, referred to as HB. With respect to the magnitudes of the adsorption energy, however, there seems to be a controversy we show in Table 2. We carried out our calculations using sufficiently large supercell (in terms of B$_2$C$_6$ unit cells) per adsorption atom and inspected several possible sources of controversy. Without much details given in the papers cited, good “suspects” could be the basis set superposition error (BSSE,\cite{18}), potentially dangerous in methods with atom-centered basis functions (e.g., the study by Bafekry et al.,\cite{9}), and the neglection of the magnetic state for an isolated potassium atom, both factors tending to overestimate the adsorption energy. Our result shown in Table 2 is obtained from comparing the energies of two sufficiently “thick” supercells of identical size, possessing the same 73 atoms: the relaxed system upon K adsorption, and the pristine BC$_3$ layer with the K atom removed away from the layer at a distance that would preclude the overlap of their basis functions. This does not fully removes the BSSE (that could have been done by introducing ghost atoms), but substantially cancels systematic errors.

#### 3.1. Siesta Calculations for Single Adsorbed Atoms (Na and K)

A smooth variation of the total energy and magnetic moment on approaching an alkali metal atom (K and Na have been tested) to the BC$_3$ sheet (without performing any structure relaxation and only converging the electronic structure) is shown in Figure 1. For the record, the lattice parameter in these trial calculations done with Siesta was fixed at $a = 5.170$ Å. The idea of this exercise was to inspect the sharpness of the potential energy minimum, and, in the case of Na, to test the stability of results against the choice of pseudopotential, in the construction of which the arguments could have been found to explicitly include the semicore Na$^{2p}$ states among the “valence” ones, or attribute them to the core. As shown in Figure 1 (right panel), the difference in the potential energy profiles stemming from these two choices is acceptably small yet noticeable. For the subsequent study of Na–Na interactions, we “pragmatically” opted for using the “small core” Na pseudopotential with 2p treated as valence.

### Table 1. Calculated properties of single-layer BC$_3$.

| Method     | Ref.  | $d_{\text{C-C}}$ [Å] | $d_{\text{C-B}}$ [Å] | $a$ [Å] | $E_{\text{gap}}$ [eV] |
|------------|-------|----------------------|-----------------------|--------|---------------------|
| Siesta GGA | Present work | 1.428 | 1.564 | 5.183 | 0.67 |
| QE GGA     | Present work | 1.421 | 1.564 | 5.170 | 0.51 |
| VASP GGA   | \cite{17} | 1.422 | 1.565 | 5.174 | 0.62 |
| VASP GGA   | \cite{5}   | 1.42 | 1.57 | 5.17 | 0.66 |
| Siesta GGA | \cite{9}   | 1.422 | 1.562 | 5.170 | 0.67 |
This choice results in more accurate estimation of equilibrium atom-to-monolayer distance and yields a better pronounced discrimination between the adsorption energies of Na and K atoms, which seems to be consistent with general trend found by other calculations listed in Table 2 (whatever would be the sources of error in reported absolute energy values). The depth of the total energy profile gives a fair estimate of the adsorption energy. The magnetic moment exhibits instability throughout the range of distances 3–7 Å for K, or 5–8 Å for Na, as the outer s state of the corresponding alkali metal, which carries an unpaired spin in a free atom, starts to interact with the wavefunctions of the BC3 layer. The corresponding part is therefore not shown in the magnetic moment plots in Figure 1. Upon adsorption and after atomic and electronic relaxation, the magnetic moment is fully dissolved (differently, e.g., from the situation with graphene, on which the adsorbed K atom retains its magnetic moment). The asymptotic value of the magnetic moment corresponding to large distances in Figure 1 does not reach $1\mu_B$ – probably due to a purely technical drawback that very fine k and energy mesh is needed to cope with very narrow s-states energy levels).

The results obtained in the course of relaxing atomic positions within a supercell of a fixed size, corresponding to the lattice parameter $a = 5.17$ Å without structure relaxation. For Na, the results are shown for two norm-conserving pseudopotentials, for the cases of Na 2p states treated as valence states or attributed to the core. See text for details.

### Table 2. Calculated parameters of alkali metal atoms adsorbed at C6 hollow site of BC3. $E_a$: adsorption energy (defined positive, i.e., corresponding to energy gain on adsorption, in all cases); $h$: the height of the adsorbed atom over the BC3 plane. See text for detail.

| Method          | Ref.        | Supercell | $E_a$ [eV] | $h$ [Å] |
|-----------------|-------------|-----------|-----------|---------|
| OpenMX or Siesta (GGA) | [9]         | $2 \times 2 \times 1$ | 0.81     | 2.31    |
| VASP (GGA)      | [8]         | $2 \times 2 \times 1$ | 5.13     | 1.74    |
| VASP (GGA)      | [5]         | $3 \times 3 \times 1$ | 1.26     | 1.77    |
| Siesta (GGA)    | Present work | $3 \times 3 \times 1$ | 1.53     | 2.18    |
| QE (GGA)        | Present work | $3 \times 3 \times 1$ | 2.56     | 1.73    |

*With Grimme-D2; for results with Grimme-D2 correction, see next table; $a = 5.17$ Å fixed.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Total energy (upper plots, blue curves, axes on the left) and magnetic moment (lower plots, red dots, axes on the right) as functions of the height of the alkali metal atom (left panel: K, right panel: Na) over the BC3 layer. Calculations are done with lattice constant fixed at $a = 5.17$ Å without structure relaxation. For Na, the results are shown for two norm-conserving pseudopotentials, for the cases of Na 2p states treated as valence states or attributed to the core. See text for details.

