Unusual semimetal-semimetal transition of layer-stacked borophene under pressure

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The 8-Pmnn borophene, a boron analogue of graphene, hosts tilted and anisotropic massless Dirac fermion quasiparticles owing to the presence of the distorted graphene-like sublattice. First-principles calculations reveal that the bulk layer-stacked 8-Pmnn borophene inherits the Dirac band dispersion resulting in the topological nodal-line semimetal phase. At a pressure 3 GPa, the stacked 8-Pmnn borophene is transformed into the fused three-dimensional borophene that preserves the graphene-like substructure, and thereby leading to an unusual semimetal-semimetal transition, which contrasts greatly to the transformation of graphite into diamond associated with the semimetal-insulator transition.

Graphene, a monolayer material exfoliated from graphite, has attracted immense interest partially owing to its remarkable thermal stability, superior mechanical strength and unique Dirac-semimetallic band structure [1–3]. Graphene shows a significant potential for applications in the fields of electronics, batteries, sensors, structural materials and more. Boron, the element that neighbors carbon in the second row of the periodic table and forms a nonmetallic solid, has also been proved to own its two-dimension (2D) form, termed borophene [4–6]. Borophene shares a lot in common with graphene, but has its own uniqueness due to the complex multicenter bonds. Both theoretical simulations and experiments extensively explored the diverse geometrical configurations (i.e., planar, quasi-planar, or multilayer structures) and versatile properties (i.e., superconductivity, magnetism, or negative Poisson’s ratio) in various borophenes [4–8]. For instance, the 8-Pmnn borophene, featured by an 8-atom orthorhombic unit cell with the Pmnn symmetry [9], is composed of distorted graphene-like boron sheet and attached boron chains. More specifically, the boron chains attach above and below the distorted graphene-like sheet. Each B-B pair along the chain direction donates two electrons to the distorted hexagonal lattice, satisfying the iso-electronic state of graphene and resulting in the tilted and anisotropic Dirac cone at the Fermi level \( (E_F) \), which is quite different from that of graphene (isotropic Dirac cone) [10]. The maximum Fermi velocity of 8-Pmnn borophene along the chain direction is nearly 1.5 times that of graphene [9]. Such unique band structure stimulated further study of the electronic properties of 8-Pmnn borophene, such as anisotropic plasmons, magnetotransport properties, anomalous Klein tunneling, valley-dependent electron retroreflection, Veselago focusing, Ruderman-Kittel-Kasuya-Yosida exchange interaction, metal-insulator transition, and the photoinduced Hall effect [11–20]. Most recently, a variety of exotic electronic states, including flat-band phases, superconductivity, magnetism, and the Chern insulators phases, were discovered moiré superlattice systems based on multilayer graphene [21–25]. These new discoveries made a very strong impact in condensed matter physics and beyond. Obviously, it is interesting to investigate the ambient pressure bulk stacked borophenes as well as their high-pressure phases.

In this work, boron polymorphs derived from 8-Pmnn borophene have been studied using the projector augmented wave (PAW) method [26] as implemented in the VASP code [27]. The exchange correlation energy was treated within the generalized gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof (PBE). The plane-wave energy cutoff of 500 eV, energy convergence criterion of \( 10^{-7} \) eV, force criterion of 0.003 eV/Å, and \( k \)-point resolution of \( 2\pi \times 0.04 \) Å\(^{-1}\) were employed for the density functional theory (DFT) calculation, which showed excellent convergence of the total energy, stress tensors and lattice parameters. To examine the accurate energetic stability, the semimipirical dispersion-correction method (DFT-D3) was applied to the various boron allotropes [28]. Phonon spectrum was calculated by the PHONOPY code [29] within the density functional perturbation theory (DFPT) framework.

Two layer-stacked borophene configurations are constructed from the parent 8-Pmnn structure, and designated as the AA-8-Pmnn and AB-16-Amnn borophenes. Two sublattices of the 8-Pmnn borophene are illustrated in Fig. 1 using different colors. The AA-8-Pmnn configuration was constructed from the 8-Pmnn...
FIG. 1. (a)-(c) Projection along the [100] direction of the AA-8-Pmnm (1×2×1 supercell), AB-16-Amam (conventional cell), and the fused AB-16-Pnnm phase. (d)-(f) Projection along the [001] direction of the AA-8-Pmnm, AB-16-Amam, and the fused AB-16-Pnnm phases. The distorted graphene-like sublattice is colored in green while the attached boron chains are colored in purple.

FIG. 2. (a) Enthalpy and (b) lattice parameter $b$ as a function of pressure.

