Topological phase transition from T-carbon to bct-C$_{16}$

Xian-Yong Ding$^{1}$, Chao Zhang$^{2}$, Li-Yong Gan$^{2}$, Yu Cao$^{1}$, Lei-Lei Chen$^{1}$ and Rui Wang$^{1,2}$

$^{1}$ School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, People’s Republic of China

$^{2}$ Institute for Structure and Function & Department of Physics, Chongqing University, Chongqing 400044, People’s Republic of China

E-mail: chaozhang@mail.bnu.edu.cn and rcwang@cqu.edu.cn

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Abstract

The realization of nontrivial fermions in three-dimensional carbon allotropes greatly facilitates topological applications in carbon based-materials. In this work, we find a topological phase transition from T-carbon to bct-C$_{16}$ based on first principles calculations. After carrying out a heating or a doping process on T-carbon, a new carbon phase termed bct-C$_{16}$ is obtained. The potential energy and the crystal orbital Hamilton population confirm the phase transition process, respectively. Importantly, we also investigate the quantized Berry phase and drumhead surfaces states, confirming the topological nodal line semimetallic features of bct-C$_{16}$. Due to the extremely weak spin–orbital coupling effect in carbon, the nodal ring in bct-C$_{16}$ can be guaranteed to be nearly intact. This work not only provides two methods to obtain the carbon phase bct-C$_{16}$, but also an avenue for bct-C$_{16}$ to observe nontrivial fermions.

1. Introduction

Carbon is a high-profile element due to its ability to form numerous allotropes with emergent properties. The most famous carbon allotropes are graphite and diamond. At ambient conditions, graphite is the thermodynamically most stable phase with layered honeycomb lattices. Based on graphite, many structural transformations can be occurred at high pressures and temperatures [1–4]. For instance, cubic and hexagonal diamond can be obtained from graphite at pressures above 15 GPa and temperatures above 1300 K [3, 4]. Besides, graphite can be converted into diamond-like cold-compressed phases at the room temperature [5–9]. Distinguished from semimetallic graphite that possesses an all sp$^2$ bonding state, the metastable carbon allotropes mentioned above host the sp$^3$ hybridization and thus are insulators. Furthermore, graphite can also be exfoliated or wrapped to other structures with sp$^2$ bonding states, such as zero-dimensional (0D) fullerenes [10], one-dimensional (1D) nanotubes [11], and two-dimensional (2D) graphene [12]. Among these lower dimensional sp$^2$ carbon allotropes graphene is particularly important. As is well-known, topological semimetallic features in graphene have significantly impacted on the field of topological materials [13]. Motivated by great achievements in graphene, it is promising to investigate symmetry-protected topological fermions in three-dimensional (3D) carbon allotropes.

To design 3D carbon allotropes with semimetallic phases, we recall electron configurations of a carbon atom, which possesses 2s$^2$2p$^2$ valence electrons. Thus, the conductivity requires that 3D carbon allotropes with nontrivial fermions must be in all sp$^2$ structures or sp$^2$–sp$^3$ hybridized network structures. With this guidance, a series of 3D conductive carbon allotropes with sp$^2$ bonding or sp$^2$–sp$^3$ hybridized structures
have been intensively predicted [16–24]. As expected, most of them host topological semimetallic features, such as nodal line fermions in 3D graphene networks [16], body-centered orthorhombic C_{16} [17], and body-centered tetragonal C_{12} [18], C_{16} [19], and C_{40} [20], as well as beyond [21–24]. These advancements greatly inspire us to find more novel 3D carbon allotropes with nontrivial fermions. However, the topological fermions in 3D carbon allotropes have been not verified in experiments. We find that most of reported topological 3D carbon allotropes possess complicated crystal structures and many atoms in a unit cell. Therefore, the discovery of high-symmetric topological 3D carbon allotropes is highly desirable. Of equal importance is the realization that there are fewer atoms in a unit cell, which can intuitively exhibit the relation between topological orders and symmetries and even realize topological applications in carbon based-materials.