3.2. Adsorption Energies Calculated with QE; Role of Dispersion Interactions

Independently, we calculated the adsorption energy of $M = \{\text{Li}, \text{Na}, \text{K}\}$ atoms at HC, HB and AB sites by the QE method, also for
In the next section, we come to the analysis of interaction between adsorbed alkali metal atoms.

4. Interaction of Alkali Metal Atoms Adsorbed on BC₃

4.1. Spatial Map of M–M Interaction Energies on the BC₃ Surface

To gain a substantial and reliable information concerning the interaction between alkali metal atoms M adsorbed on BC₃ (specifically, Na and K have been studied), we staged a series of simulations on large supercells containing two adsorbed atoms. One of them, the “reference atom,” was placed in a (lowest-energy) HC position over the center of a C₆ ring, and the other, “trial” atom—at different local-minima positions at different distances from the reference atom. Within the 5 × 5 supercell (200 atoms), all nonequivalent adsorption positions have been explored within the “irreducible wedge” (shown in inset of Figure 2) closest to a given HC site. This amounted to four HC positions, 9 HB positions (over the center of C₆B₂ hexagons), and 7 AB positions (atom of a boron atom), hence the positions confirmed (see previous section) correspond to stable (local energy minima) adsorption sites. Moreover, the configurations in which the second (trial) atom was adsorbed at the opposite side of the BC₃ monolayer have been tested—all the HC, HB, and AB sites, mentioned earlier, plus directly at the reference site, in a mirror position from the reference atom. In all cases, an unconstrained relaxation has been performed (fixing however the supercell parameters), which yielded the total energy and the equilibrium geometry.

For M–M distances starting from ≈7 Å onwards, the relaxation patterns are barely visible: the adsorbed atoms reside in their nominal positions, so that only tiny modifications of interatomic distances come about. The BC₃ layer in all cases looks extremely rigid and planar, without a marked tendency toward bending or warping. At shorter distances, the repulsion between the adsorbed atoms pushes them out of symmetry positions; the examples of this will be discussed in the following text. In fact, the stabilization of the trial atom in the nearest HB or AB position to the reference atom becomes impossible, because the atoms drift away from such configuration. This refers to the atoms adsorbed at the same side of the CB₁ plane. The atoms

| Table 3. Adsorption energy (defined positive for energy gain) and height over BC₃ layer for Li, Na, and K atoms in three symmetric positions, according to QE calculations with PBE (upper line in each block for a given atom) and with Grimme-D2 correction included (lower line; the value in parentheses gives the difference with respect to the PBE value). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Adsorption energy [eV] |                 | Height over layer [Å] |                 |                 |                 |
|                 | HC   | HB   | AB   | HC   | HB   | AB   |
| Li              | 2.56 | 2.47 | 2.09 | 1.73 | 1.72 | 1.91 |
|                 | 2.91 (+0.36) | 2.85 (+0.39) | 2.41 (0.32) | 1.80 (+0.08) | 1.73 (+0.06) | 1.73 (+0.18) |
| Na              | 1.85 | 1.83 | 1.69 | 2.26 | 2.22 | 2.28 |
|                 | 2.23 (+0.38) | 2.22 (+0.40) | 2.02 (0.33) | 2.28 (0.02) | 2.23 (0.01) | 2.23 (+0.05) |
| K               | 2.31 | 2.25 | 2.20 | 2.63 | 2.62 | 2.65 |
|                 | 2.61 (+0.29) | 2.56 (+0.30) | 2.48 (+0.28) | 2.63 (+0.00) | 2.62 (+0.00) | 2.58 (+0.07) |
adsorbed “across the plane” remain practically insensitive to the closeness of the reference atom, exhibiting no perturbations in their relaxation pattern, and the energies which are largely independent on the in-plane distance to the reference atom.

The “interaction energies” shown in Figure 2 are defined as total energies from each calculations, expressed relative to the energy of supercell in which the two atoms are at maximally separated HC positions, within the given type of placement (i.e., either both above, or one below the BC3$_{\text{layer}}$), effectively setting the “infinity limit” within the given supercell size. We note that these “infinity limit” energies are not exactly equal for the trial atom being on the same side of the BC3$_{\text{plane}}$ as the reference atom, or on the opposite side. In fact, the second energy is lower by 0.03 eV for Na adsorption and by 0.05 eV for K adsorption. This disparity (which would disappear be the atoms at really sufficiently far distance) can be considered as a measure of the effect of our limited supercell size.