The stacking sequence play a decisive role in the relative stability of vdW-coupled stacked borophenes. Both the AA-8-Pmnm and AB-16-Amam borophene configurations are close in energy compared to other predicted three-dimensional (3D) boron phases (see Table I), but are higher in energy relative to bulk $\alpha$-B$_{12}$, indicating these are metastable phases. While various structures of borophene have been reported, neither stacked nor fused borophenes have been explored extensively [32, 33], even less for their high-pressure phases.

Graphite can be converted into a novel form of diamond (cold compressed graphite) at high pressure or cubic diamond at high pressure and high temperature as a resulting of the $sp^2$-$sp^3$ transition [34, 35]. It is interesting to study the behavior of the stacked borophenes under pressure. The calculated pressure-enthalpy curves of the stacked borophene configurations are presented in Fig. 2(a). One observes that the AA-8-Pmnm phase is thermodynamically more stable than the AB-16-Amam phase up to 2.75 GPa. Strikingly, the enthalpy of the AB-16-Amam borophene decreases abruptly at 3 GPa, suggesting a structural phase transition. The variation of lattice parameter $b$ as a function of pressure is shown in Fig. 2(b). This quantity also exhibits an abrupt decrease at the phase transition point for the AB-16-Amam borophene. By analyzing the relaxed structure of the AB-16-Amam phase at 3 GPa, we conclude that the phase transition takes place by overcoming the weak vdW interaction with bond breaking and bond reforming, leading to the connection of the adjacent layers. The relaxed structure is termed as the fused AB-16-Pnnm borophene [Figs. 1(c) and 1(f)]. Compared to the AB-16-Amam structure, the graphene-like sublattice in the fused AB-16-Pnnm borophene is retained, while the boron chains in the adjacent layers are connected in a puckered arrangement. Although the interlayer distance in the AA-8-Pmnm phase (3.09 Å) is shorter than that in the AB-16-Amam phase (3.37 Å), as shown in Figs. 1(a) and 1(b), the nearest B-B distance between the adjacent layers in the AA-8-Pmnm phase (3.82 Å) is longer than its interlayer distance (3.09 Å), whereas it is the same for the AB-16-Amam borophene (3.37 Å). The
longer B-B distance between adjacent layers in the AA-8-Pmmn borophene seems to prevent the occurrence of direct phase transformation compared in contrast to AB-16-Amam structure [Fig. 2(a)]. However, because of the peculiar puckered structure and weak vdW interactions between the adjacent layers, the AA-8-Pmmn borophene can easily transform into the AB-16-Amam phase by interlayer slipping along the [001] direction under shear stress, the phase transition sequence of AA-8-Amam → AB-16-Amam → fused AB-16-Pmmn borophene is therefore expected under certain conditions.

The 8-Pmmn borophene hosts tilted and anisotropic massless Dirac fermion quasiparticles owing to its unique crystal structure. For the 2D 8-Pmmn phase, as the interlayer distance is larger than 10 Å (along y direction), there is no interaction between adjacent layers [Figs. 3(a) and 3(b)]. As the interlayer distance is decreased to a certain value (e.g., 3.37 Å), the AB-16-Amam borophene is formed. The interlayer coupling transforms the Dirac points of 8-Pmmn borophene into the nodal lines of AB-16-Amam borophene [Figs. 3(c) and 3(d)]. As the interlayer distance is further decreased, AB-16-Amam borophene may transform into the fused AB-16-Pmmn phase under pressure (or under uniaxial compression). The mechanism underlying the band structure evolution is complex but intriguing. As shown in Fig. 3(e), the orbital-resolved band structure shows that the fused AB-16-Pmmn borophene is a semimetal with several crossing points at the vicinity of the Fermi level $E_F$. Furthermore, the electrons at the crossing points 1 and 3 and the holes at the points 2 and 4 lead to nonzero density of states (DOS) at $E_F$. The densities of the electrons and holes are evaluated by integrating their occupations of four bands overlapping nodal loops in the Brillouin zone (BZ) [Figs. 3(f) and 4(a)], consisting of two sets of nodal lines which are orthogonal and intersect at the crossing point 3 [Fig. 3(e)].

