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Stabilizing honeycomb borophene by beryllium decoration: a computational study

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Supplementary information

I. Computational details, convergence and adsorption: Values used for plane wave cut-off, number of k-points and size of the vacuum layer in *c*-axis direction separating periodic images were fixed through rigorous convergence tests, with total energies converged to 1 meV. Using the converged values of cut-off, number of k-points and size of the vacuum layer, the structure of the honeycomb borophene was relaxed and the geometry is shown in Figure 1.

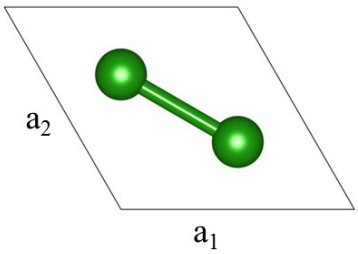

Figure 1: The unit cell of hexagonal honeycomb borophene.

The unit cell is hexagonal (space group P6mm) with lattice parameters $a_1=a_2=2.92$Å and the angle between them is 120°. The bond length is 1.68Å and the structure is completely planar. All the adsorption calculations were carried out on the three probable sites on *hc*-B, viz. hollow (H), Bridge (B) and Atop (A) as shown in Figure 2.

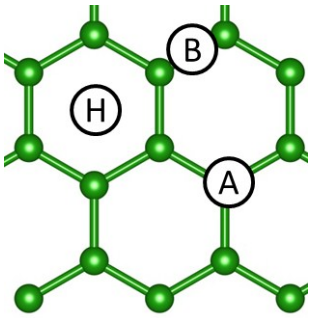

Figure 2: The hollow (H), Bridge (B) and Atop (A) adsorption sites on *hc*-B.

Table I shows a comparison of cohesive energy and adsorption energy for light metal atoms adsorbed at the most probable site of *hc*-B. Since the adsorption energy is greater than cohesive energy for each atom, we conclude that there will be no tendency for the metals to form a cluster and agglomerate on *hc*-B.

Table I: The cohesive energies and adsorption energies of light metal atoms on the most probable site of *hc*-B.

Atom	E_{coh} (eV)[1]	E_{ads} (eV)
Li	1.63	2.83
Be	3.32	5.12
Na	1.113	1.49
Mg	1.51	2.40
Al	3.39	4.40

Table II: Calculated adsorption energy of most elements of alkali metal and alkaline earth metal group, made to compare trend in adsorption energy down a group of elements. It is clearly seen that adsorption energy decreses down a group, owing to increase in atomic size. The negative values mean no adsorption or binding to the surface, and in these cases, one cannot see any trend, except that these are not adsorbed on to *hc*-B. The second column in table II pertains to the height of the adsorbed atom above the sheet.

Atom	E_{ads} (eV)	*h* (Å)
Li	2.83	1.45
Be	5.12	0.68
Na	1.49	2.13
Mg	2.40	1.75
K	-0.72	2.38
Ca	1.88	1.53
Rb	-0.33	2.54
Sr	0.79	2.25

II. Phonon dispersion in metal adsorbed *hc*-B: The phonon dispersion of Li, Na and Mg adsorbed on *hc*-B are shown in Figure 3, as calculated with the program PHONOPY. From these its perfectly clear that all of them will furnish thermally unstable structures owing to the imaginary frequencies in the dispersion.

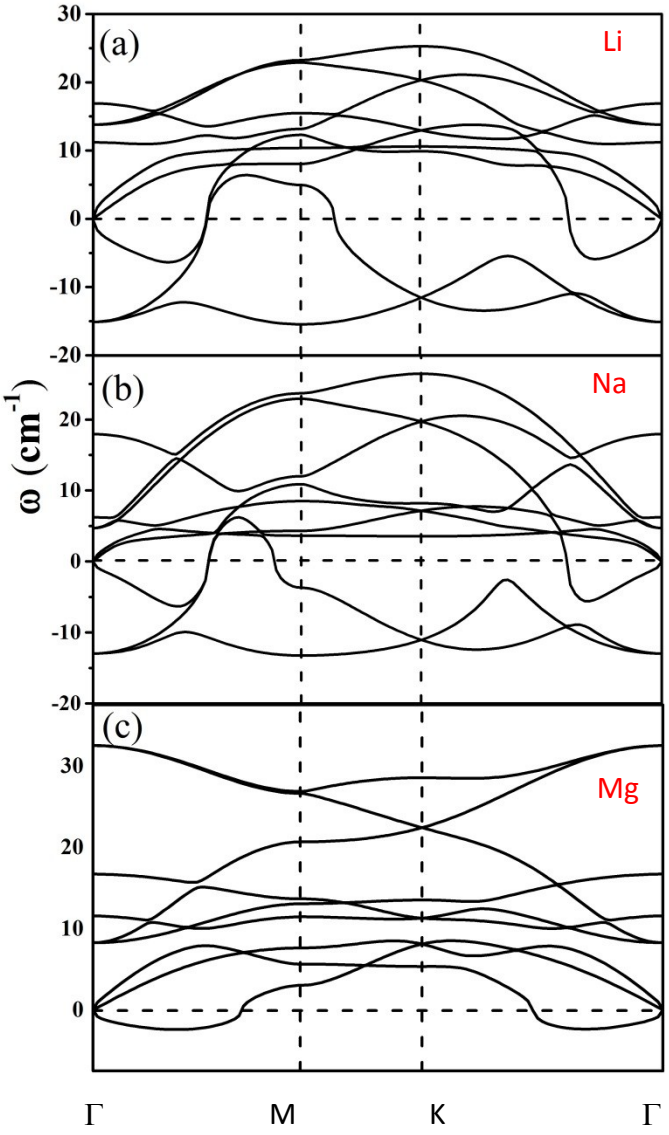

Figure 3: The phonon distrubutions of (a) Li (b) Na and (c) Mg adsorbed on *hc*-B.

