Low-dimensional boron: searching for Dirac materials

Xiang-Feng Zhou and Hui-Tian Wang

School of Physics and Key Laboratory of Weak-Light Nonlinear Photonics, Nankai University, Tianjin, China; National Laboratory of Solid State Microstructures and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, China

ABSTRACT

Two-dimensional (2D) boron, as an analog of graphene, can serve as a building block for fullerenes, nanotubes, and nanoribbons. Understanding its structure and stability is a prerequisite for studies of all those boron nanostructures. Based on an ab initio evolutionary structure search, novel 2D boron structures with nonzero thickness were predicted. In particular, the formation of 2D Dirac boron was reviewed.

KEYWORDS

Two-dimensional boron allotrope; distorted Dirac cones; evolutionary algorithm; first-principle calculation

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61.46.-w Structure of nanoscale materials; 68.65.-k Low-dimensional, mesoscopic, nanoscale and other related systems: structure and nonelectronic properties; 73.22.-f Electronic structure of nanoscale materials and related systems; 71.20.-b Electron density of states and band structure of crystalline solids

The element boron had long attracted enormous attention owing to its fascinating properties, such as exceptional structural complexity, superhardness, unusual partially ionic bonding, and superconductivity at high pressure [1–5]. As carbon's neighbor in the periodic table, boron is in many ways an analog of carbon and its nanostructures (clusters, nanotubes, nanowires, nanobelts, fullerenes, and so on) [6–22]. Meanwhile, it is also a natural candidate in the hopes of replicating or even surpassing the unique properties and diversity of the forms of carbon. For example, graphene has a unique isotropic Dirac cone, and the resultant transport properties may revolutionize transistor technology [23]. By analogy with graphene, two-dimensional (2D) boron sheet was also expected to have similar or
even better electronic properties than graphene. Previously, the single-walled and multiwalled boron nanotubes were successfully synthesized [7]. However, their crystal structures are not fully resolved. It is therefore unknown whether 2D boron is experimentally stable and whether its structure would reflect the simplicity of planar boron clusters or the complexity of bulk boron phases. A recent prediction of the B_{80} buckyball has aroused extensive interest because of structural similarity to the C_{60} fullerene [9]. It was followed immediately by the proposal of stable 2D boron sheets with triangular and hexagonal motifs (named as α-sheet), which can serve as precursors for boron nanostructures [14], such as B_{80}. However, recently the stability of B_{80} fullerene was challenged [18]. Furthermore, the α-sheet was dynamically unstable and transformed to its analogs (nonplanar α’-sheet) by removing the soft mode near the M (0.5 0 0) point [21]. In addition, using a particle swarm optimization technique, some similar planar structures were predicted to have the same or slightly lower energy than the α-sheet [20,21]. In comparison to the well-studied boron sheets, there were few reports for the structures of bilayer 2D boron. Several bilayer phases were constructed by connecting monolayers with van der Waals interactions or strong covalent B–B bonds [15,21].

Our recent works focused on the multilayered 2D boron material because their structures are poorly understood and lack of experimental evidences. To be distinguished from the previous results, 2D structure prediction was implemented in USPEX using plane group symmetry technology [24–29]. The most striking advantage for structure search is to produce 2D structures with a user-defined thickness. The energetic stability is sensitive to the thickness. That is, in general, 2D structures become more thermodynamically stable with increasing thickness because the dangling bonds were minimized as much as they can. According to the experimental evidence for the spacing (∼3.2 Å) between two adjacent layers of multiwalled boron nanotubes [7], the initial thickness was set to 3 Å and allowed to change during relaxation. The structural relaxations used the all-electron-projector augmented wave method [30] as implemented in the Vienna ab initio simulation package [31]. The exchange–correlation energy was treated within the generalized gradient approximation (GGA), using the functional of Perdew, Burke, and Ernzerhof (PBE) [32]. In addition, the hybrid HSE06 functional with the screening parameter (ω) of 0.2 Å⁻¹ was also employed to confirm the energetic stability and the band structures of several 2D boron structures [33].

