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Letter

Fused borophenes: A new family of superhard light-weight materials

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The search of new superhard materials has received a strong impulse by industrial demands for low-cost alternatives to diamond and *c*-BN, such as metal borides. In this Letter we introduce a new family of superhard materials, "*fused borophenes*" (FBs), containing 2D boron layers that are interlinked to form a 3D network. These materials, identified through a high-throughput scan of B_xC_{1-x} structures, exhibit Vicker's hardness comparable to those of the best commercial metal borides. Due to their low formation enthalpies, FBs could be synthesized by high-temperature methods, starting from appropriate precursors, or through quenching of high-pressure phases.

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Introduction- The revamped interest in superhard materials has been driven not only by scientific curiosity but also by the increasing technological interest in several industrial applications [1,2]. Diamond, with a reported Vicker's Hardness (V_H) of 120 GPa, holds by far the record among all known materials, but its chemical reactivity at high temperatures and high production cost restrain its practical usability. Improvements over the current alternatives, such as cubic-BN (*c*-BN) or cubic-BC_2N [3–5] and metal borides [6–8], which also present serious limiting issues such as high synthesis price, or limited hardness, are being intensively sought.

The phase diagrams of elements such as boron, carbon, nitrogen, and oxygen and their compounds represent ideal hunting grounds for potential superhard materials to explore with *ab-initio* methods for crystal structure prediction (CSP) and high-throughput (HT) screening, which are rapidly expanding the scope of material research [2,9–15].

In this paper, applying a combination of CSP (minima hopping) [16,17] and HT screening techniques to the boron-carbon (B-C) phase diagram, we uncover a family of metastable boron and boron-rich carbon structures, "*fused borophenes*" (FBs), with hardness and elastic properties comparable to those of the best metal borides.

Fused borophenes, as the term suggests, can be seen as a stacking of different types of 2D boron layers (BLs), connected through covalent bonds to form 3D bulk structures. Being structurally related to the high-pressure α-Ga phase, considered to be the most likely candidate to explain superconductivity observed in boron above 160 GPa [18–20], FBs ideally represent the missing link between the two known families of boron structures: 2D borophenes [21–25] and 3D bulk structures based on B_{12} icosahedral (IC) units, such as α, β, and γ boron [25–27]. The idea that bulk boron structures may be obtained by stacking different boron sheets was originally introduced by Boustani [21] and later by Kunstmann in 2008 [28], based on a generalized Aufbau principle. In this work, we confirm that FBs appear as metastable structures in an unbiased exploration of the boron and boron-carbon phase diagram and may also exhibit motifs that deviate from the conventional triangular/hexagonal network of borophenes. FBs are metastable at ambient conditions, but our calculations suggest that quenching from high pressure may be used to stabilize some of the most competitive phases.

In the following, after discussing the general elastic and thermodynamic properties of superhard fused borophenes, we will introduce a general classification scheme into three families based on the structural motifs; after this, we will discuss the origin and nature of the exceptional elastic properties, with a detailed analysis of the three hardest structures in each family.

Fused Borophenes in the B-C Phase Diagram- Fused borophenes were identified through a HT search of hard materials on a database of ∼2700 distinct B-C structures, obtained through an unbiased minima hopping search [16,17], on 8–15 atom unit cells with variable B/C composition [29]. The left panel of Fig. 1 shows the location of all resulting structures in the formation energy (ΔE) vs Boron fraction plane; C-graphite and α-B_{12} were used to compute the reference energy [30]

Through HT screening of the initial set, we singled out 71 B-C structures with Vicker Hardness (V_H) $\geqslant$ 40 GPa, which is the conventional threshold for superhard materials. They are shown as different colored symbols in the left panel of Fig. 1. Among these 71 superhard materials, 40 are diamondlike C-rich structures (green diamonds). Based on the atomic arrangement, the remaining 31 B-rich compounds can be classified in two groups: 4 are IC-like (inverted pentagons), while 27 of them can neither be classified as B_{12} IC nor be classified as triangular/hexagonal 2D boron sheets (borophenes). We termed this new class of B-rich B-C structures as FBs and indicate them in the plot as colored (inverted) triangles and asterisks. The colors of the IC-like and FB symbols indicate the fraction of B present in these