III. Adsorption of transition metals: Adsorption of various transition metal atoms on *hc*-B surface was tried out. Only Ag and

Au display a tendency to cluster, based on a comparison of the value of their cohesive energy and adsorption energy (Table II). All transition metal atoms considered showed a preferential adsorption at the hollow site, except in case of Au, Pd and Pt, where the bridge was preferred. The charge transfer in the adsorbed state was calculated with Bader analysis of charge density (Table III). The charge transfer in these systems is reversed, ie, from *hc*-B to metal atom. The DOS is shown in Figure 4. The DOS shows mixing of the boron and transition metal states, presenting a different kind of bonding, unlike the case of alkali or alkaline earth metals considered in the paper.

Table II: The cohesive energies and adsorption energies of transition metal atoms on the most probable site of *hc*-B.

TM Atom	E_{coh} (eV)[1]	E_{ads} (eV)
Fe	4.28	5.53
Co	4.39	5.79
Ni	4.44	5.42
Cu	3.49	3.66
Zn	1.35	1.49
Ag	2.95	2.89
Au	3.81	3.52
Pd	3.89	4.36
Pt	5.84	6.12

Table III: The preferred site of each transition metal atom (S), their cohesive energies (E_{coh}), adsorption energies on hc-B (E_{ads}), height at which the atom is adsorbed (h) and charge transferred from the metal atom to the boron sheet (C). Minus sign shows reverse transfer.

TM atom	Site	h(Å)	C
Fe	hollow	1.91	0.61
Co	hollow	1.09	0.41
Ni	hollow	1.23	0.29

Cu	hollow	1.51	0.28
Zn	hollow	1.74	0.37
Ag	hollow	2.06	0.11
Au	bridge	2.27	-0.05
Pd	bridge	1.96	-0.07
Pt	bridge	2	-0.17

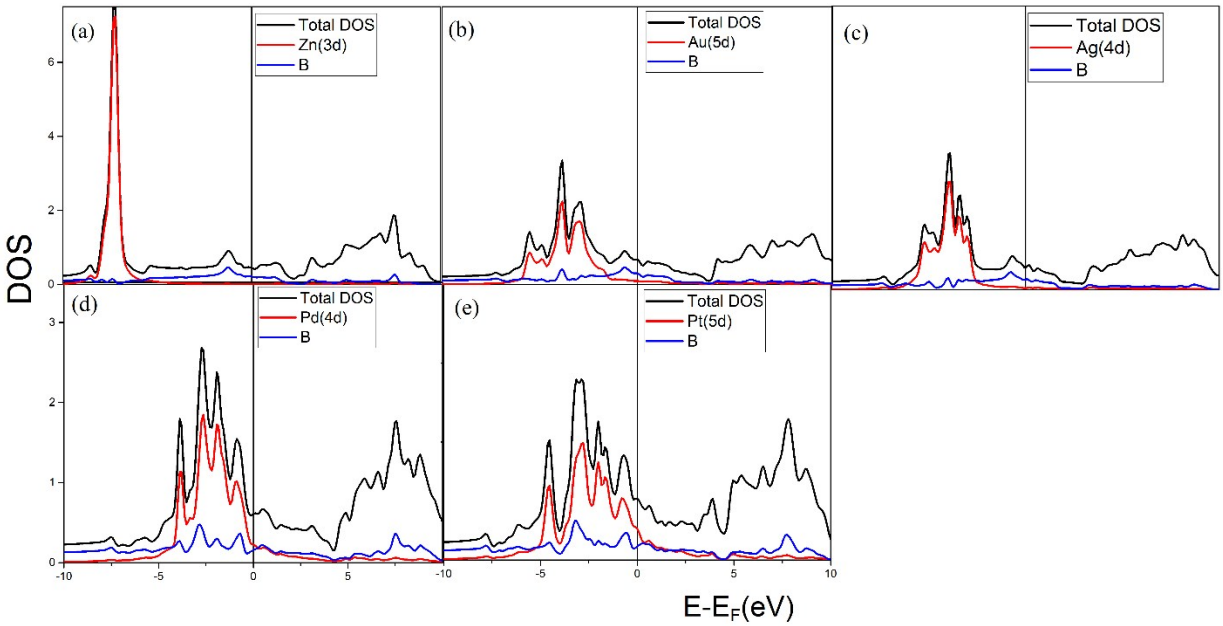

Figure 4: The total density of states, PDOS of the TM metal atom and PDOS of borophene.

References:

[1] C. Kittel, Introduction to Solid State Physics, 8 (Wiley, 2004)