Many 2D structures (such as 2D-B_{14} and 2D-B_{16}, which contain 14 and 16 atoms per unit cell, respectively) are much lower in energy than the α-sheet [27]. They were completely different from each other in structural form, which reveal that the nonzero thickness plays an important role in decreasing the total energy, leading rich structural diversity in 2D boron system. To verify the correctness and efficiency of USPEX, an 8-atom (8 atoms/cell) structure searching was illustrated in Figure 1. As shown in Figure 1(a), the α-sheet structure was really reproduced, which establishes the reliability and accuracy of the USPEX calculations. Moreover, there were other many low-symmetry (e.g. P-1) structures (more stable
than the α-sheet), indicating that 2D boron is a frustrated system, and favors to be the buckled structure. Two stable symmetric phases are designated as Pmmn boron and Pmmm boron (Figure 1(b)–(d)). The GGA-PBE results show that

![Figure 1](image_url)

**Figure 1.** (a) Typical enthalpy evolution for an 8-atom 2D boron system during an evolutionary structure search. The inset shows the structure of the α-sheet. (b) and (c) Projections of Pmmn boron structure along [0 0 1] and [1 0 0] directions. (d) and (e) Projections of Pmmm boron structure along [0 0 1] and [1 0 0] directions. Figures were extracted from Ref. [27].
Pmmm boron and Pmmn boron are 0.08 and 0.05 eV/atom lower in energy than the α-sheet structure, but are 0.32 and 0.35 eV/atom higher in energy than bulk α boron, indicating that the two 2D phases are metastable. Moreover, the HSE06 calculations show the total energies for α-sheet, Pmmn boron, Pmmm boron, and bulk α boron are $-6.94$, $-7.03$, $-7.05$, and $-7.43$ eV/atom compared with the corresponding values of $-6.28$, $-6.33$, $-6.36$, and $-6.68$ eV/atom from GGA-PBE calculations; i.e. GGA-PBE and HSE06 give the same ranking of structures by stability [27]. Therefore, the energetic stability shows that 2D boron prefers the buckled multilayered structures than flat monolayer sheets.

Both α-sheet and Pmmm boron were metallic. Surprisingly, Pmmn boron was a zero-gap semiconductor. Its band structure showed valence and conduction bands met in a single point $(0, 0.3, 0)$. The density of states (DOS) of Pmmn boron was

**Figure 2.** Electronic structure of Pmmn boron. (a) Band structure, (b) DOS, (c) Dirac cone. Figures were extracted from Ref. [27].
zero at the Fermi level (Figure 2(a) and (b)). So this meeting point was a Dirac point which elaborated in Figure 2(c). The valence and the conduction band of Pmmn boron in the vicinity of the Dirac point showed the presence of a distorted Dirac cone which is very similar to that of 6, 6, 12-graphyne [34]. These bands exhibit a linear dispersion in both \( k_x \) and \( k_y \) directions, i.e. like in graphene, the effective mass of the mobile electron is zero. The Fermi velocity of the Dirac fermions was calculated by the formula 
\[
\nu_F = \frac{E(k)}{\hbar k}
\]
. The slope of the bands in the \( k_x \) direction is \( \pm 23 \) eV \( \AA \), equivalent to a Fermi velocity \( 0.56 \times 10^6 \) m/s. In the \( k_y \) direction, the slope of the bands equal \( -48 \) eV \( \AA \) (\( \nu_F = 1.16 \times 10^6 \) m/s) and \( 19 \) eV \( \AA \) (\( \nu_F = 0.46 \times 10^6 \) m/s), compared to \( \pm 34 \) eV \( \AA \) (\( \nu_F = 0.82 \times 10^6 \) m/s) in graphene when approaching a Dirac point along the \( \Gamma-K \) direction. [34]. The anisotropy of the Dirac cones with different slopes at the Dirac points in the \( k_x \) and \( k_y \) directions, implies direction-dependent electronic properties. It also should note that the distorted Dirac cone of Pmmn boron is a robust feature and is found also when using the HSE06 functional, its position shifts 0.18 eV above the Fermi level [27]. As shown in Figure 3, the charge density of the highest valence band is mainly derived from the out-of-plane states (\( p_z \) orbitals, see Figure 3(a) and (c)). By comparison, the in-plane states (\( p_{x,y} \) orbitals, see Figure 3(b) and (d)) are dominantly responsible for the charge density of the lowest conduction band at the Dirac point. The charge density distributions for both the conduction band and the valence band at the Dirac point have mirror symmetry along \( x \) and \( y \) directions. Therefore, the

