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Energy decomposition analysis of neutral and negatively charged borophenes

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ABSTRACT

The effect of external static charging on borophenes – 2D boron crystals – is investigated by using first principles calculations. The influence of the excess negative charge on the stability of the 2D structures is examined using a very simple analysis of decomposition of the binding energy of a given boron layer into contributions coming from boron atoms that have different coordination numbers. This analysis is important to understand how the local neighbourhood of an atom influences the overall stability of the monolayer structure. The decomposition is done for the α-sheet and its related family of structures. From this analysis, we have found a preference for 2D boron crystals with very small or very high charges per atom. The structures with intermediate charges are energetically not favourable. We have also found a clear preference in terms of binding energy for the experimentally seen γ-sheet and δ-sheet structures that is almost independent on the considered excess of negative charge of the structures. On the other hand, we have shown that a model based solely on nearest-neighbour interactions, although instructive, is too simple to predict binding energies accurately.

1. Introduction

Like carbon, boron can adopt bonding configurations that favor the formation of low-dimensional structures such as nanotubes, fullerenes, and sheets. With these different forms (or allotropes) could come interesting and novel properties distinct from those of the bulk structures. Two-dimensional (2D) allotropes of boron have been studied theoretically more extensively during the last ten years [1]. There are different proposals based on first principles calculations for the atomic structure of 2D boron crystals: buckled triangular (bt) sheet [2–4], α-sheet and related planar and quasi-planar layers [5–8], non-zero thick layers and bilayers [9–11], B_{12}-based layers [9], and other structures [12,7]. However, the experimental realization came just recently and confirmed only some of those structures.

Tai et al. [13] reported the synthesis of 2D boron structures on copper foils by chemical vapor deposition (CVD), by combining boron and B_2O_3 to make B_2O_2 vapour and reducing it with hydrogen while passing it over copper foil. Their 2D boron structure consists of B_{12} icosahedra held together by B_2 dumbbells and behaves as a direct band gap semiconductor. The same year, Mannix et al. [14] reported the synthesis of 2D boron sheets grown on a single crystal Ag(111) substrate using molecular beam epitaxy (MBE) under ultrahigh-vacuum (UHV) conditions. Two distinct forms of 2D boron structures have been observed, both consisting of triangular layers with some fraction of missing atoms (empty hexagons, hexagonal holes or vacancies) in the hexagonal lattice. In one form (labeled in this work as γ-sheet, see Fig. 1b) rows of filled hexagons are separated by chains of empty hexagons; in the other (labeled in this work as δ-sheet, see Fig. 1b), boron atoms take up narrow zig-zag stripes separated by arrays of empty hexagons. Should be noted that the first form was initially proposed to be the bt sheet (see Fig. 1a) [14], and then recently confirmed to be the γ-sheet [15]. Similarly, Feng et al. [16] used MBE to grow 2D sheets of boron on a metallic Ag(111) substrate by direct evaporation of a pure boron source under UHV conditions. They also observed two different structures corresponding to the described above γ and δ sheets. According to this study, both sheets are flat, metallic in character, and quite stable against oxidation in air. Moreover, the sheets appear to be robust and only weakly bound to their substrate, indicating that it might be possible to obtain freestanding sheets, but the question of how to detach the sheets from the substrates is still open. Finally, in the most recent experimental study [17] two reproducible metallic phases of 2D boron are found on Ag (111), one of them being the γ-sheet and the other one presumably being the α-sheet. All these experimental studies pave the way to fascinating applications in nanoelectronic and nanophotonic devices [1,13,18].

