

Unexpected Reconstruction of the α -Boron (111) Surface

Xiang-Feng Zhou,^{1,2,*} Artem R. Oganov,^{2,3,4} Xi Shao,¹ Qiang Zhu,² and Hui-Tian Wang^{1,5}

¹*School of Physics and Key Laboratory of Weak-Light Nonlinear Photonics, Nankai University, Tianjin 300071, China*

²*Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York 11794, USA*

³*Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny City, Moscow Region 141700, Russian Federation*

⁴*School of Materials Science, Northwestern Polytechnical University, Xi'an 710072, China*

⁵*National Laboratory of Solid State Microstructures and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China*

(Received 30 July 2014; published 21 October 2014)

We report a novel reconstruction of the α -boron (111) surface, discovered using *ab initio* evolutionary structure prediction, and show that this unexpected neat structure has a much lower energy than the recently proposed (111)- $I_{R,(a)}$ surface. In this reconstruction, all single interstitial boron atoms bridge neighboring B_{12} icosahedra by polar covalent bonds, and this satisfies the electron counting rule, leading to the reconstruction-induced metal-semiconductor transition. The peculiar charge transfer between the interstitial atoms and the icosahedra plays an important role in stabilizing the surface.

DOI: 10.1103/PhysRevLett.113.176101

PACS numbers: 68.35.bg, 71.15.Mb, 73.20.At

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) have aroused extensive interest, in the hopes of replicating or even surpassing the unique properties and diversity of the forms of carbon [6–12]. By analogy with graphene [13,14], two-dimensional boron sheets with triangular and hexagonal motifs are predicted to be the most stable phases and likely precursors for boron nanostructures [15–22]. However, buckled bilayer structures appeared to be massively more stable; some of them turned out to have novel electronic properties, such as a distorted Dirac cone [23]. Hayami and Otani systematically studied the energies of low-index bare surfaces in the α -boron, β -boron, and two tetragonal phases (t -I and t -II), which suggested that t -I and t -II can be more stable than α -boron and β -boron for sufficiently small nanoparticles [24,25]. Amsler *et al.* performed the first study of the reconstruction of the α -boron (111) and predicted several low-energy surface reconstructions by using the minima hopping method. In particular, a metallic reconstructed phase of (111)- $I_{R,(a)}$ was predicted to be the most stable configuration, where a conducting boron sheet was adsorbed on a semiconducting substrate, leading to numerous possible applications in nanoelectronics [26]. However, this seems to be in conflict with the general principle that the reconstructions usually lower their energies by atomic rearrangement leading to a semiconducting (as opposed to metallic) surface state [27]. Such an unexpected metallic reconstruction encourages us to explore other

likely reconstructions and the stabilization mechanisms by first-principles calculations.

α -boron structure is composed of B_{12} icosahedra [28], has two inequivalent atomic sites, polar (B_p) and equatorial (B_e) sites, the B_p atoms form upper and lower triangles of an icosahedron, and the B_e atoms form a slightly nonplanar hexagon along the equator of an icosahedron [2]. The arrangement of icosahedra in α -boron can be described as a cubic close packing with the layer sequence ABC [1]. Compared with the (111)- $I_{R,(a)}$ surface built along the [111] direction of the primitive rhombohedral cell with surface vectors $\mathbf{U}(2\bar{1}\bar{1})$ and $\mathbf{V}(11\bar{2})$, we cleaved the surface along the [111] direction with surface vectors $\mathbf{U}(\bar{1}\bar{1}2)$ and $\mathbf{V}(1\bar{1}0)$, which allowed us to reduce the computational costs drastically. The calculations were based on four layers of B_{12} icosahedra in the (111)-I substrate, and then the (111)-II substrate was also tested [25,26]. In both cases we obtained exactly the same reconstruction, regardless of the type of substrate if enough atoms and sufficient thickness were used. Searches for the stable reconstruction were performed using the *ab initio* evolutionary algorithm USPEX [29–31], which has been successfully applied to various materials (e.g., [32–34]). The number of surface atoms was allowed to vary from 1 to 20, constrained within a surface layer of thickness 4 Å, and we used vacuum regions of 10 Å thickness. Given that the thickness of B_{12} icosahedron is ~ 3.7 Å, there is enough space to fully explore the chemical landscape (more than 2500 structures were sampled, to achieve full confidence in the final result) in our calculations. The all-electron projector-augmented wave method [35] was employed, as implemented in the Vienna *ab initio* simulation package (VASP) [36], in combination with the generalized gradient approximation (GGA) and functional of Perdew, Burke, and Ernzerhof (PBE) [37]. A plane-wave