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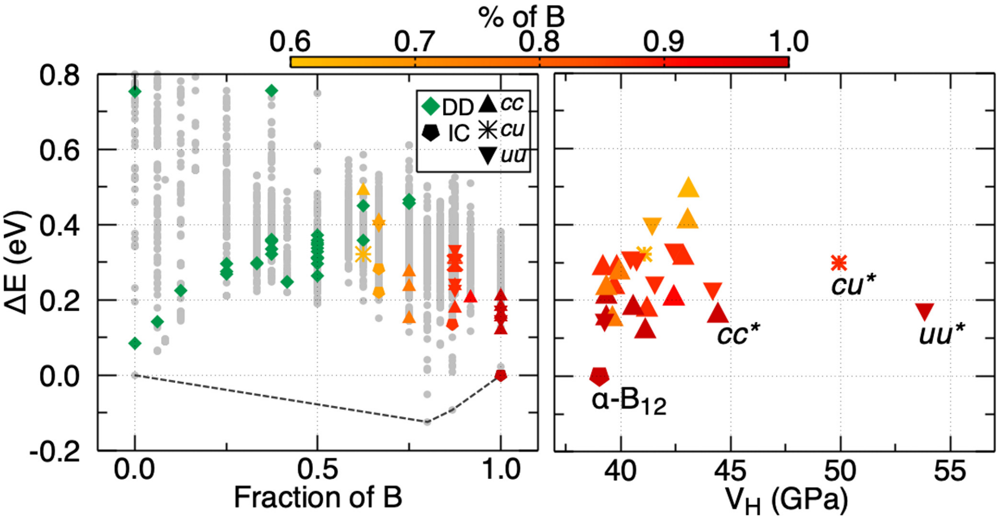

FIG. 1. The left panel shows the relative energy ΔE(eV/atom) vs B fraction of all the ∼2700 B-C structures at 0 GPa. The reference structures for C and B are C-graphite and α-B_{12}, respectively. The dashed black line represents the convex hull. The right panel shows the relative energy as a function of Vicker's hardness V_H (GPa) of only the superhard B-C structures. The B fraction in these structures is indicated by the color bar at the top. The colored triangles, inverted triangles, and asterisks represent the 17 *cc*, 2 *cu*, and 8 *uu* superhard FB, respectively. The green diamond and inverted pentagons represent diamond and IC structures, respectively. The remaining B-C structures are shown as gray circles.

structures, according to the color bar at the top. The remaining structures are shown as gray circles.

FBs appear in the B-C phase diagram at a minimum B concentration $B_{7/12}C_{5/12}$, with relative energies ΔE $\geqslant$ 293 meV/atom and become gradually more stable as the B fraction increases. There is a total of 306 FB structures in the whole database of ∼2700 B-C structures. Among them only 27 have $V_H \geqslant 40$ GPa, i.e., ∼9 % of FB structures are superhard materials.

The right panel of Fig. 1 displays a plot of the ΔE against V_H (GPa) of the 27 FB superhard structures, plus α-B_{12} for reference. The colors of the symbols indicate the fraction of boron for the structure.

Depending on the nature and relative arrangement of the-BLs, FBs have been divided into three families: *cc* (triangles), *cu* (asterisk), and *uu* (inverted triangles). The hardest FBs in each family are marked as *cc**, *cu**, and *uu**. The plot clearly shows that there is no evident correlation between the ΔE and the V_H of the FBs. Based on the amorphous thermodynamic limit criteria of synthesizability in Ref. [31], the upper limit of formation energy for synthesizability for B, C, or B-C systems is ∼1 eV/atom. In this context, it is encouraging to observe that all superhard FBs shown in Fig. 1 have ΔE $\leqslant$ 500 meV/atom, indicating that under appropriate conditions with suitable precursors, synthesis is viable.

As for the hardness, most structures have a V_H close to the threshold value of 40 GPa. A few structures, however, stand out as exceptional, with V_H exceeding 45 GPa: among these, we selected one structure per prototype, indicated as *cc**, *cu**, and *uu** in Fig. 1, which will be discussed in detail in the following.

Classification of Fused Borophenes in Different Families - Like other known boron polymorphs, Fused borophenes exhibit a large diversity of motifs, reflecting the electron-deficient multicentered bonding nature of this element [32]. FBs identified in our search may contain: (i) Boron layers (BL) of different types and (ii) single or V-shaped nearest neighbor connecting one atom in a layer to two atoms in another layer. Furthermore, (iii) a structure may comprise BL all of the same type or of different types, and (iv) their stacking along the vertical axis may also be different [33].