In this paper, by using first-principle calculations, it is found that an all-quasi-sp° bonding carbon allotrope named bct-C_{16}, which crystallizes in a body-centered tetragonal (bct) lattice, can be obtained from T-carbon phase [25]. bct-C_{16} hosts the high symmetry (i.e., D_{4h}) and there are only eight carbon atoms in one unit cell. We show by a symmetry and effective model analysis that bct-C_{16} belongs to the Dirac node-line semimetal phase, in which an ideal nodal ring exactly crosses the Fermi level and is protected by the coexistence of inversion and time reversal symmetries. Our work provides an avenue for obtaining the carbon phase bct-C_{16} and exploring the nodal line fermions in this carbon phase.

2. Computational methods

First-principles calculations are performed using the Vienna \textit{ab initio} simulation package with the projector augmented wave method [26]. A plane wave expansion with an energy cutoff of 600 eV is used in all calculations. The generalized gradient approximation with Perdew–Burke–Ernzerhof (PBE) functional is chosen to describe exchange–correlation energy [27, 28]. \textit{Ab initio} molecular dynamic simulation (AIMD) is also implemented to investigate the temperature effect on T-carbon. An initial temperature of 100 K according to a Boltzmann distribution is assigned to the T-carbon in a 2 × 2 × 1 supercell with 128 carbon atoms. A series of temperatures from 100 K to 600 K with a temperature step of 50 K in an NVT ensemble are considered in 2 ps, and each equilibrium structure at a constant temperature maintains 20 ps with Nose thermostat. The timestep of this AIMD simulation is 1 fs. We also check the band inversion and topology in Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [29]. The ionic relaxation and electronic self-consistent iteration are converged to 0.01 eV Å$^{-1}$ and 10$^{-6}$ eV with a Γ-centered k-mesh of 11 × 11 × 11. In order to reveal topological electronic features of bct-C_{16}, we construct a tight-binding (TB) Hamiltonian based on maximally localized Wannier functions projected from the bulk Bloch wave function in the WANNIER90 package [30]. The crystal orbital Hamilton populations (COHPs) [31–33] of T-carbon and bct-C_{16} are implemented in the LOBSTER code [34].

3. Results and discussions

As shown in figures 1(a) and (b), according to the \textit{ab initio} molecular dynamic simulations (AIMD), it is found that the T-carbon phase undergoes a structural phase transition to bct-C_{16} at the temperature of \(~500 K\) (figure 1(b)). In this process, the internal carbon-tetrahedron of T-carbon is destroyed to form a non-planar carbon-square, i.e., bct-C_{16} is present. The dynamical process of this AIMD simulation is shown in a video (see the Video SM, which is available online at \url{https://stacks.iop.org/NJP/22/073036/mmedia}). To understand the intrinsic mechanism of the phase transition from T-carbon to bct-C_{16}, we calculated the COHP of T-carbon and bct-C_{16}, respectively. As shown in figure 2(b), the absolute integral values of COHP confirm that the bonding network of T-carbon will be translated to a more stable carbon phase bct-C_{16} in thermal fluctuations. Moreover, the potential energy of this system is also shown in figure 2(a), which shows that there exists a dramatic reduction of potential energy in 500 K, also confirming the phase transition from T-carbon to bct-C_{16}. These results insure that the phase transition is properly exist during the heating process of T-carbon. Furthermore, figure 1(d) shows that the T-carbon phase are transformed to the bct-C_{16} carbon phase by doping the transition elements (Cu, Fe), which might be experimentally realized by ion implantation, or being introduced in preparation. These results indicate that bct-C_{16} is a fairly stable carbon phase and could be synthesized from T-carbon.

As shown in figures 3(a) and (b), the carbon phase bct-C_{16} is constructed to investigate the corresponding properties. The optimized lattice parameters of bct-C_{16} are $a = 6.588$ Å, $c = 3.378$ Å. Each carbon atom is connected by three neighbors, forming non-planar geometries composed by four- and eight-membered rings. Different from the unique bond length \(~1.414\) Å in graphite, there are two non-equivalent carbon-carbon bond lengths denoted as $d_1 = 1.361$ Å and $d_2 = 1.483$ Å in bct-C_{16}, which
Figure 1. The AIMD simulation structure of T-carbon in (a) 300 K and (b) 500 K. (c) The initial doped (Cu, Fe) structure which the doped elements replace the carbon tetragon of T-carbon and the corresponding (d) optimized structure at the temperature of 0 K.