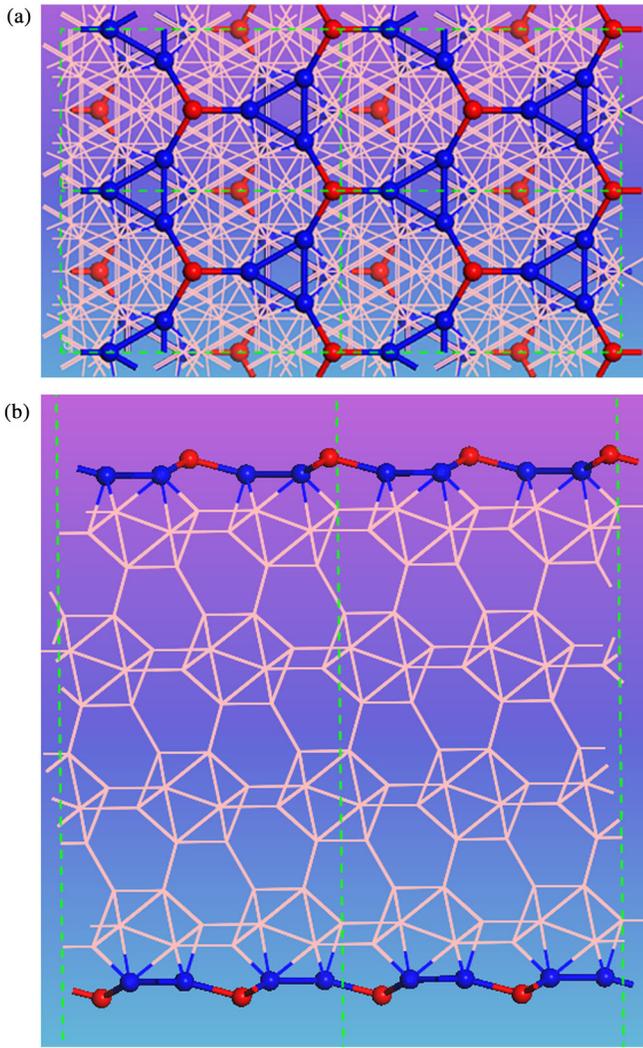


FIG. 1 (color online). (a) Projection of the $2 \times 2 \times 1$ supercell of the $(111)\text{-}I_{R,(z)}$ structure along the $[111]$ direction. (b) Projection of the $2 \times 2 \times 1$ supercell of the $(111)\text{-}I_{R,(z)}$ structure along the $[\bar{1}\bar{1}2]$ direction. The inequivalent surface atoms are shown by different colors.

cutoff energy of 500 eV and for sampling the Brillouin zone we used uniform gamma-centered k -points grids with resolution $2\pi \times 0.04 \text{ \AA}^{-1}$. In addition, the hybrid HSE06 functional with the screening parameter (ω) 0.2 \AA^{-1} was also employed to check the robustness of surface energies [38].

For the $(111)\text{-}I_{R,(a)}$ reconstruction, proposed by Amsler *et al.*, there is buckling and coupling among three outer atomic layers above the icosahedral B_{12} units, which results in structural complexity [26]. In contrast to $(111)\text{-}I_{R,(a)}$, our reconstruction [designated as $(111)\text{-}I_{R,(z)}$] has an unexpected neat structure, as shown in Fig. 1(a), where a single boron atom occupies the interstitial position (named as B_i , colored in red), connects the B_p atoms (colored in blue), and forms bridges with bond lengths of 1.793 \AA and bond angles of 113.06° . The B_i atoms are slightly above the topmost icosahedral atoms (B_p), see Fig. 1(b), and together