We classify a BL as *conventional* if it exhibits only triangular and hexagonal patterns, as found in synthesized/theoretically predicted borophenes [22,23,34,35] and *unconventional* if it contains other polygonal motifs. Based on the type of BLs they contain, we classify FB into three families: (i) Conventional-conventional (*cc*), (ii) conventional-unconventional (*cu*), and (iii) unconventional-unconventional (*uu*).

In order to uniquely identify all structures generated, we assigned each FB a unique alphanumeric ID of the form: TYPE-XYZ(HH)-XYZ(HH).... Here, TYPE indicates the family, *cc*, *cu*, or *uu*; the XYZ numerals denote the polygonal motif present in each BL; while HH is the hexagonal-hole concentration of the BL if applicable. The XYZ(HH) notation is introduced for each type of BL in the structure; the unconventional BL precedes the conventional BL. Following this description, the XYZ(HH) is mentioned only once if a FB is made of only one type of BL. Within this classification scheme, the α-Ga structure, formed by stacking two identical triangular conventional BLs with 0 HH concentration, would be assigned the ID *cc*-3(0).

Examples of structures belonging to each of the three families are shown in Fig. 2. In particular, the figure depicts the three structures indicated as *cc**, *cu**, and *uu**. The two different BLs in these FBs are shown by orange/blue color; *cc** [*cc*-36(2/25)] comprises two identical conventional BL with 2/25 HH concentration, interconnected through V-shaped nearest neighbors [Figs. 2(a) and 2(b)]; *cu**, with composition $B_{7/8}C_{1/8}$

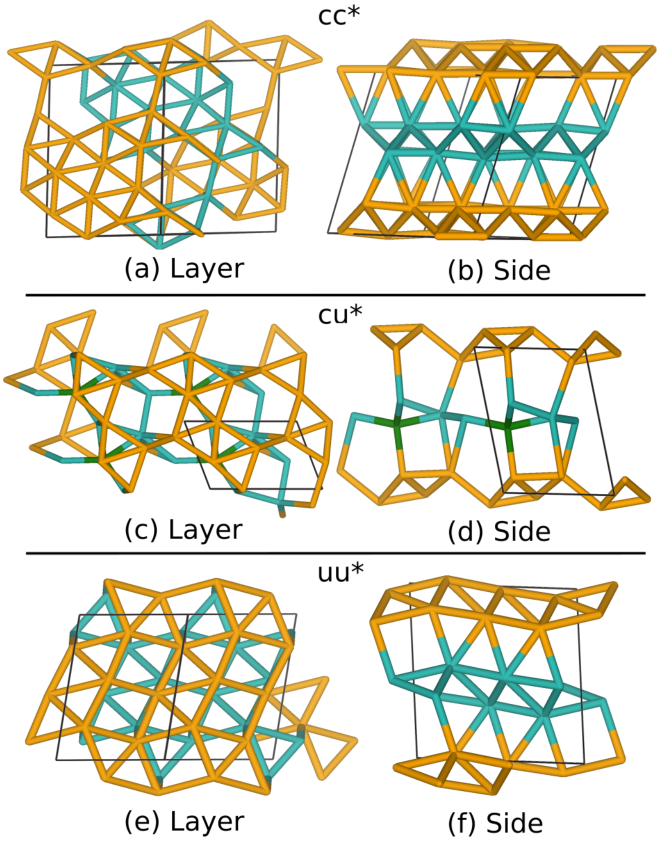

FIG. 2. Top and side views of BL in the three best superhard FB: *cc** (a,b), *cu** (c,d), and *uu** (e,f), respectively. The orange- and blue-colored sticks indicate different BLs. Dark green sticks are centered on C atoms in one of the BL of *cu**. The unit cell is shown as a black line.

[*cu*-356-36(1/5)] comprises an unconventional BL with a triangular-pentagonal-hexagonal motif and a conventional BL [Fig. 2(c)] with 1/5 HH concentration. These two BLs are connected by single bonds as shown in Fig. 2(d); *uu** (*uu*-34) comprises two identical unconventional BL interconnected through a V-shaped nearest neighbor [Figs. 2(e) and 2(f)].

In all three structures, bonds within and between the BLs are of comparable length, indicating that boron is forming multicenter bonds. Indeed, electronic localization function (ELF) plots, shown in Fig. 1 of the supplemental material [36], show that the electronic charge tends to accumulate both along the bonds connecting atoms in the same BLs and between different layers. Thus, FBs should be described rather as a bulk-like interconnected network of BLs and not as quasi-2D van-der-Waals systems. This peculiar bonding characteristic of FBs is at the heart of their remarkable elastic properties.