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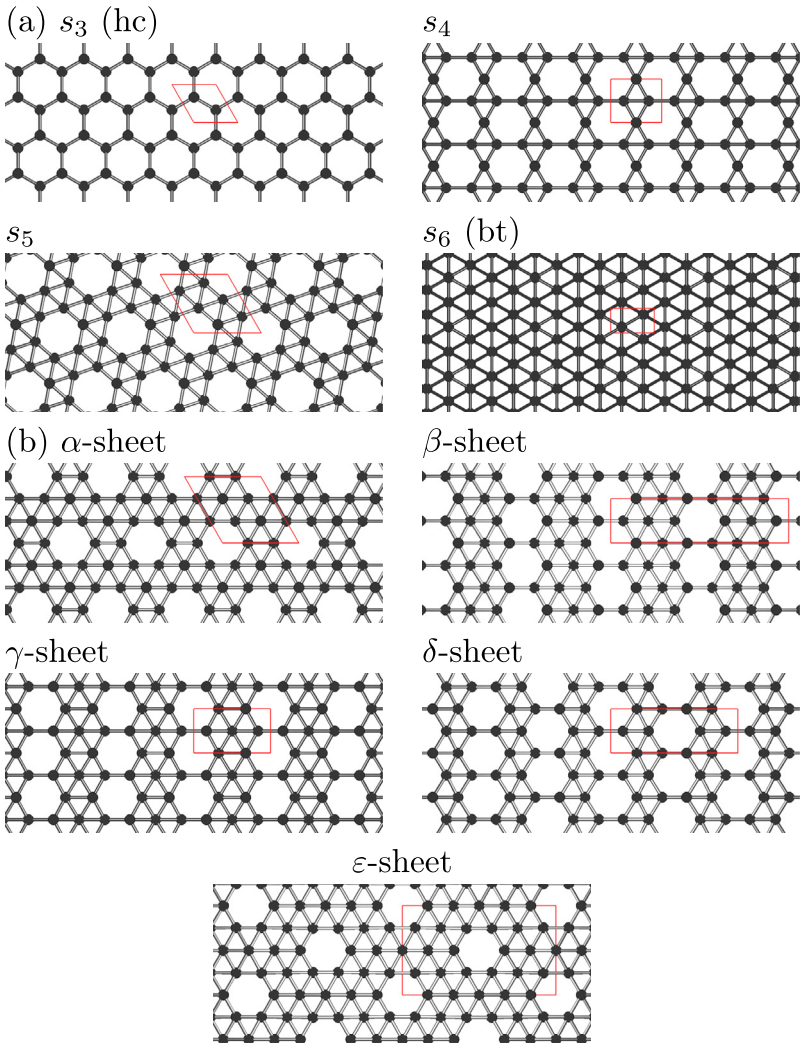

Fig. 1. 2D boron layers considered in this study. (a) Structures that are used to calculate the values of the e_i energies in our model. (b) Structures that are used to test the accuracy of our model. In all cases, the conventional unit cells are shown in red.

There are still many unanswered questions about the structure and properties of 2D boron structures. In this work, we concentrate only on monolayer boron structures. For these structures it is not clear, for instance, why from the vast number of distinct 2D boron sheets reported theoretically [18], only some of them seem to be favored and realized experimentally. Also, the high-symmetry α-sheet that has been predicted to be one of the most stable one-atom-thick forms of 2D boron is believed to be obtained just very recently [17]. As of our understanding, the main factors that may influence the structure of 2D boron crystals are the strain induced by the substrate and the amount of negative charge that is transferring from the substrate [18]. In this study, we propose a simple model to predict the structure of 2D boron crystals exposed to static negative charge. The model does not include the strain but may serve as a first step in the search for stable charged boron sheets.

2. Computational approach

Our first principles calculations are based on density functional theory (DFT) and the projector augmented wave (PAW) method as implemented in the Quantum espresso simulation package [19]. For the exchange and correlation functional, we use a revised Perdew-Burke-Ernzerhof spin-polarized generalized gradient approximation (PBEsol-GGA) functional. The plane-wave basis set is converged using a 60 Ry energy cutoff. A $8 \times 8 \times 1$ $\boldsymbol{k}$-point mesh and a Gaussian smearing of 0.005 Ry is used in the Brillouin Zone integration. The calculations are done using supercells ensuring a 50 Å separation between adjacent layers. For the charged structures, the amount of negative charge (excess of electrons) is specified in units of the charge of an electron per boron atom. For each considered structure, we do a full atomic position and lattice parameter relaxation. The 2D bulk modulus for the hc-sheet (s_3) is obtained from the Murnaghan equation of state.

Images of the crystal structures shown in Fig. 1 were created using the VESTA visualization program [20]. The space group symmetries are found by using the FINDSYM software package [21] and later on reduced to plane group symmetries. The k-point mesh used in the density of states (DOS) and charge density post-processing calculations was $10 \times 10 \times 1$.

3. Results and discussion

3.1. Static charging of 2D boron structures

The structure of all the theoretically and experimentally reported one-atom-thick 2D boron crystals can be easily compared to that of graphene, with that difference that part of the hexagons in the boron layers are filled with additional boron atoms. Should

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