they form the modulated “3 + 9” membered rings on the topmost surface (the calculated lattice constants and atomic positions of the related surfaces are given in the Supplemental Material [39]). We have computed the surface energy as $\sigma = (1/2A) (N\epsilon_{\text{bulk}} - E_{\text{slab}})$, where A denotes the surface area, ϵ_{bulk} is the energy per atom in the bulk α -boron, and E_{slab} is the energy of the substrate containing N atoms [26]. Surface energies of $(111)\text{-}I$ and $(111)\text{-}I_{R,(a)}$ obtained using the GGA-PBE and HSE06 functionals (Table I), are in excellent agreement with previous results [26]. This establishes the reliability and accuracy of our calculations. Strikingly, the surface energy of $(111)\text{-}I_{R,(z)}$ is 128.23 meV/\AA^2 for GGA-PBE and 136.79 meV/\AA^2 for HSE06, which is considerably, by 42 and 60 meV/\AA^2 , respectively, lower than the energy of the $(111)\text{-}I_{R,(a)}$ surface reconstruction. As an additional check, we performed a structure search with the same substrate proposed in Ref. [26], and obtained the same reconstruction and energy, and found that there is no dependence on the choice of the surface vectors or cleavage plane: it is the general rule that the ratio of B_i atoms to the exposed B_{12} icosahedra should be 1 : 1 on the α -boron (111) surface.

Figure 2 shows band structures of the unreconstructed $(111)\text{-}I$ and the reconstructed $(111)\text{-}I_{R,(z)}$ surfaces from the GGA-PBE calculations. Because of the unsaturated dangling bonds, the $(111)\text{-}I$ surface is metallic, as shown in Fig. 2(a). In contrast, Figure 2(b) shows that the $(111)\text{-}I_{R,(z)}$ surface is semiconducting, with a direct density functional theory band gap of 1.13 eV compared with the band gap of 1.50 eV of bulk α -boron. The reconstruction-induced metal-semiconductor transition is consistent with the general principle that reconstructions usually lower their energies by atomic rearrangements that lead to a semiconducting surface [27]. According to Wade’s rule [42,43], a B_{12} icosahedron has 36 valence electrons, 26 of which may be used for intricosahedral bonds and 10 for intericosahedral bonds. Each icosahedron forms six two-electron-two-center ($2e2c$) bonds with the icosahedra of neighboring layers, which requires $6 \times 2/2 = 6$ electrons, as well as six closed two-electron-three-center ($2e3c$) bonds with the neighboring icosahedra in its own layer, these multicenter bonds require $6 \times 2/3 = 4$ electrons [1]. The $(111)\text{-}I$ surface cuts three intericosahedral bonds ($2e2c$) per

TABLE I. Surface energies of the unreconstructed $(111)\text{-}I$, reconstructed $(111)\text{-}I_{R,(a)}$, and $(111)\text{-}I_{R,(z)}$ structures obtained using different functionals, in units of meV/\AA^2 .

Surface	(111)-I	(111)-I _{R,(a)}	(111)-I _{R,(z)}	Reference
PBE	219.29	170.64	128.23	This work 26
	218.80	170.61		
HSE	248.43	197.39	136.79	This work 26
	247.50	196.31		