| Structure (symmetry) | Lattice parameters (Å) | Atomic position (fractional coordinates) | Total energy (eV/atom) |
|----------------------|------------------------|------------------------------------------|------------------------|
| AA-8-Pmmn            | $a = 3.25, b = 5.27, c = 4.51$ | B1(0.000,0.424,0.184) B2(0.247,0.707,0.000) | -6.420                |
| AA-16-Amam           | $a = 3.25, b = 11.10, c = 4.51$ | B1(0.000, 0.152, 0.033) B2(0.184, 0.286, 0.250) | -6.415                |
| AA-16-Pmmn           | $a = 3.20, b = 8.48, c = 4.50$ | B1(0.171, 0.074, 0.000) B2(0.159, 0.352, 0.500) B3(0.136, 0.690, 0.188) | -6.519                |
| $\alpha$-$\text{B}_1_2$ (R-3m) | $a = b = c = 5.03$ $\alpha = \beta = \gamma = 58.0^\circ$ | B1(0.010, 0.010, 0.654) B2(0.222, 0.222, 0.630) | -6.808                |
| 8-Pmmn [9]           | $a = 3.25, b = 4.52, c = 13.00$ | B1(0.000, 0.316, 0.531) B2(0.253, 0.000, 0.584) | -6.395                |
| 3D borophene [33] (1mmn) | $a = 5.14, b = 1.85, c = 2.80$ $\alpha = \beta = \gamma = 90^\circ$ | B1(0.167, 0.000, 0.000) | -6.429                |
| 3D-$\alpha'$ boron [42] (Cmcm) | $a = 7.82, b = 8.00, c = 5.05$ $\alpha = \beta = \gamma = 90^\circ$ | B1(0.000, 0.398, 0.568) B2(0.168, 0.289, 0.084) B3(0.176, 0.304, 0.750) | -6.431                |
| $\alpha$ sheet [43] (P6/mmmn) | $a = b = 5.06, c = 15.00$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ | B1(0.000, 0.332, 0.500) B2(0.333, 0.667, 0.500) | -6.332                |
According to the space group $Pnmm$, the point groups on the $10YS$ and $1YTS$ planes are both $C_s$. The nodal loops in the $k_x-k_y$ plane are protected by the mirror operator $M_z$, whereas others in the $k_y-k_z$ plane are protected by the glide operator $\{M_y|a/2+b/2+c/2\}$ [36]. Overall, the fused $AB-16-Pnmm$ borophene can be classified as a nodal-chain semimetal.

One of the most interesting features of the nodal-line materials is the presence of drumhead surface states, which may provide a route to higher-temperature superconductivity [37, 38]. The surface states of the fused $AB-16-Pnmm$ borophene are calculated using the fifteen-layer-thick (010) slab model. As shown in Fig. 4(b), the drumhead-like surface state (colored in red) connects nodal points 1 and 2 in the $\Gamma\Sigma0\Gamma$ path. The dispersion is flat around the high-symmetry point $\Sigma$, which is expected to facilitate the detection in the future experiment. We would like to point out that spin-orbit coupling (SOC) can break the symmetry and open a band gap at the crossing point. However, due to the very weak SOC in the studied light-element systems, only a tiny gap opens at the nodal points, e.g. $\sim1.35$ meV at the fourfold degenerate point, which is too weak to affect the semimetal properties. Finally, we shown that the fused $AB-16-Pnmm$ borophene is dynamically stable at ambient conditions as there are no imaginary frequencies in the entire BZ [Figs. 4(c) and 4(d)]. If the fused $AB-16-Pnmm$ borophene can be synthesized, the strong covalent bond nature and the remarkable dynamical stability imply the possibility of quenching this material to the ambient pressure.

In conclusion, we investigated the stacked $8-Pnmm$ borophene in different forms. Under increasing pressure, the interatomic distances typically decreased. The valence and conduction bands are thus expected to broaden, leading to the pressure-induced metalization [39]. The AB-stacked borophene is transformed into the fused borophene at $\sim3$ GPa associated with the bond breaking and reforming between the adjacent boron chains. However, due to the preserved graphene-like substructure, the pressure-induced semimetal-semimetal transition takes place in the stacked $8-Pnmm$ borophene—that is, a nodal-line semimetal ($AB-16-Amam$ phase) transforms to a nodal-chain semimetal (fused $AB-16-Pnmm$ phase), which is different from the common semimetal-metal (semimetal-semiconductor) transition. Furthermore, it was previously predicted that the $8-Pnmm$ borophene may be grown on the metal substrates because its lattice constants match with the (110) surface of several metals and metal oxides [9, 40]. Most recently, bilayer borophene was successfully synthesized on the Ag(111) substrate [41]. It is therefore anticipated that layer-stacked borophenes might be synthesized in the near future. If the synthesis succeeds, new bulk allotropes of boron could be formed under pressure and may be quenchable to ambient condition. These would extremely expand the phase diagram...
of elemental boron.

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