**Figure 3.** The band decomposed charge density of Pmmn boron at the Dirac point: (a) and (c) projections of the charge density of the highest valence band along [001] and [100] directions; (b) and (d) projections of the charge density of the lowest conduction band along [001] and [100] directions. Figures were extracted from Ref. [27].
emergence of massless Dirac fermions can be attributed to the mirror symmetry, which could be explained by the minimal two-band model in other work [35].

Pmmn boron exhibits massless Dirac fermions with anisotropic Dirac cones, which may be superior to graphene, i.e. transport properties of these Dirac fermions will depend on direction, which gives an additional degree of freedom (with faster-than-graphene and slower-than-graphene directions) for electronic applications. This exotic electronic property further inspires experimental works [36–39]. A. J. Mannix et al. grew atomically thin, boron sheets under ultrahigh vacuum conditions using a solid boron atomic source. An atomically clean Ag (1 1 1) substrate provided a well defined and inert surface for 2D boron growth. During growth, the substrate was maintained between 450° and 700 °C under a boron flux between ~0.01 and ~0.1 monolayer (ML) per minute. After boron deposition at a substrate temperature of 550 °C, In situ scanning tunneling microscopy (STM) topography images revealed two distinct boron phases: a homogeneous phase and a more corrugated ‘striped’ phase. STM images show the emergence of planar structures exhibiting anisotropic corrugation as increasing growth temperatures [36]. The linearity in the central region of I–V curves showed that borophene was a metal. At first, 2D Pmmn boron was speculated to be the candidate for the above graph and caption: Figure 4. Projections of monolayer borophene structure on Ag (1 1 1) surface, (a) along [0 0 1] direction, (b) along [0 1 0] direction, (c) band structure of freestanding borophene.
the striped phase because its lattice constants are close to the measured value. Secondly, Pmmn boron was a metal when interactions from Ag (1 1 1) substrate were included. However, the measured thickness of ~2.7 to 3.1 Å was less than the distance between Pmmn boron and Ag (1 1 1) substrate (>4 Å). Furthermore, the calculations showed that Pmmn boron was mechanically unstable due to small lattice mismatch and interactions from the substrate. Therefore, the possibility for the candidate of Pmmn boron was excluded. To resolve the crystal structures of borophenes, *Ab initio* structure predictions were performed using the USPEX code with surface prediction module. The Ag (1 1 1) substrate was constructed by rectangular and hexagonal lattices, respectively. The lattice vectors are \( a = 5.004 \, \text{Å} \) and \( b = 2.889 \, \text{Å} \) for rectangular lattice and \( a = b = 5.778 \, \text{Å} \) for hexagonal lattices. The structure searches were conducted with 6, 8, 10, 12, 14, and 16 atoms per

**Figure 5.** (a), (b) Simulated STM images (Vs = 1.0 V) of borophene compared with experimental results (Vs = 0.1 V, It = 1.0 nA). The atomic structure and the unit cell were overlaid for illustration. (c), (d) simulated and experimental (Vs = 0.1 V, It = 3.0 nA) STM topography images. Figures were extracted from Ref. [36].
unit cell for the hexagonal substrate; and 6, 7, 8, 10, 12, 14, and 16 atoms per cell for the rectangular lattice, respectively. The thickness of the surface layer and the vacuum layer were set to 3 and 10 Å during the searching, but allowed to change for postprocessing [36]. In rectangular lattice, the buckled triangular structure is shown in Figure 4(a) and (b), which is constructible from distorted B$_7$ clusters proposed by Boustani [10,11]. The symmetry (space group Pmmn) and calculated lattice constants agree well with the STM data, with $a$ and $b$ equal to 5.0 and 2.89 Å, respectively. The simulated STM topography images are in excellent agreement with experimental results (Figure 5). In hexagonal lattice, the monolayer 2D boron with 1/6 vacancies (Figure 6) was also found during the structure searching. 