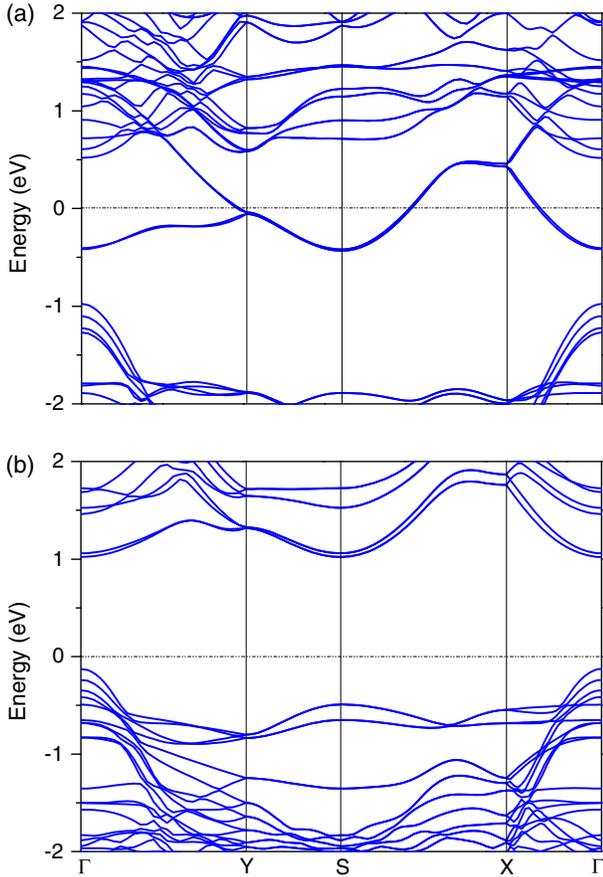


FIG. 2 (color online). Band structures of (a) (111)-I and (b) (111)- $I_{R,(z)}$, the special k points are labeled as $\Gamma(000)$, $Y(00.50)$, $S(-0.50.50)$, and $X(-0.500)$, respectively.

icosahedron, and there are two B_{12} icosahedra per stacking layer of the (111)- $I_{R,(z)}$ surface. Therefore, the unsaturated dangling bonds of the (111)- $I_{R,(z)}$ surface need additional $3 \times 2 \times 2/2 = 6$ valence electrons. Two B_i atoms per surface unit cell, connect six B_p atoms, as shown in Fig. 1(a), form six bridging B_i - B_p bonds (these are $2e2c$ bonds), which perfectly satisfy the electron counting rule (ECR) [27,44], and are responsible for the reconstruction-induced metal-semiconductor transition.

Projected density of states (PDOS) of the topmost atoms is plotted in Fig. 3. The (111)-I surface exhibits metallic character, see Fig. 3(a), predominantly due to the out-of-plane states (p_z orbitals), arising from the unsaturated B_p atoms, and located at the bottom of the conduction band. In comparison, strongly hybridized bonding states present in the vicinity of the Fermi level in Fig. 3(b), mainly derive from the B_p : p_z and B_i : p_{xy} orbitals, and are completely filled. The (111)- $I_{R,(z)}$ surface is therefore a semiconductor. PDOS [Figs. 3(c) and 3(d)] clearly shows that the out-of-plane p_z states and in-plane p_{xy} states near the valence band edge are predominantly from the B_p and B_i atoms, respectively. Because the B_i atoms are located above empty space, there is no p_z state for the B_i below the Fermi level in

Fig. 3(d). Moreover, the distance between the B_i and B_e atoms is clearly non-bonding, 2.926 Å. All of these facts indicate that there is no interaction or bonding between the B_i and B_e atoms, which further confirms the reliability of the surface bonding configuration and the ECR applied for the (111)- $I_{R,(z)}$ surface.

Symmetry breaking of B_{12} icosahedra results in charge asymmetry on some B-B bonds, and in fact a small degree of ionicity of B-B bonds in the B_{12} icosahedron was predicted in α -boron [3], while a much greater degree of ionicity was found in the high-pressure partially ionic γ -boron [4]. It is interesting to study charge transfer or ionicity for the (111)- $I_{R,(z)}$ surface. Chemical effects of the B_i adsorption can be seen in Fig. 4, which shows charge density difference [45]. There is a notable charge transfer from B_i to the neighboring B_{12} icosahedra through B_p atoms. Bader charges for B_i are $+0.17e$, and $+0.04e$ for B_p [46]. Strikingly, the charge of B_p is close to the value in the bulk ($\sim +0.05e$) [4,23], and the significant charge transfer between the B_i atoms and B_{12} icosahedra indicates that the bridging B_i - B_p bonds are unique polar covalent bonds, in contrast with the intericosahedral purely covalent B_p - B_p

