Topological nodal line semimetal in an all-\(sp^2\) monoclinic carbon

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Abstract

Topological nodal line semimetal is an exotic class of quantum materials featuring the continuous line of nodes inside the first Brillouin zone. Here we identify by systematical \textit{ab initio} calculations a new all-\(sp^2\) hybridized carbon allotrope with monoclinic \(C_2/c\) (\(C_{2h}^8\)) symmetry which is termed as \(bcm-C_{16}\). Total energy calculations show that our proposed \(bcm-C_{16}\) carbon is energetically comparable to or stable than the previously proposed bco-\(C_{16}\), bct-\(C_{16}\), and oP16 carbon. Its dynamical stability has been confirmed by phonon mode calculations. Detailed analysis of the electronic properties show that \(bcm-C_{16}\) carbon is a topological nodal line semimetal with a single closed nodal ring around the \(\Gamma\) high symmetric point, protected by spatial inversion (\(P\)) and time-reversal (\(T\)) symmetry. When the nodal ring is projected onto the (001) surface, a topologically protected drumhead-like surface state can be seen inside or outside the nodal ring depending on the different surface terminations. Moreover, we also examined the tensile-strain robustness of the electronic properties of \(bcm-C_{16}\) carbon. The nodal ring is robust under a tensile-strain along the crystalline \(x\)- and \(z\)-directions up to 20%. In addition, the simulated x-ray diffraction pattern (XRD) of \(bcm-C_{16}\) carbon matches with the experimental pattern found in the detonation and chimney soot experiment. The present proposal has enriched the family of carbon allotropes with topological nodal lines, and pave the way for further theoretical and experimental studies.

1. Introduction

Topological semimetals as a new class of quantum materials have been attracting tremendous research interests due to their fundamental physics and also intriguing device applications [1–8]. In general, topological semimetals can be classified into Weyl semimetals with isolated two-fold degenerate Weyl points [9, 10], and Dirac semimetals with isolated four-fold degenerate Dirac points [11–13], and nodal line semimetals [14–17] with continuous line of nodes inside the first Brillouin zone (BZ). Especially, nodal line semimetal is usually enforced due to the band inversion mechanism and protected by spatial inversion (\(P\)) and time-reversal (\(T\)) symmetry [15]. Recently, topological nodal line semimetals states have been theoretically and experimentally realized in large number of materials including 3D icosahedron-based boron \(B_{60}\) [18], CaP\(_3\) family [19], Ca\(_3\)P\(_2\) [20], CaAg\(_X\) (\(X = P, As\)) [21], CaTe [22] and transition metal phosphides [23], etc.

Carbon can form a rich variety of allotropes due to its ability to form \(sp\), \(sp^2\), and \(sp^3\) carbon–carbon bonds [24–26]. In recent years, a series of carbon allotropes have been proposed with topological nodal lines [27–39]. The topological nodal lines in carbon networks can be roughly classified into type-A with

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close nodal ring such as Mackay–Terrones carbon crystal (MTC) [28], body-centered orthorhombic C₁₆ (bco-C₁₆) [30], body-centered tetragonal C₁₆ (bct-C₁₆) [31] and base-centered orthorhombic ors-C₁₆ [32] carbon in all-\(sp^2\) hybridized network; or type-B with two separate nodal lines such as interpenetrated graphene network C₆ (ign-C₆) [33], orthorhombic C₂₄ (oC₂₄) [34], and simple orthorhombic C₁₂ (so-C₁₂) [36] carbon in \(sp^2–sp^3\) hybridized network. Recently, a new hexagonal series of topological nodal line carbon phases was proposed for all-\(sp^2\) hybridized networks but with B-type paired nodal lines on the edge of the first BZ rather than A-type closed nodal rings [38], and soon after an \(sp^2–sp^3\) hybridized oP₁₆ carbon [39] with two closed A-type nodal rings is proposed and it is pointed out that the type-A/B nodal line behavior is actually affected by the \(lattice\ anisotropy\) while the bonding type is not the essence.