Thermodynamical and Mechanical Properties of cc, cu*, and uu* FBs* - Table I contains selected thermodynamic, geometric, and elastic properties of *cc**, *cu**, and *uu** FBs calculated at the local density approximation (LDA)-DFT level [37]. The table also reports, for comparison, the calculated properties for other well-known superhard covalent materials and metal borides, as well as for graphite (C-gra) and hexagonal BN (*h*-BN), as representative examples of quasi-2D van-der-Waals systems.

TABLE I. Summary of the calculated properties of the three best superhard FB: *cc**, *cu**, and *uu**, indicated in Fig. 1. We also include (i) different hard covalent system including carbon diamond (C-Dia) and α-B$_{12}$ and (ii) hard metal borides for reference and quasi-2D materials such as graphite (C-Gra) and hexagonal BN (*h*-BN). The ID of the structures is shown in the first column, while the relative energy (ΔE) with respect to C-graphite and α-B$_{12}$ in meV/atom, volume (Vol) in Å^3/atom, and density in g/cm^3 are listed in the second, third, and fourth columns, respectively. The remaining columns contain mechanical properties: Bulk modulus (B), shear modulus (G), Young's modulus (Y), and Vicker's hardness (V$_H$) in GPa. The Poisson's ratio ν and the universal elastic anisotropy index A^U are listed in columns 9 and 10, respectively.

ID	ΔE	Vol	Density	B	G	Y	V$_H$	ν	A^U
	(meV)	(Å^3)	(g/cm^3)	(GPa)					
Fused Borophene									
*cc**	164	6.68	2.69	245	236	547	44	0.136	0.362
*cu**	278	6.53	2.79	242	246	558	48	0.121	0.190
*uu**	177	6.35	2.83	270	279	631	53	0.115	0.247
Other Covalent Systems									
C-Dia	85	5.52	3.61	454	537	1155	93	0.076	0.046
c-BN	0	5.75	3.58	409	407	916	64	0.126	0.200
α-B$_{12}$	0	7.00	2.57	225	210	480	39	0.145	0.192
γ-B$_{28}$	24	6.74	2.68	239	247	553	49	0.116	0.061
α-Ga	253	6.17	2.93	277	314	684	64	0.088	0.130
B$_6$O	–	7.11	2.67	239	211	496	37	0.158	0.239
Metal Borides									
TiB$_2$	–	8.20	4.70	282	282	638	51	0.125	0.123
CrB$_4$	–	7.14	4.44	300	277	647	46	0.148	0.347
ReB$_2$	–	8.89	12.95	370	296	711	40	0.184	0.193
Quasi-2D vdW System									
C-Gra	0	8.56	2.33	165	119	803	19	0.209	93.489
h-BN	59	8.65	2.39	146	99	654	16	0.224	57.663

With the exception of diamond (C-Dia) and *c*-BN, the calculated V$_H$ of *cc**, *cu**, and *uu** FBs is larger than that of all other superhard materials listed in the Table I. Their formation energies are relatively low (ΔE $\leqslant$ 280 meV/atom). Furthermore, the three phases satisfy the general stability criteria, i.e., the elastic tensor C_{ij}, are positive definite, have positive eigenvalues, and are dynamically stable. While *cc** and *cu** FBs are both metallic, *uu** is a small gap semiconductor. The gap calculated with modified Becke-Johnson functional [38] turns out to be 0.46 eV.

Additional details on the calculations are reported in the supplemental material [36], together with electronic and phononic spectra.

The three elastic moduli, i.e., the bulk (B), shear (G), and Young's (Y) moduli, are considerably smaller than the covalent superhard materials with a sp^3 tetragonal arrangement, such as C-Dia and *c*-BN, but comparable or larger than the other hard nontetragonal covalent systems (α-B$_{12}$ and B$_6$O) and hard metal borides. The Poisson's ratio ν and universal elastic anisotropy index A^U [39] are in line with those of other bulk systems, but sensibly different from those of C-Gra and *h*-BN, confirming the bulk nature of FBs.