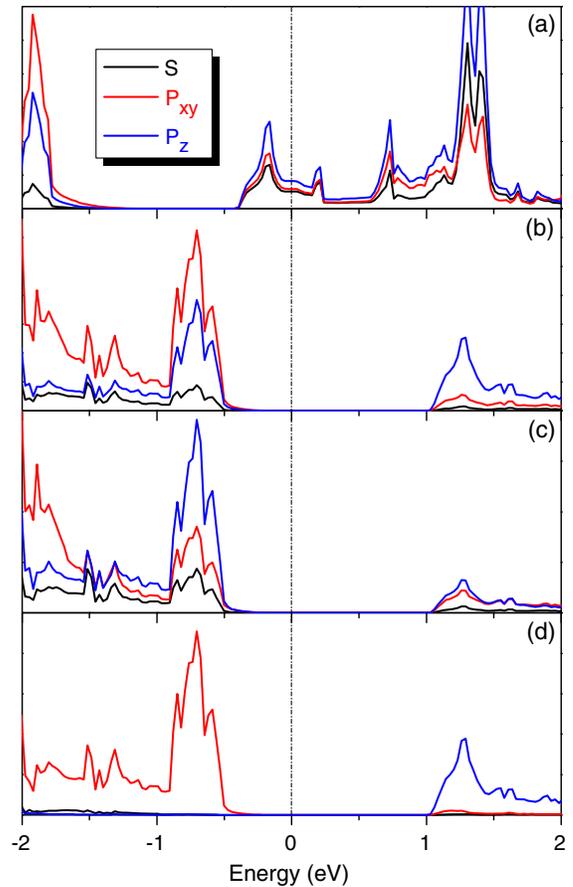


FIG. 3 (color online). [(a) and (b)] PDOS of the (111)-I and (111)- $I_{R,(z)}$ structures. [(c) and (d)] PDOS of the B_p and B_i atoms in (111)- $I_{R,(z)}$ structure.

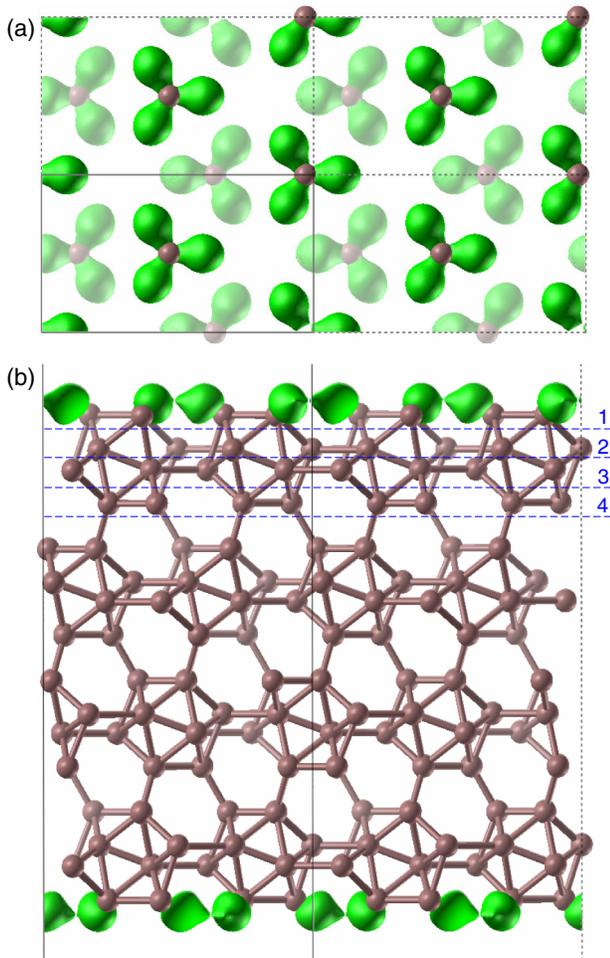


FIG. 4 (color online). Charge density difference isosurface [45] showing bonding between the adsorbed boron atoms and the substrate. (a) Top view (for clarity, only the adsorbed atoms are shown), (b) side view (showing the substrate).

bonds [3]. Consistent with significant charge transfer, the B_i - B_p bonds (1.793 Å) are much weaker and longer than the B_p - B_p bonds (1.673 Å). In Fig. 4(b), each B_{12} icosahedron comprises four atomic layers (labeled from 1 to 4); the charge transfer for these four layers should be in the “+ - - +” order with the values of +0.56, -0.46, -0.46, and +0.36 e , compared with the corresponding values of +0.20, -0.22, -0.22, and +0.24 e in α -boron. It is clear from these numbers that the surface region as a whole is charge-neutral. The charge transfer of the (111)- $I_{R,(z)}$ surface is rebalanced within the top four atomic layers (including the B_i atoms and B_{12} icosahedra), which plays an important role in stabilizing the surface.