In this paper, we identify through \textit{ab initio} calculations a new three-dimensional (3D) all-\(sp^2\) hybridized carbon allotrope in \(C2/c (C_{6h}^g\) space group No. 15) symmetry. This new carbon phase has 16-atom base-centered monoclinic unit cell, thus termed as bcm-C₁₆ carbon. Total energy calculations show that our proposed bcm-C₁₆ carbon is energetically comparable to or stable than the previously proposed bco-C₁₆ [30], bct-C₁₆ [31], and oP₁₆ [39] carbon. Its dynamical stability has been confirmed with phonon mode calculations. Detailed analysis of the electronic properties show that bcm-C₁₆ carbon is a topological nodal line semimetal with a single closed nodal ring around the high symmetry \(\Gamma\) point, protected by \(P\) and \(T\) symmetry. When the nodal ring is projected onto the (001) surface, a topologically protected drumhead-like surface state can be seen inside or outside the nodal ring depending on the different surface terminations. In addition, we also examined the tensile-strain robustness of the electronic properties of bcm-C₁₆. The nodal ring is robust under a tensile-strain along the crystalline network with five distinct kinds of bond lengths: \(d_{1}(1.376 \text{ Å}), d_{2}(1.437 \text{ Å}), d_{3}(1.475 \text{ Å}), d_{4}(1.401 \text{ Å})\), and \(d_{5}(1.460 \text{ Å})\), associated with \(C_1(sp^2) = C_1(sp^2), C_2(sp^2) = C_2(sp^2), C_1(sp^2) = C_1(sp^2), C_2(sp^2) = C_2(sp^2),\) and \(C_1(sp^2) = C_2(sp^2)\), respectively. There are also three kinds of bond angles are: \(\angle C_1−C_1−C_2 = 123.05^\circ, \angle C_2−C_1−C_1 = 124.29^\circ, \angle C_2−C_2−C_2 = 119.57^\circ, \angle C_1−C_2−C_2 = 123.25^\circ, \angle C_1−C_1−C_2 = 112.39^\circ, \angle C_2−C_2−C_2 = 117.18^\circ\). The primitive cell of bcm-C₁₆ carbon contains eight atoms as shown in figure 1(b). It has only four symmetry operations including an inversion center and lack of mirror symmetry unlike the reported all-\(sp^2\) topological semimetals bco-C₁₆ [30] and bct-C₁₆ [31].

Figure 2 shows the calculated energy versus volume curves of bcm-C₁₆ carbon comparing with graphite, diamond [55], and the reported bco-C₁₆ [30], bct-C₁₆ [31], ors-C₁₆ [32], and oP₁₆ [39] carbon that also have 16 carbon atoms in unit cell. It is seen that the equilibrium energy of bcm-C₁₆ carbon is
Figure 1. (a) The unit cell of crystalline structure of monoclinic carbon (bcm-C16) in C2/c (C16e, No. 15) symmetry with one-third double (d1, d2) and two-third single (d3, d4, d5) carbon–carbon bonds. The lattice constants are: a = 3.321 Å, b = 9.174 Å, and c = 4.281 Å, and the carbon atoms occupying two 8f Wyckoff positions of (0.7851, 0.5531, 0.9258), and (0.8628, 0.6847, 0.0884), denoted by C1 (black) and C2 (red). (b) The primitive cell of bcm-C16 carbon.

Figure 2. Calculated total energy per atom as a function of volume for bcm-C16 carbon compared to graphite, diamond [55] and other reported bco-C16 [30], bct-C16 [31], oP16 [39], and ors-C16 [32] carbon allotropes. 

−8.659 eV/atom, which is very close to −8.671 eV/atom for bco-C16 carbon, and lower than −8.570 eV/atom for oP16 carbon and −8.369 eV/atom for bct-C16 carbon, while slightly higher than −8.810 eV/atom for ors-C16 carbon, showing its good energetic stability. We have also calculated the bulk modulus (B0) by fitting with Murnaghan’s equation of state [57] to the energy–volume curve of bcm-C16 as 301 GPa, which is smaller than 451 GPa for diamond, 315 GPa for bco-C16, and larger than 250 GPa for bct-C16 carbon and 298 GPa for ors-C16 carbon. The calculated equilibrium structural parameters, total energy per atom, equilibrium volume per atom and bulk modulus are listed in table 1, comparing with available experimental and reported data [30–32, 37, 39, 55].

To further examine the dynamical stability of bcm-C16 carbon, we have calculated the phonon band structure and phonon density of states (PDOS) as shown in figure 3. The highest phonon frequency is located at the high-symmetric X point with a value of ~1561 cm⁻¹, which is comparable to the highest phonon frequency ~1571 cm⁻¹ of all-sp² bco-C16 [30] and lower than but close to ~1600 cm⁻¹ for graphite [58]. There are two main peaks at around 1524 and 1381 cm⁻¹ in the PDOS of bcm-C16 carbon. The peak at around 1524 cm⁻¹ and 1381 cm⁻¹ are related to C1 and C2 carbon atoms, respectively. There is no imaginary phonon frequency through the entire BZ and in PDOS, thus confirming the dynamical stability of bcm-C16.

