Computational prediction of body-centered cubic carbon in an all-sp^{3} six-member ring configuration
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Body-centered cubic carbon in an all-\(sp^3\) six-membered-ring configuration

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Recent shock compression experiments produced clear evidence of a new carbon phase, but a full structural identification has remained elusive. Here we establish by \textit{ab initio} calculations a body-centered cubic carbon phase in \(Ia\bar{3}d\) (\(O_\text{h}^{23}\)) symmetry, which contains twelve atoms in its primitive cell, thus termed BC12, and comprises all-\(sp^3\) six-membered rings. This structural configuration places BC12 carbon in the same bonding type as cubic diamond, and its stability is verified by phonon mode analysis. Simulated x-ray diffraction patterns provide an excellent match to the previously unexplained distinct diffraction peak found in shock compression experiments. Electronic band and density of states calculations reveal that BC12 is a semiconductor with a direct band gap of \(\sim 2.97\) eV. These results provide a solid foundation for further exploration of this new carbon allotrope.

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I. INTRODUCTION

Carbon is one of the most versatile elements in its ability to assemble diverse structural types. In pure elemental form, there are three naturally occurring carbon allotropes, graphite, diamond, and amorphous carbon, which contain \(sp^2\), \(sp^3\), and mixed \(sp^2/sp^3\) bonding types, respectively. A rich variety of carbon phases also have been synthesized under laboratory conditions, including, most notably, carbon nanotubes (CNT),\(^1\) fullerenes,\(^2\) and graphene.\(^3\) These discoveries have stimulated great interest in search of more carbon allotropes.\(^4\)–\(^8\) A particularly appealing approach is to explore new carbon phases under extreme conditions, such as high pressure or shock compression, which can induce new bonding modifications. A prominent example is the recent discovery of cold-compressed graphite\(^9\) that has led to the identification of several new carbon forms.\(^10\)–\(^18\) In addition, cubic modifications of carbon have been produced during the heating of carbon soot or shock compression of polycrystalline graphite,\(^19\)–\(^21\) which led to a proposed simple cubic carbon phase termed SC24 in \(Pa\bar{3}\) symmetry.\(^22\) Moreover, a body-centered cubic carbon denoted BC8 is suggested to be the high-pressure modification of carbon derived from cubic diamond under pressure of \(\sim 1100\) GPa.\(^23\)–\(^25\) Among all these carbon structures, only BC8 carbon comprises entirely a diamond-like six-membered-ring bonding structure, while other reported \(sp^3\) hybridized carbon structures contain mixedbonding configurations, such as the \((5+6+7)\)-membered-ring in \(M\) carbon,\(^10\) \((4+6+8)\)-membered-ring in \(Z\) carbon,\(^13\) or \((3+6+7)\)-membered-ring in SC24 carbon.\(^22\)

In this paper, we report by \textit{ab initio} calculations a body-centered cubic carbon phase with a 24-atom unit cell in \(Ia\bar{3}d\) symmetry with all-\(sp^3\) six-membered rings, which is the same bonding type as cubic diamond (8-atom unit cell in \(Fd\bar{3}m\) symmetry) and BC8 carbon (16-atom unit cell in \(Ia\bar{3}\) symmetry). This new carbon phase has a twelve-atom primitive cell (thus termed BC12 carbon hereafter) with a single bond length (1.566 Å) but two distinct bond angles (99.59° and 131.81°), placing it between cubic diamond, which has a single bond length and a single bond angle, and BC8, which has two distinct bond lengths and two bond angles. Electronic band and density of states calculations reveal that BC12 carbon is a semiconductor with a direct band gap of 2.97 eV, and its dynamic stability is verified by phonon mode analysis. Simulated X-ray diffraction (XRD) patterns suggest the presence of BC12 carbon in shock compressed soot carbon,\(^20\) and this finding resolves previously unexplained experimental data and lays the foundation for further exploration of this new carbon form.