In conclusion, the most stable reconstruction of the α -boron (111) surface has been predicted using an *ab initio* evolutionary structure search. Our results show the (111)- $I_{R,(z)}$ reconstruction is lower in energy than the earlier reported structures [26], and confirm that the classical ECR governs the reconstructions, and is

satisfied through adsorption of extra boron atoms that occupy non-icosahedral sites and form $2e2c$ bonds with substrate, leading to the metal-semiconductor transition. These newly formed bonds involve a significant charge transfer and can be characterized as polar covalent bonds. Charge redistribution between the B_i atoms and the B_{12} icosahedra contributes to the stabilization of this reconstruction.

X. F. Z. thanks Philip B. Allen and Maria V. Fernandez-Serra for valuable discussions. This work was supported by the National Science Foundation of China (Grants No. 11174152 and No. 91222111), the National 973 Program of China (Grant No. 2012CB921900), the Program for New Century Excellent Talents in University (Grant No. NCET-12-0278), and the Fundamental Research Funds for the Central Universities (Grant No. 65121009). A. R. O. thanks the National Science Foundation (Grants No. EAR-1114313, No. DMR-1231586), DARPA (Grants No. W31P4Q1310005 and No. W31P4Q1210008), DOE [Computational Materials and Chemical Sciences Network (CMCSN) Project No. DE-AC02-98CH10886], the Government of Russian Federation (Grant No. 14.A12.31.0003), and the Foreign Talents Introduction and Academic Exchange Program (Grant No. B08040). Calculations were performed on XSEDE facilities and on the cluster of the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the DOE-BES under Contract No. DE-AC02-98CH10086.

*xfzhou@nankai.edu.cn; zxf888@163.com

- [1] B. Albert and H. Hillebrecht, *Angew. Chem., Int. Ed.* **48**, 8640 (2009).
- [2] M. Fujimori, T. Nakata, T. Nakayama, E. Nishibori, K. Kimura, M. Takata, and M. Sakata, *Phys. Rev. Lett.* **82**, 4452 (1999).
- [3] J. He, E. Wu, H. Wang, R. Liu, and Y. J. Tian, *Phys. Rev. Lett.* **94**, 015504 (2005).
- [4] A. R. Oganov, J. H. Chen, C. Gatti, Y. Z. Ma, Y. M. Ma, C. W. Glass, Z. X. Liu, T. Yu, O. O. Kurakevych, and V. L. Solozhenko, *Nature (London)* **457**, 863 (2009).
- [5] M. I. Eremets, V. V. Struzhkin, H.-k. Mao, and R. J. Hemley, *Science* **293**, 272 (2001).
- [6] H. J. Zhai, B. Kiran, J. Li, and L. S. Wang, *Nat. Mater.* **2**, 827 (2003).
- [7] F. Liu, C. Shen, Z. Su, X. Ding, S. Deng, J. Chen, N. Xu, and H. Gao, *J. Mater. Chem.* **20**, 2197 (2010).
- [8] C. J. Otten, O. R. Lourie, M. F. Yu, J. M. Cowley, M. J. Dyer, R. S. Ruoff, and W. E. Buhro, *J. Am. Chem. Soc.* **124**, 4564 (2002).
- [9] Y. Sato, M. Terauchi, K. Kirihara, T. Sasaki, K. Kawaguchi, N. Koshizaki, and K. Kimura, *J. Phys. Conf. Ser.* **176**, 012029 (2009).
- [10] N. Gonzalez Szwacki, A. Sadrzadeh, and B. I. Yakobson, *Phys. Rev. Lett.* **98**, 166804 (2007).
- [11] D. L. V. K. Prasad and E. D. Jemmis, *Phys. Rev. Lett.* **100**, 165504 (2008).