Figure 6. Top and side views of 2D boron sheet with 1/6 vacancies on Ag (1 1 1). (a), (b) Hexagonal form. (c), (d) Rectangular form.
Because this structure was almost a flat sheet, it was not studied thoroughly for the candidate of striped phases. However, other independent groups synthesized 2D boron sheets also by growing boron on Ag (1 1 1) substrate with molecular beam epitaxy technique. These borophenes with different kinds of vacancies were constructed and clarified for their experimental findings [38,39].

The band structure of the relaxed, freestanding monolayer borophene showed that metallic conduction along the $\Gamma$–$X$ and $Y$–$S$ directions (Figure 4(c)). However, the out-of-plane corrugation opens a band gap along the $\Gamma$–$Y$ and $S$–$X$ directions. As a result, borophene is a highly anisotropic metal, where electrical conductivity is confined along the chains. The calculated DOS is likewise metallic [36].

Figure 7. (a), (b) Top and side views of borophane, (c) band structure, (d) Dirac cone.
phonon dispersion curve showed that the free standing borophene is dynamically unstable. The small imaginary frequencies near the Γ point are consistent with instability against long-wavelength transversal waves. This instability may be fixed by defects, such as ripples or grain boundaries, which do not allow these waves by limiting the size of boron sheets. This may contribute to the observed stripe formation and would likely distort the structure of the borophene upon removal from the substrate [36]. To make the borophene be stable for future potential applications, Xu et al. proposed that it can be stabilized by passivation with hydrogen atoms [40]. Indeed, the imaginary phonon frequencies were disappeared when all of B atoms were passivated by H atoms. Interestingly, the hydrogenated borophene (designated as borophane) would be a 2D Dirac material with ultra-high Fermi velocity (Figure 7). The Dirac cone is distorted and asymmetric, with slopes of +72 and −40 eVÅ around the Dirac cone. In the $k_x$ direction, the Fermi velocity is
1.74 × 10^6 and 0.97 × 10^6 m/s, which are 1–2 times higher than that of graphene (0.82 × 10^6 m/s). The charge density at the Dirac points clearly confirms that in-plane \( p_x \) and \( p_y \) orbitals lead to the formation of a Dirac cone (Figure 7(b)). The bonds between \( p_x \) orbitals forms \( \sigma \)-conjugated linear chain, while the coupling between \( p_y \) orbitals leads to the formation of \( \pi \) bonding-like framework \[40\]. This leads to remarkable anisotropy of Dirac fermion. Therefore, borophane may be synthesized under similar conditions as borophene or exfoliated from the weakly bonded high-pressure BH phases \[41\].

In addition, a specific bilayer borophene had also been considered as an alternative candidate for the experimental striped phases because the simulated STM image is also in good agreement with experimental result. Bilayer borophene is 0.14 eV/atom lower in energy than monolayer one. However, its thickness (~6 Å) was larger than the measured value (~3 Å). Therefore, bilayer borophene was less likely to be the candidate for experimental phase \[36\]. Band structure shows that bilayer borophene also has a distorted Dirac cone near and below the Fermi level along the Y–S direction at the point (−0.155 0.5 0) (Figure 8). However, this advantage was restrained by metallic property within the first Brillouin zone. The Dirac fermions in bilayer borophene may be reserved and improved by doping or passivation, which need further study latter.

In summary, beside graphene, many other 2D carbon allotropes had been predicted to have distorted Dirac cones, such as \( \alpha, \beta, \delta, 6,6,12-, 14,14,14-, 14,14,18 \)-graphyne, and phagraphene \[34,42–44\]. In contrast, only two stable elemental 2D Dirac boron (Pmmn boron and P6/mmm boron) were predicted \[27,45\], not yet realized in experiment. Since the 2D boron sheets had been successfully synthesized recently \[36–39\], there is great possibility to grow 2D Dirac boron on different kinds of substrates. Therefore, more borophenes with Dirac cones will be found in near future.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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