II. COMPUTATIONAL METHOD

We performed calculations using the density functional theory as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^26\) Both the local density approximation (LDA) in the form of Ceperley-Alder\(^27\) and generalized gradient approximation (GGA) developed by Perdew, Burke, and Ernzerhof (PBE)\(^28\) are adopted for the exchange-correlation potential. The all-electron projector augmented wave (PAW)\(^29\) method is adopted with \(2s^22p^2\) treated as valence electrons. We used a plane-wave basis set with an energy cutoff of 800 eV and sampled the Brillouin zone with an \(8 \times 8 \times 8\) \(k\)-point grid. The geometries are optimized with symmetry constraints until the remaining atomic forces are less than \(10^{-6}\) eV/Å and the energy convergence criterion is set at \(10^{-8}\) eV. Electronic band structures are calculated using the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06).\(^30\) Phonon calculations are performed using the phonopy package\(^31,\)\(^32\) with the forces calculated from VASP.
TABLE I: Calculated equilibrium structural parameters (space group, lattice parameter $a$, volume per atom $V_0$, density $\rho$, bond lengths $d_{C-C}$, bond angles $\angle C-C-C$), total energy per atom $E_{tot}$, electronic band gap $E_g$, and bulk modulus $B_0$ for diamond, BC8, BC12, and SC24 carbon at zero pressure, compared to available experimental data.$^{20,35}$

<table>
<thead>
<tr>
<th>Structure</th>
<th>Space group</th>
<th>Method</th>
<th>$a$ (Å)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$d_{C-C}$ (Å)</th>
<th>$\angle C-C-C$ ($^\circ$)</th>
<th>$E_{tot}$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>$Fd\bar{3}m$</td>
<td>LDA</td>
<td>3.534</td>
<td>5.52</td>
<td>3.616</td>
<td>1.530</td>
<td>109.47</td>
<td>-10.134</td>
<td>5.43</td>
<td>452</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>3.572</td>
<td>5.70</td>
<td>3.502</td>
<td>1.547</td>
<td>109.47</td>
<td>-9.094</td>
<td>5.34</td>
<td>418</td>
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<td></td>
<td></td>
<td>Exp$^{35}$</td>
<td>3.567</td>
<td>5.67</td>
<td>3.520</td>
<td>1.544</td>
<td>109.47</td>
<td>5.47</td>
<td>442</td>
<td></td>
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<tr>
<td>BC8</td>
<td>$Ia\bar{3}$</td>
<td>LDA</td>
<td>4.425</td>
<td>5.41</td>
<td>3.684</td>
<td>1.611,1.446</td>
<td>101.22, 116.31</td>
<td>-9.447</td>
<td>3.58</td>
<td>409</td>
</tr>
<tr>
<td>BC12</td>
<td>$Ia\bar{3}d$</td>
<td>LDA</td>
<td>5.116</td>
<td>5.58</td>
<td>3.576</td>
<td>1.566</td>
<td>99.59, 131.81</td>
<td>-9.235</td>
<td>2.97</td>
<td>428</td>
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<td></td>
<td></td>
<td>PBE</td>
<td>5.172</td>
<td>5.76</td>
<td>3.461</td>
<td>1.583</td>
<td>99.59, 131.81</td>
<td>-8.205</td>
<td>2.98</td>
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<tr>
<td></td>
<td></td>
<td>Exp$^{20}$</td>
<td>5.140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC24</td>
<td>$Pa\bar{3}$</td>
<td>LDA</td>
<td>5.304</td>
<td>6.22</td>
<td>3.192</td>
<td>1.523,1.525</td>
<td>60, 102.71</td>
<td>-9.169</td>
<td>3.05</td>
<td>323</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>5.368</td>
<td>6.45</td>
<td>3.094</td>
<td>1.539,1.542</td>
<td>60, 102.75</td>
<td>-8.168</td>
<td>2.96</td>
<td>299</td>
</tr>
</tbody>
</table>