Next we discuss the electronic properties of bcm-C16 carbon. Figure 4(a) depicts the calculated bulk band structures at equilibrium lattice parameters using HSE06 functional [49] with the Fermi energy (EF)
Table 1. Calculated equilibrium lattice parameters \((a, b, c, \text{ and } \beta)\), volume per atom \(V_0\), bond lengths \(d_{C-C}\), total energy per atom \(E_{tot}\), electronic band gap \(E_g\) and bulk modulus \(B_0\) for diamond, bct-C\(_{16}\), bcm-C\(_{16}\), bco-C\(_{16}\), ors-C\(_{16}\) and oP16 carbon at zero pressure, compared to available experimental and reported data [30–32, 37, 39, 55, 56].

| Structure | Space group | Method | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(\beta\) \((^\circ)\) | \(V_0\) (Å\(^3\)) | \(d_{C-C}\) (Å) | \(E_{tot}\) (eV) | \(E_g\) (eV) | \(B_0\) (GPa) |
|-----------|-------------|--------|-----------|-----------|-----------|----------------|----------------|----------------|----------------|-------------|-------------|
| Diamond   | Fd\(\bar{3}\)m | AM05   | 3.552     |           |           | 5.60          | 1.538          | −9.018         | 5.36           | 451         |             |
| Exp [35]  | 3.567       |        |           |           |           | 5.67          | 1.544          | 5.47           | 446         |             |
| bco-C\(_{16}\) | Imma | AM05 [30] | 7.806     | 4.877     | 3.237     | 7.70          | 1.382–1.459    | −8.671         | Semimetal     | 315         |             |
| bct-C\(_{16}\) | I4/ amd | AM05 [31] | 6.578     | 3.330     |           | 9.01          | 1.360–1.477    | −8.369         | Semimetal     | 250         |             |
| ors-C\(_{16}\) | Ccm | AM05 [32] | 3.318     | 8.372     | 4.915     | 8.02          | 1.421–1.438    | −8.810         | Semimetal     | 298         |             |
| oP16       | Pccn       | AM05 [39] | 4.646     | 4.277     | 5.133     | 6.37          | 1.353–1.691    | −8.570         | Semimetal     | 370         |             |
| bcm-C\(_{16}\) | C2/c | AM05 | 3.321     | 9.174     | 4.281     | 106.42        | 7.04          | 1.401–1.475    | −8.659         | Semimetal     | 301         |             |
| Graphite   | P6\(_3\)/mmc | AM05 | 2.462     | 2.462     | 6.710     | 8.81          | 1.422         | −9.045         | Semimetal     | 280         |             |

![Figure 3](https://stacks.iop.org/043007/mmedia)  

Figure 3. Calculated phonon band structure and partial density of states (PDOS) for bcm-C\(_{16}\) with equilibrium lattice parameters. The peaks around 1524 and 1381 cm\(^{-1}\) are related to \(C_1\) and \(C_2\) atomic sites, respectively.

set to zero. It can be seen that the highest occupied band and lowest unoccupied band cross each other along the high-symmetric \(X–\Gamma\) direction and exhibit a linear dispersion due to the band inversion mechanism \([59, 60]\) with opposite parity eigenvalues. Further analysis of the electronic band structure in 3D BZ shows that the band crossing nodes form a continuous nodal ring around the \(\Gamma\) point inside the 3D BZ as shown in figure 4(b), which is protected merely by \(PT\) symmetry. Unlike bct-C\(_{16}\), bco-C\(_{16}\), CaP\(_3\) \([19]\) or CaTe \([22]\) nodal line semimetals, whose nodal lines lie in a certain mirror plane, in our case the nodal ring is twisted around the high symmetric \(\Gamma\) point due to the lack of mirror symmetry.

It is well known that, when the nodal line is projected into some planes, there is a drumhead like surface state inside or outside the nodal ring depending on the surface terminations. In order to investigate the topological surface states in our system, we have constructed an eight-band tight-binding (TB) model for bcm-C\(_{16}\) carbon with the MLWFs method based on the \(p_z\) orbitals of carbon atoms by using the WANNIER90 package \([51, 52]\). The calculated electronic density of states and TB band structures are shown in figure S1 of the supplemental materials (https://stacks.iop.org/NJP/24/043007/mmedia) \([61]\). The TB band structures match well with the DFT band structures, confirms the effectiveness of our established TB models.

Based on this TB model, we have calculated the surface states along \(H–\Gamma–X\) high-symmetric directions for the (001) surface as shown in figures 4(c) and (d) with the iterative surface Green’s function method as implemented in WannierTools package \([54]\). When the surface termination is a zigzag type, a drumhead-like surface state is seen outside the projected nodal ring as shown in figure 4(c) and when the surface termination is a arm-chair type, the drumhead like surface state seen inside the projected nodal ring as in figure 4(d); while the different types of surface terminations are shown in figure S2 of the supplemental materials \([61]\). The calculated surface states can be detected by the angle resolved photoemission spectroscopy (ARPES) experiments \([62]\).