Figure 2. (a) The potential energy of T-carbon in 500 K during the AIMD simulation. (b) The COHP of bct-C16 and T-carbon between C1, C2 and C3 corresponding to the left structure.

alternately arrange in an eight-membered ring. In figure 3(c), we plot the bulk bct BZ and the corresponding (001) surface BZ, in which high-symmetry points are highlighted as red-solid points. The dynamical and thermal stabilities of bct-C16 is confirmed by phonon spectra (in the SM) and a 5 ps AIMD simulation. The AIMD simulation is performed in 500 K with a $3 \times 3 \times 3$ supercell.

Next, we focus on the electronic properties of bct-C16. The electronic band structure along high-symmetry paths of the BZ is shown in figure 4(a). Comparing to the semiconductor T-carbon phase in which the band gap is 3.0 eV [25], the bands of bct-C16 possess semimetallic features. The partial density of
Figure 3. Crystal structure and Brillouin zone (BZ). (a) Top and (b) side views of bct-C_{16} with a space group I4_1/amd (no. 141). Two different bond lengths \(d_1, d_2\) and bond angles \(\theta_1, \theta_2\) are also denoted. (c) The bct BZ and the corresponding (001) surface BZ.

Figure 4. (a) The electronic structure of bct-C_{16}, HSE06 (blue dotted line) and PBE (red solid line) results. (b) Partial density of states of bct-C_{16}. (c) The zoom-in view marked by rectangle region in panel (a). The red and black lines represent two crossing bands belonging to opposite eigenvalues \(\pm 1\). (d) Energy difference map between the lowest conduction band and the highest valence band in the \(k_z = 0\) plane is shown.

states depicted in figure 4(b) indicate that \(p_z\) orbital dominates the contributions near the Fermi level, confirming the quasi-sp\(^2\) bonding features of bct-C_{16}. Remarkably, two bands exactly cross each other with linear dispersions at the Fermi level in the \(\Gamma-X\) and \(\Gamma-M\) directions (see figure 4(c)). The two crossing bands belong to opposite eigenvalues \(\pm 1\) of mirror symmetry \(M_z\). Considering this \(M_z\) symmetry, two crossing bands with an inversion gap of \(\sim 1.75\) eV at the \(\Gamma\) point form a continuous topological nodal ring in the \(k_z = 0\) plane. Figure 4(d) shows a map of energy difference between the lowest conduction band and highest valence band, and the nodal ring is denoted as the white feature, indicating a zero gap in the \(k_z = 0\) plane. Besides, we carry out HSE06 calculations with more accurate correlations than PBE functional to check band inversion in bct-C_{16}. The results show that HSE06 functional only slightly shift the band profile and confirm the same band topology (see figure 4(a)). Moreover, we also consider the spin–orbital coupling (SOC) effect on the band structures of bct-C_{16}. The results show that the global gap is present (see the SM). In this case, bct-C_{16} is converted to a strong topological insulator with \(Z_2\) index \((1;001)\). However, the values of gap are very tiny (<1 meV) due to the weak SOC effect of the carbon.
Figure 5. (a) The Berry phase varies along the high-symmetry directions $X$–$\Gamma$–$M$. (b) The LDOS projected on the seminfinite (001) surface of bct-C16. The occupied drumhead surface states lie inside the projection of nodal ring. (c) Projected Fermi surface on a (001) surface as a function of $E - E_F$. (d) Projected Fermi surface at $E = E_F - 0.3$ eV. A continuous Fermi arc is clearly visible.

element, so the nodal ring in bct-C16 can be guaranteed to be nearly intact even though the SOC is present.