Having established that FBs with low formation energy have mechanical properties comparable to other classes of

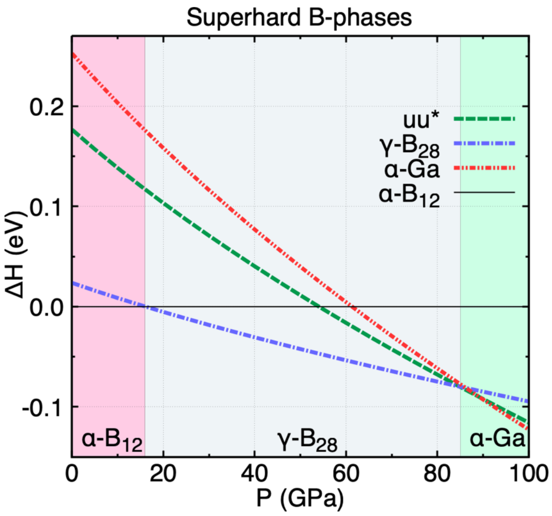

FIG. 3. Relative enthalpy ΔH (eV/atom) vs pressure P (GPa) of the most promising *uu** FB (green dashed), γ-B_{28} (blue dashed), and α-Ga (red dashed) phases of B. The ΔH is estimated with respect to α-B_{12}(black line).

widely used superhard materials, two obvious questions remain to be asked: What is the origin of their record hardness? What strategies can be used to synthesize them?

The reasons underlying the exceptional hardness of known superhard materials have been extensively investigated, revealing two different mechanisms: Diamond and other sp^3 materials, such as *c*-BN and *c*-BC_2N, contain a dense lattice of strong covalent bonds that are hard to compress; in metal borides, on the other hard, regions of incompressible electronic densities associated with the large metal ions limit the overall compressibility of the materials [40–42]. Clearly, it is the first mechanism that is at play in FBs: Inspection of Table I reveals that the atomic volumes are sensibly smaller than in metal borides and, although larger than in C-Dia or *c*-BN, absolutely in line with those of other covalent borides. Moreover, FBs including α-Ga exhibit lower atomic volumes than α-B_{12} due to the collapse of IC units.

A very attractive property of FBs compared with other superhard materials is their low density; in fact, despite the increase in atomic volume, due to the light mass of B atoms, FBs are lighter than C-Dia and *c*-BN and comparable to other covalent systems in Table. I. On the other hand, in metal borides, the heavy metal ions required to achieve high hardness lead to a significant (∼1.5–5) increase of the density, compared with FBs. This makes FBs an extremely new attractive family of superhard lightweight materials.

Concerning possible strategies to synthesize FBs, one option is to resort to high-temperature reactions, starting from appropriate precursors. The predicted enthalpies of formation of *cc**, *cu**, and *uu** FBs ($\Delta E \leqslant 280$ meV/atom) are within typical stabilization energies of metastable polymorphs, i.e., ∼1 eV/atom based on the amorphous reference criteria [31]. To simulate the synthesis from amorphous precursors, we recalculated the convex hull in Fig. 1 using as reference B-C. The downward shift of relative energy of the FB systems makes the potential FBs thermodynamically favorable. Moreover, some of the record superhard borophenes, such as the *uu** structure, become thermodynamically competitive with the ground-state structures at higher pressure (80–90 GPa), as shown in Fig. 3. Although direct quenching to room pressure may be problematic, a viable alternative may be high-pressure high-temperature synthesis. Such synthesis methods are used on a regular basis at present to obtain synthetic diamonds, and their use has recently been demonstrated also to synthesize (non)-IC B crystals [43–46]. Other methods such as chemical vapor deposition could be used in combination with high-pressure high temperature to grow the crystals [47].

Conclusions- In conclusion, in this paper we presented a new class of superhard materials, FBs, identified through HT screening of B-C structures generated in a minima-hopping run. FB can be seen as a stacking of 2D boron-layers, interconnected through either a single or V-shaped double covalent bonds, which makes them distinct from other known 2D boron materials (borophenes) reported in the literature. The spatial distribution of the ELF and the generally low A^U clearly show that, due the presence of covalent bonds between the atoms of the interconnected BLs, FBs effectively behave as 3D bulk structures, although geometrically they appear to be composed of 2D BLs. In this sense, FB represent the missing link between the 2D borophenes and the 3D bulk IC structures.