FIG. 1: (Color online) Schematic depiction of the bonding structure of BC12 carbon. (a) The cubic crystalline structure of BC12 carbon in $Ia\bar{3}d$ ($O_{h}^{10}$) symmetry with the lattice parameter of 5.116 Å. All the carbon atoms are equivalent and occupy the 24d (0.375, 0, 0.25) Wyckoff position. (b) The primitive cell of BC12 carbon containing twelve carbon atoms, consisting of zigzag $C_6$ rings ($C_6$ unit is marked in yellow). (c) The viewpoint along the $c$ axis of the (3,0)-CNT structure. (d) A hexagonal representation of BC12 carbon, corresponding to the (3,0)-CNT.

III. RESULTS AND DISCUSSION

We first characterize the structural property of BC12 carbon, which is in $Ia\bar{3}d$ ($O_{h}^{10}$) symmetry, as shown in Fig. 1(a), has an $sp^3$ bonding network purely consisting of connected zigzag $C_6$ benzene rings. In cubic representation, the equilibrium lattice parameter is estimated to be $a = 5.116$ Å with only one inequivalent crystallographic site, occupying the 24d (0.375, 0, 0.25) Wyckoff position. In the primitive unit cell, it has twelve atoms with lattice parameters $a = 4.430$ Å, $\alpha = \beta = \gamma = 109.47^\circ$ [Fig. 1(b)]. All the C-C bonds in BC12 carbon are of equal length of 1.566 Å, which is only slightly larger than 1.544 Å for diamond. Meanwhile there are two different bond angles of 99.59$^\circ$ and 131.81$^\circ$ in BC12 carbon, which also occurs in BC8 carbon where the two bond angles are 101.22$^\circ$ and 116.31$^\circ$. When each six-membered rings of the (3,0)-CNT [see Fig. 1(c)] is twisted around the $c$-axis, a hexagonal structure [Fig. 1(d)] can be obtained. The viewpoint along the [111] direction of BC12 carbon resembles the viewpoint along the $c$-axis of this hexagonal structure. This structural relation suggests that BC12 carbon may be synthesized by the polymerization of properly selected CNTs as starting materials. In fact, the (3,0) CNT bundle has a higher energy of -8.93 eV per atom (see Fig. 2) and can easily convert to BC12 carbon with an energy gain of 0.29 eV per carbon atom.

Figure 2 shows the calculated total energy versus the volume per atom for diamond, BC8, BC12, and SC24 carbon. It is clearly seen that BC12 carbon is less stable than diamond and BC8 carbon, but more stable than bond angles of 99.59$^\circ$ and 131.81$^\circ$ in BC12 carbon, which also occurs in BC8 carbon where the two bond angles are 101.22$^\circ$ and 116.31$^\circ$. When each six-membered rings of the (3,0)-CNT [see Fig. 1(c)] is twisted around the $c$-axis, a hexagonal structure [Fig. 1(d)] can be obtained. The viewpoint along the [111] direction of BC12 carbon resembles the viewpoint along the $c$-axis of this hexagonal structure. This structural relation suggests that BC12 carbon may be synthesized by the polymerization of properly selected CNTs as starting materials. In fact, the (3,0) CNT bundle has a higher energy of -8.93 eV per atom (see Fig. 2) and can easily convert to BC12 carbon with an energy gain of 0.29 eV per carbon atom.

Figure 2: (Color online) The total energy as a function of volume per atom for BC12 carbon in comparison with diamond, BC8, SC24, Rh6, oC8 carbon, and (3,0)-CNT.
modulus for BC8 (409 GPa) and the value for diamond (452 GPa), but larger than the value for Murnaghan’s equation of state, fitting the calculated total energy as a function of volume. The equilibrium volume per atom of BC12 carbon is comparable to that of cubic diamond, but it is smaller than that of SC24 carbon. These energetic results strongly suggest that bond-angle deviation from that of cubic diamond has a significant influence on the total energy of cubic carbon allotropes in all of soot.