Next we investigate the robustness of the nodal ring against the applied tensile strain along the crystalline \(x\)- and \(z\)-directions (denoted as \(\varepsilon_x\) and \(\varepsilon_z\), respectively). The change of the band crossing points near the Fermi level is depicted in figure 5(a) with an increase of tensile strain \(\varepsilon_x\), from 5 to 25\%, respectively. It can be seen that the band crossing point around the Fermi level robust within the applied
strain limit along \( x \)-direction. However, with an increase of strain \( \varepsilon_x \), the band crossing point slightly move toward \( X \) high symmetric point and below to the Fermi level due to the change in BZ. Further analysis of band crossing point in 3D BZ with the applied tensile strain along \( x \)-direction demonstrates that the size of the nodal ring becomes larger with an increase of applied strain along \( x \)-direction as shown in figures S3(a) and (b) in the supplementals materials [61]. On the other hand, when the tensile strain is applied along \( z \)-direction from 5 to 20% the band crossing point move toward \( \Gamma \) point and near to Fermi level as depicted in figure 5(b). While in 3D BZ the size of nodal ring becomes smaller with an increase of applied strain as shown in figures S3(c) and (d) in the supplementals materials [61]. At 25% tensile strain along \( z \)-direction, the band crossing point is not robust and the bcm-C\(_{16}\) nodal line semimetal has been converted into a direct band gap semiconductor. This change in the topological phase is associated with the change of double bond (\( d_1 \)) into a single bond in the crystal structure of bcm-C\(_{16}\) carbon at 25% strain along \( z \)-direction. On the other hand, with the applied strain along \( x \)-direction the double bond remain conserve within the applied strain limit, due to which band crossing is robust. The changes in bond lengths with the applied strain along \( x \)- and \( z \)-directions are given in table S1 in the supplementals materials [61].

Finally, to guide for experimental observations, we simulated XRD pattern of bcm-C\(_{16}\) carbon with wavelength 1.5406 Å, along with those of diamond, graphite, bco-C\(_{16}\) [30], bct-C\(_{16}\) [31], ors-C\(_{16}\) [32], and compare with experimental data from detonation soot of TNT and diesel oil [40] and chimney soot [41] as shown in figure 6. It can be observed that in XRD pattern of bcm-C\(_{16}\) carbon, the first dominant peak at \( 2\theta \approx 30^\circ \) matches well with the peaks at \( 2\theta \approx 30^\circ \) of detonation soot of TNT and diesel oil [40] and chimney soot [41]. Simulated XRD patterns of the bcm-C\(_{16}\) carbon also exhibit a main peak at a position slightly higher than 30°, similar to bco-C\(_{16}\) carbon [30]. The high energetic stability and well agreement of XRD pattern between the simulated and experiments XRD patterns suggest the existence of the bcm-C\(_{16}\) carbon in the detonation and chimney soot.
Figure 5. Strain-robust band crossing point in the bcm-C\textsubscript{16} carbon. (a) The change of band crossing point around the Fermi level with an increase of tensile strain along the $x$-direction from 5 to 25\%, respectively. (b) The change of band crossing point around the Fermi level with an increase of tensile strain along the $z$-direction from 5 to 25\%, respectively. Conversion from nodal line semimetals phase to semiconductor at 25\% tensile strain along $z$-direction can be seen in (b).

Figure 6. (a) Simulated XRD patterns for diamond, graphite, bco-C\textsubscript{16} [30], bct-C\textsubscript{16} [31], ors-C\textsubscript{16} [32], and bcm-C\textsubscript{16} carbon phases. (b) Experimental XRD patterns for detonation soot [40] and chimney soot [41]. The x-ray wavelength is 1.5406 Å with a copper source.

4. Summary

In conclusion, we have identified based on \textit{ab initio} calculations a new all-$sp^2$ hybridized bcm-C\textsubscript{16} carbon. Total energy calculations have confirmed its energetic stability and its dynamical stability has been confirmed with phonon mode analysis. The electronic band structures show that it is a topological nodal line semimetal with a single nodal ring around the high symmetric $\Gamma$ point, and the nodal line is robust under a large tensile strain $\varepsilon_x$ and $\varepsilon_z$ along the crystalline $x$- and $z$-directions up to 20\%. Simulated XRD patterns show a good match with the experimental findings in the detonation and chimney soot.
experiments, suggesting that it may be one of the experimental phases. Our findings have enriched the family of carbon allotropes with topological properties and pave the way for further theoretical and experimental researches.

Conflict of interest

There are no conflicts to declare.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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[61] See the supplemental materials for the partial electron density of states (figure S1(a)); the tight-binding band structure for bcm-C16 (figures S1(b)); zigzag-like termination and armchair-like termination along (001) directions (figure S2). The nodal rings formed by band crossing point figure S3(a) 5%, figure S3(b) 10%, strain along \( x \)-direction, figure S3(c) 5%, and figure S3(d) 10%, strain along calculated value of double bond length between carbon atoms table S1. The supplemental material includes references [51, 52].
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