Due to their relatively low formation energies and low densities, FBs could be very interesting lightweight alternatives to existing hard materials for industrial applications, which may be synthesized through one or more of the methods that are currently routinely used to synthesize other boron crystals: High-temperature, high-pressure, or CVD synthesis techniques, starting from appropriate precursors. Furthermore, our calculations hint that *uu** FB, with V_H of 53 GPa, becomes thermodynamically competitive with other boron structures at high pressures and may hence be stabilized through controlled quenching from high pressure.

Note added. Recently, a preprint has appeared [48], which reports layered structures of boron discovered by CSP with evolutionary algorithms. The authors propose a different classification scheme of FBs into *derivatives of the α-Ga* and *channel* structures. The *Channel-I* structure is analogous to our *uu** structure. The main results of that work, which is totally independent from ours, are in good agreement with ours.

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[1] V. L. Solozhenko and Y. Le Godec, J. Appl. Phys. **126**, 230401 (2019).

[2] A. G. Kvashnin, Z. Allahyari, and A. R. Oganov, J. Appl. Phys. **126**, 040901 (2019).

[3] M. Wakatsuki, K. Ichinose, and T. Aoki, Mater. Res. Bull. **7**, 999 (1972).

[4] Y. Zhang, H. Sun, and C. Chen, Phys. Rev. B **73**, 144115 (2006).

[5] V. L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, and D. C. Rubie, Appl. Phys. Lett. **78**, 1385 (2001).

[6] Q. Gu, G. Krauss, and W. Steurer, Adv. Mater. **20**, 3620 (2008).

[7] J. B. Levine, S. H. Tolbert, and R. B. Kaner, Adv. Funct. Mater. **19**, 3519 (2009).

[8] Y. Liang, Z. Zhong, and W. Zhang, Comput. Mater. Sci. **68**, 222 (2013).

[9] S. Curtarolo, G. L. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, Nat. Mater. **12**, 191 (2013).

[10] J. A. Flores-Livas, L. Boeri, A. Sanna, G. Profeta, R. Arita, and M. Eremets, Phys. Rep. **856**, 1 (2020).

[11] W.-C. Chen, J. N. Schmidt, D. Yan, Y. K. Vohra, and C.-C. Chen, npj Comput. Mater. **7**, 114 (2021).

[12] P. Avery, X. Wang, C. Oses, E. Gossett, D. M. Proserpio, C. Toher, S. Curtarolo, and E. Zurek, npj Comput. Mater. **5**, 89 (2019).

[13] Y. Fujii, M. Maruyama, N. T. Cuong, and S. Okada, Phys. Rev. Lett. **125**, 016001 (2020).

[14] S. Saha, W. von der Linden, and L. Boeri, arXiv:2007.09254.

[15] V. Brazhkin, M. Kondrin, A. Kvashnin, E. Mazhnik, and A. Oganov, arXiv:2007.08912.

[16] S. Goedecker, J. Chem. Phys. **120**, 9911 (2004).

[17] M. Amsler and S. Goedecker, J. Chem. Phys. **133**, 224104 (2010).

[18] M. I. Eremets, V. V. Struzhkin, H.-k. Mao, and R. J. Hemley, Science **293**, 272 (2001).

[19] D. Papaconstantopoulos and M. Mehl, Phys. Rev. B **65**, 172510 (2002).

[20] Y. Ma, J. S. Tse, D. D. Klug, and R. Ahuja, Phys. Rev. B **70**, 214107 (2004).

[21] I. Boustani, Phys. Rev. B **55**, 16426 (1997).

[22] H. Tang and S. Ismail-Beigi, Phys. Rev. Lett. **99**, 115501 (2007).

[23] X.-F. Zhou, X. Dong, A. R. Oganov, Q. Zhu, Y. Tian, and H.-T. Wang, Phys. Rev. Lett. **112**, 085502 (2014).

[24] X. Sun, X. Liu, J. Yin, J. Yu, Y. Li, Y. Hang, X. Zhou, M. Yu, J. Li, G. Tai *et al.*, Adv. Funct. Mater. **27**, 1603300 (2017).

[25] Z.-Q. Wang, T.-Y. Lü, H.-Q. Wang, Y. P. Feng, and J.-C. Zheng, Front. Phys. **14**, 33403 (2019).

[26] A. Oganov and V. Solozhenko, J. Superhard Mater. **31**, 285 (2009).

[27] E. S. Penev, S. Bhowmick, A. Sadrzadeh, and B. I. Yakobson, Nano Lett. **12**, 2441 (2012).