Choosing such “distant M–M” limit of two adsorbed atoms as the reference level leaves the adsorption energy at a HC site out of our grasp; however, this issue has been separately addressed in the previous section. In fact, the differences between adsorption energies at HC, HB, and AB sites, or otherwise the barrier heights, are easily readable from Figure 2, and are instructive to discuss.

We note first that for “inverted” adsorption of a trial atom (cf. bottom panels in Figure 2), the energy of its interaction with the reference one is practically independent on interatomic distance, and follows the universal trend that HB positions are, on the average, higher in energy by $\approx 0.03$ eV than the HC ones, whereas the AB positions are higher than the HC by $\approx 0.08$ eV, in case of K adsorption. As for the Na adsorption, the energies at HC and HB positions are almost identical within the “numerical noise,” the HB ones being just a bit higher, whereas the energies in AB positions are much higher, by $\approx 0.12$ eV. This simply passes the information about barrier heights (differences between adsorption energies at different sites), which was already addressed in the previous section, see e.g., Table 3. However, here it appears not as a “random” number but as a “statistically credible” result.

We can again refer to the similarity of the present estimation of barrier heights with those given by Zhao et al.,\textsuperscript{[5]} notably in Figure 5c,d of this publication.

The bottom panel of Figure 2 suggests that the alkali metal atoms “do not see each other” across the BC3$_{\text{plane}}$ till the $M–M$ distance becomes really short, within the closest

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Figure 2. Map of interaction energies between alkali metal atoms (two panels on the left refer to K–K, two on the right to Na–Na), adsorbed at different sites of the BC3$_{\text{layer}}$ (marked by circles, squares, and triangles in the “irreducible part” of the 5 x 5 supercell schematically shown in the inset), and the reference atom in the HC position (the bottom blue point in the inset). HC positions (over C$_{\text{h}}$ hexagons), HB positions (over C$_{\text{b}}$B$_{\text{2}}$ hexagons), and AB positions (over B atoms) are indicated by different symbols. The two upper panels refer to the interactions between atoms adsorbed at the same side of the BC3$_{\text{plane}}$, the bottom panels—between atoms adsorbed at the opposite sides, in both cases—as function of the in-plane distances between the adsorption sites. Positions included in the mapping are marked by symbols, as in the main plot. A primitive cell of BC3 is outlined by a dashed contour in the inset.
adsorption sites. Still, this does not bring about neither an “asymmetric” relaxation nor noticeable augmentation of the z-coordinate; the adsorbed atoms remain well centered at their respective sites. The “double occupation” of a HC adsorption site from both sides of the BC₃ plane, whereby the two K atoms remain stable at a distance 5.4 Å (hence at a regular height above the layer) is by far not so energetically unfavorable as it could have been a priori anticipated; it costs only 0.1 eV to bring a K atom from a distant HC site onto this “antipode” reference site; for Na atoms the corresponding energy is 0.18 eV.

The established hierarchy of barrier heights, revealed via interaction energies being independent on the M–M distance, is also valid for adsorptions at the same side of the BC₃ plane (see upper panels of Figure 2), provided the M atoms are placed not closer than ≃10 Å. At shorter distances, the energy barrier rapidly increases, forming a nearly rigid core of the radius of ≃5 Å for Na and ≃6 Å for K, irrespectively of the adsorption site concerned.

4.2. Unusual Relaxation Patterns of Closely Placed Adsorbed Atoms

The placement of trial atoms at adsorption sites close (within ≃8 Å) of the reference atom resulted in a noticeable repulsion of both atoms in their relaxed configurations, as shown in Figure 3 for the case of potassium. The reference atom displaces in its “nest” over the C₆ ring without however leaving the latter, whereas the trial atom could have been pushed from its initial “on top of B” position onto that above the C–B bond; see the case AB in Figure 3. It was not possible to stabilize the trial atoms in AB or HB positions closest to the reference atom, since the interacting atoms were pushed apart into “second-neighbors” configurations, shown in Figure 3. This strengthens an idea of “hard core” repulsion potential which effectively prevents the potassium atoms to come closer than about 6 Å. This minimal distance corresponds to both atoms residing over the second-neighbor C₆–C₆ or C₆–C₆B₂ hexagons, slightly pushed apart from the respective centers, as shown in Figure 3. We note that the z-coordinates of potassium atoms are not much affected by their relaxation “situation”; also the warping of the BC₃ layer, although noticeable around such “strong” relaxations, remains small and difficult to make sense of.

5. Conclusion

Summarizing, we found that alkali metal atoms, sodium and potassium, adsorbed over the BC₃ monolayer, interact strongly repulsively at distances smaller than ≃10 Å, and otherwise remain relatively insensitive to the mutual presence, feeling the “usual” landscape of potential barriers of ≲0.1 eV (case of K) or ≲0.15 eV (case of Na) in their movement over the BC₃ plane. A combination of relatively high adsorption energy with respectively low barriers, especially prominent for potassium, known already from early works, suggested a quite interesting interplay of sticking and mobility. Now we conclude that even relatively high concentration of adsorbed K atoms might not prevent them from acting as a highly mobile “gas” on the BC₃ surface. This may open perspectives for further more realistic simulations and interesting applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.
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