To insightfully understand the band topology in bct-C16, we perform a symmetry analysis and effective $k \cdot p$ model to demonstrate that the nodal ring exist in the $k_z = 0$ plane. The symmetry of bct-C16 at the band inversion $\Gamma$ point is $D_{4h} = D_4 \otimes C_i$, including an inversion symmetry $I$, two-fold rotational symmetries $C_{2x}$ and $C_{2y}$, a four-fold rotational symmetry $C_{4z}$, and a mirror symmetry $M_z$. Two crossing bands with a band inversion can be generally described by a $2 \times 2$ $k \cdot p$ Hamiltonian,

$$H(k) = f_x(k)\sigma_x + f_y(k)\sigma_y + f_z(k)\sigma_z,$$

where $H$ is referenced to the Fermi level, $k$ is the momentum vector related to the $\Gamma$ point, $f_i(k) (i = x, y, z)$ are real functions, and $\sigma_j$ are Pauli matrices. The two inverted bands have opposite mirror eigenvalues $\pm 1$, so we can represent the inversion symmetry as $I = \sigma_z$. Besides, the time-reversal symmetry $T$ exists in a non-magnetic system of bct-C16. As a result, the presence of $I$ and $T$ symmetries constrain the Hamiltonian as

$$IH(k)I^{-1} = H(-k), \quad TH(k)T^{-1} = H(-k),$$

which leads to that $f_x(k) \equiv 0, f_y(k)$ is an odd function, and $f_z(k)$ is an even function. The zero-energy solutions of two crossing bands [i.e., $f_x(k) = 0$ and $f_y(k) = 0$] induce codimension 1, signaling the presence of nodal lines in momentum space. Additionally, the four-fold rotational symmetry $C_{4z}$ and mirror symmetry $M_z$ constrain $f_y(k)$ and $f_z(k)$. These symmetries guarantee the nodal ring locating in the $k_z = 0$ plane with respect to four-fold rotational $z$ axis. In this case, only $f_z(k)$ is nonzero and it can be expanded in the low-energy as

$$f_z(k_x, k_y, 0) = A_0 + A_2(k_x^2 + k_y^2) + \cdots ,$$

When the parameters $A_0$ and $A_2$ satisfy $A_0A_2 < 0$, the closed nodal ring is present in the $k_z = 0$ plane.

The topological nodal ring in bct-C16 connects to a quantized Berry phase $\nu$, 

$$\nu = -i \oint \sum_{\lambda} \langle \varphi_{\lambda}(k)|\nabla_k|\varphi_{\lambda}(k) \rangle \cdot dk$$
which is related to wave functions \( \varphi_\ell (k) \) of valence bands cumulated from a symmetric circle \( \ell \) surrounding the nodal ring. The circle \( \ell \) can be continuously deformed into 1D subsystem along the \( k_3 \) directions with one inside the nodal ring and the other outside. As shown in figure 5(a), it is found that the Berry phase inside the nodal ring is nontrivial, i.e., \( \nu = \pi \mod 2\pi \). From the bulk-boundary correspondence, the nontrivial Berry phase leads to topologically-protected drumhead surface states lying inside the projection of the nodal ring on the surface BZ. To obtain the topological surface states, we employ the iterative Green’s function method with a Wannier TB Hamiltonian [35, 36]. We plot the local density of states (LDOS) projected on the seminfinite (001) surface of bct-C\(_{16}\) in figure 5(b). As expected, we can see that occupied drumhead surface states cover the internal region of the projection of nodal ring on the (001) surface BZ. Panel (c) of figure 5 shows the evolution of the projected Fermi surface with respect to \( E - E_F \). For the energy \( E = E_F - 0.3 \) eV (see figure 5(d)), a continuous Fermi arc is clearly visible on the projected Fermi surface.

4. Conclusions

In summary, by using first-principle calculations, we find a phase transition from T-carbon to bct-C\(_{16}\). Importantly, there exist two ways to realize this phase transition. The first way is to heat T-carbon to 500 K and the second way is to dope some transition elements (i.e., Cu, Fe) to break the carbon-tetrahedron. Furthermore, based on a symmetry and effective model analysis, we reveal that the Dirac node-line semimetal phase of bct-C\(_{16}\) is protected by the coexistence of inversion and time reversal symmetries. The nodal ring in bct-C\(_{16}\) can be guaranteed to be nearly intact even though the SOC is present since carbon element possesses extremely weak SOC effects. The calculated Berry phase and drumhead surfaces states further support nodal line semimetallic features. Our work provides an avenue for obtaining the carbon phase bct-C\(_{16}\), and exploring the nodal line fermions in this carbon phase.

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ORCID iDs

Chao Zhang https://orcid.org/0000-0002-4481-1476
Rui Wang https://orcid.org/0000-0002-5063-5691

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