- [12] S. De, A. Willand, M. Amsler, P. Pochet, L. Genovese, and S. Goedecker, *Phys. Rev. Lett.* **106**, 225502 (2011).
- [13] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature (London)* **438**, 197 (2005).
- [14] A. K. Geim, *Science* **324**, 1530 (2009).
- [15] I. Boustani, *Surf. Sci.* **370**, 355 (1997).
- [16] I. Boustani, *Phys. Rev. B* **55**, 16426 (1997).
- [17] H. Tang and S. Ismail-Beigi, *Phys. Rev. Lett.* **99**, 115501 (2007).
- [18] A. Sebetci, E. Mete, and I. Boustani, *J. Phys. Chem. Solids* **69**, 2004 (2008).
- [19] H. Tang and S. Ismail-Beigi, *Phys. Rev. B* **80**, 134113 (2009); **82**, 115412 (2010).
- [20] S. Saxena and T. A. Tyson, *Phys. Rev. Lett.* **104**, 245502 (2010).
- [21] E. S. Penev, S. Bhowmick, A. Sadrzadeh, and B. I. Yakobson, *Nano Lett.* **12**, 2441 (2012).
- [22] X. Wu, J. Dai, Y. Zhao, Z. Zhuo, J. Yang, and X. C. Zeng, *ACS Nano* **6**, 7443 (2012).
- [23] X. F. Zhou, X. Dong, A. R. Oganov, Q. Zhu, Y. Tian, and H. T. Wang, *Phys. Rev. Lett.* **112**, 085502 (2014).
- [24] W. Hayami and S. Otani, *J. Phys. Chem. C* **111**, 10394 (2007).
- [25] W. Hayami and S. Otani, *J. Phys. Chem. C* **111**, 688 (2007).
- [26] M. Amsler, S. Botti, M. A. L. Marques, and S. Goedecker, *Phys. Rev. Lett.* **111**, 136101 (2013).
- [27] C. B. Duke, *Chem. Rev.* **96**, 1237 (1996).
- [28] B. F. Decker and J. S. Kasper, *Acta Crystallogr.* **12**, 503 (1959).
- [29] A. R. Oganov and C. W. Glass, *J. Chem. Phys.* **124**, 244704 (2006).
- [30] C. W. Glass, A. R. Oganov, and N. Hansen, *Comput. Phys. Commun.* **175**, 713 (2006).
- [31] Q. Zhu, L. Li, A. R. Oganov, and P. B. Allen, *Phys. Rev. B* **87**, 195317 (2013).
- [32] X. F. Zhou, A. R. Oganov, X. Dong, L. Zhang, Y. Tian, and H. T. Wang, *Phys. Rev. B* **84**, 054543 (2011).
- [33] X. F. Zhou, A. R. Oganov, G. R. Qian, and Q. Zhu, *Phys. Rev. Lett.* **109**, 245503 (2012).
- [34] C. H. Hu, A. R. Oganov, Q. Zhu, G. R. Qian, G. Frapper, A. O. Lyakhov, and H. Y. Zhou, *Phys. Rev. Lett.* **110**, 165504 (2013).
- [35] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [36] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); *Comput. Mater. Sci.* **6**, 15 (1996).
- [37] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [38] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- [39] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.113.176101>, which includes Refs. [40–41], an additional electronic property, and detailed structural parameters of related reconstructions.
- [40] J. Tersoff and D. R. Hamann, *Phys. Rev. B* **31**, 805 (1985).
- [41] D. E. P. Vanpoucke and G. Brocks, *Phys. Rev. B* **77**, 241308 (R) (2008).
- [42] K. Wade, *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
- [43] E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *J. Am. Chem. Soc.* **123**, 4313 (2001).
- [44] M. D. Pashley, *Phys. Rev. B* **40**, 10481 (1989).
- [45] The charge density difference $\delta\rho = \rho_{AB} - (\rho_A + \rho_B)$, where ρ_{AB} is the charge density of the (111)- $I_{R,(z)}$ surface, ρ_A is the charge density of the B_i atoms, and ρ_B is the charge density of the unrelaxed structure where the B_i atoms are removed from the (111)- $I_{R,(z)}$ surface.
- [46] W. Tang, E. Sanville, and G. Henkelman, *J. Phys. Condens. Matter* **21**, 084204 (2009).