The experimental XRD of shock-compressed TCE powder [see Fig. 3(b)] reveals the superposition of diffraction lines from two major phases, graphite and this new cubic modification of carbon with a unit cell parameter of 5.14 Å. The strongest peak around 26° is consistent with the graphite (002) diffraction; meanwhile, the peaks at 43° and 50.7° match well with the (211) and (220) spectrum for BC12 carbon, respectively. Here the (220) peak of BC12 maybe overlaps with the (102) peak of graphite. Also, in the original experimental paper, a peak was observed at 73.9°, which may be assigned as the (400) peak of BC12, while the (321) peak of BC12 is missed in the experimental XRD patterns, which may be due to the local disorder in the shock-compressed samples. These results suggest that BC12 carbon is a likely candidate structure for the unidentified carbon phases found in the shock-compressed TCE. Such BC12 carbon framework was also found in silicon dioxide as a Si (24d) network.

Meanwhile, some new XRD peaks are found in a different shock-compressed carbon black/tetracyanoethylene (CB/TCE) powder mixture [see Fig. 3(b)]. The peak at 43.74° is attributed to the diamond (111) diffraction; the peak at 30° may be associated with an all-sp\(^3\) Rh6 carbon found in detonation carbon nanoparticles and chimney soot. Also, the peaks at 35° and 62.3° may be assigned as the (110) and (311) peaks for a mixed sp\(^2\)-sp\(^3\) oC8 carbon in cmmm symmetry found in the graphite-
BC12 carbon is located at as presented in Fig. 4. The highest phonon frequency of found in detonation soot of some unknown forms of carbon. Such complicated mixture of a rich variety of carbon structures is commonly found in detonation soot.37

We also calculated the phonon spectra of BC12 carbon, as presented in Fig. 4. The highest phonon frequency of BC12 carbon is located at Γ point with a value of ~1150 cm⁻¹, which is lower than ~1350 cm⁻¹ for perfectly sp³ bonded diamond.38 Throughout the entire Brillouin zone, no imaginary frequencies are observed, confirming the dynamical stability of BC12 carbon.

We finally discuss the electronic properties of BC12 carbon. The band structure and density of states are calculated using the hybrid functionals (HSE06).30 The calculated band gap for diamond is about 5.43 eV, which is closed to the experimental data of 5.47 eV,35 suggesting the validity of HSE06 method in predicting band gaps for diamond and related sp³ bonded carbon structures. For BC12 carbon, as shown in Fig. 5, the band gap is estimated to be 2.97 eV, which is smaller than the value 5.43 eV for diamond and 3.58 eV for BC8 carbon. Moreover, both valence band maximum and conduction band minimum are at Γ point, showing a direct band gap semiconductor character. These results are essential for further study and application of this new carbon phase.

IV. SUMMARY

In summary, we have identified by means of ab initio calculations a new cubic carbon structure in Ia3d (O₃h) symmetry comprising fully sp³ hybridized six-membered rings. The structural stability is verified by phonon mode analysis. Electronic band structure calculations reveal that it is a semiconductor with a direct band gap about 2.97 eV. Simulated lattice parameter and x-ray diffraction patterns provide an excellent match to the previously unexplained new carbon allotrope found in recent shock-compressed experiments. These results strongly suggest the presence of BC12 carbon phase, which belongs to the same bonding type as diamond and BC8 carbon with all-sp³ six-membered-ring configuration. Shock compression only produced minute amount of BC12 carbon mixed with other carbon phases, and the next challenge is to find a route toward more effective synthesis. Similar challenges have been encountered and overcome in the study of other novel carbon phases, such as nanotubes and fullerenes. The full structural identification and characterization reported in the present work may stimulate further exploration for fundamental understanding and practical application of BC12 carbon.

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