[28] J. Kunstmann and A. Quandt, Density functional and linear response studies of sp materials, Ph.D. thesis, University of Stuttgart, 2008.

[29] S. Saha, S. Cataldo, M. Amsler, W. von der Linden, and L. Boeri, Phys. Rev. B **102**, 024519 (2020).

[30] *Computational methodology*- The plane-wave-based VASP [49] DFT package was employed for structural relaxations and for the calculation of total energies, electronic properties, ELF, and elastic properties. The calculation of phonon dispersions has been carried out using Quantum-Espresso-6.4.1 [50,51]. Unless otherwise specified, all the DFT calculations have been carried out using the LDA for the exchange-correlation functional. The in-built LDA projector augmented wave potentials have been used for VASP [52] calculations, whereas ONCV [53] was been used in QE. Further details of the calculations can be found in the supplemental material [36].

[31] M. Aykol, S. S. Dwaraknath, W. Sun, and K. A. Persson, Sci. Adv. **4**, eaaq0148 (2018).

[32] W. Eberhardt, B. Crawford. Jr., and W. N. Lipscomb, J. Chem. Phys. **22**, 989 (1954).

[33] All FBs discussed here contain a maximum of two layers; this is likely due to limit of 15 atoms/unit cell imposed in our initial structural search.

[34] A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest *et al.*, Science **350**, 1513 (2015).

[35] B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, and K. Wu, Nat. Chem. **8**, 563 (2016).

[36] See supplemental material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.5.L080601 for the details of the calculation and different properties of the *cc**, *cu**, and *uu** fused borophenes.

[37] *Computational details of elastic properties calculations*: The elastic properties of the systems listed in Table I were estimated from the elastic tensor, based on the Voigt-Reuss-Hill approximation [54]. The Chen's model [55] was used to estimate the hardness. The Chen's model is known to overestimate hardness values for 2D cases or molecular crystals [56]. If encountered, such spurious cases were removed. The non FB crystal structures in Table I were obtained from the Materials Project database [57]. Further details are in the supplemental material [36].

[38] F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009).

[39] S. I. Ranganathan and M. Ostoja-Starzewski, Phys. Rev. Lett. **101**, 055504 (2008).

[40] R. B. Kaner, J. J. Gilman, and S. H. Tolbert, Science **308**, 1268 (2005).

[41] R. W. Cumberland, M. B. Weinberger, J. J. Gilman, S. M. Clark, S. H. Tolbert, and R. B. Kaner, J. Am. Chem. Soc. **127**, 7264 (2005).

[42] H.-Y. Chung, M. B. Weinberger, J. B. Levine, A. Kavner, J.-M. Yang, S. H. Tolbert, and R. B. Kaner, Science **316**, 436 (2007).

[43] G. Parakhonskiy, N. Dubrovinskaia, E. Bykova, R. Wirth, and L. Dubrovinsky, High Press. Res. **33**, 673 (2013).

[44] Z. Wu, G. Tai, W. Shao, R. Wang, and C. Hou, Nanoscale **12**, 3787 (2020).

[45] Y. Le Godec, A. Courac, and V. L. Solozhenko, J. Appl. Phys. **126**, 151102 (2019).

[46] I. Chuvashova, E. Bykova, M. Bykov, V. Prakapenka, K. Glazyrin, M. Mezouar, L. Dubrovinsky, and N. Dubrovinskaia, Phys. Rev. B **95**, 180102(R) (2017).

[47] J. M. Maita, G. Song, M. Colby, and S.-W. Lee, Mater. Des. **193**, 108856 (2020).

[48] K. P. Hilleke, T. Ogitsu, S. Zhang, and E. Zurek, Phys. Rev. Mater. **5**, 053605 (2021).

[49] G. Kresse and F. J, Comput. Mat. Sci. **6**, 15 (1996).

[50] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni *et al.*, J. Phys.: Condens. Matter **29**, 465901 (2017).

[51] S. Baroni, S. De Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[52] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[53] D. R. Hamann, Phys. Rev. B **88**, 085117 (2013).

[54] R. Hill, Proc. Phys.l Soc. Sect. A **65**, 349 (1952).

[55] X.-Q. Chen, H. Niu, D. Li, and Y. Li, Intermetallics **19**, 1275 (2011).

[56] A. O. Lyakhov and A. R. Oganov, Phys. Rev. B **84**, 092103 (2011).

[57] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder *et al.*, APL Mater. **1**, 011002 (2013).