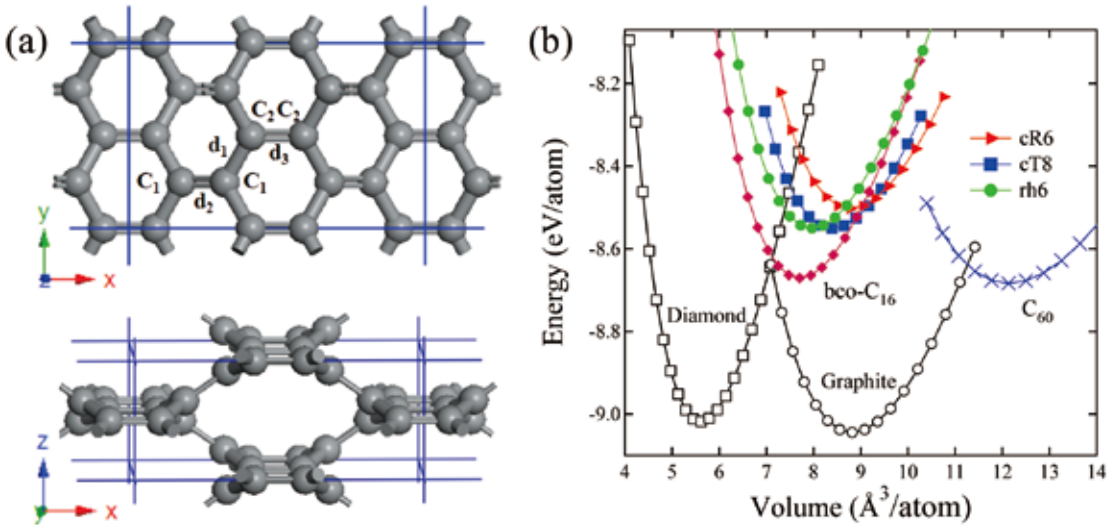
Morphed Graphene of BCO-C_{16}: A Novel Topological Node-Line Semimetal

Carbon is extremely versatile in its ability to form a rich variety of allotropes with a wide range of fascinating properties. At ambient conditions graphite is the thermodynamically most stable carbon allotrope, and many structural transformations and modifications of carbon structures in various sp^2 and sp^3 bonding networks can be produced under various pressure and temperature conditions. For example, under high static pressure and high temperature conditions, graphite can be converted to cubic diamond or twinned cubic diamond with {111} hexagonal-diamond-like stacking faults in all-sp^3 bonding networks; meanwhile, the discovery of fullerenes, nanotubes, and graphene ignited tremendous interest in recent years to explore additional carbon structures in all-sp^2 bonding networks. As a result, various hypothetical sp^2 carbon modifications have been proposed, including the hexagonal H6 carbon, fcc-C_{20}, $ThSi_2$-type tetragonal bct4 carbon, and $SrSi_2$-type cubic K_4 carbon. Most of them, however, are dynamically unstable due to the presence of twisted π states. Recent studies further unveiled a new type of stable chiral framework structures comprising 3-fold, 4-fold and 6-fold helical chains in all-sp^2 bonding networks connected by ethene-type planar π conjugation.

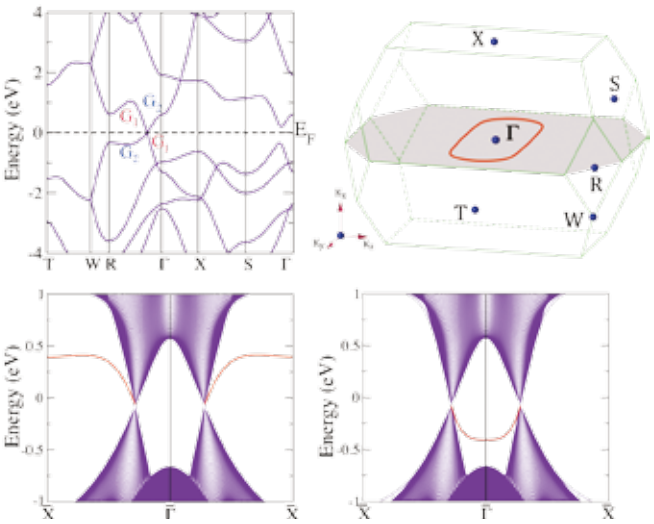
For three-dimensional chiral crystalline modification of carbon in all-sp^2 bonding networks, structures with matching helical chains of complementary chirality are energetically more favorable than those with helical



Structure of bco-C_{16} and its energy-volume curve. (a) Top and side view of the all-sp^2 bco-C_{16} in Imma symmetry with one-third double (d_2, d_3) and two-thirds single (d_1) carbon-carbon bonds. It has a 16-atom body-centered orthorhombic structure with lattice parameters a = 7.8061 Å, b = 4.8772 Å, c = 3.2372 Å, occupying the 8i (0.3231, 0.25, 0.1258) and 8f (0.0885, 0.5, 0.5) Wyckoff positions, denoted by C1 and C2, respectively. (b) Calculated energy versus volume per atom for bco-C_{16} compared to graphite, fcc-C_{60}, cR6, cT8, and rh6 carbon in all-sp^2, and diamond in all-sp^3 bonding networks. (Image by IOP)

chains of the same chirality. Based on this concept, recently, researchers led by Profs. WANG Jiantao, WENG Hongming, and FANG Zhong at the CAS Institute of Physics (IOP), including graduate student NIE Simin, reported a new all-sp^2 carbon allotrope in Imma symmetry in collaboration with Prof. KAWAZOE Yoshiyuki from Tohoku University, Japan and Prof. CHEN Changfeng from University of Nevada, Las Vegas, USA. This new carbon phase, named bco-C_{16} after its 16-atom body-centered orthorhombic unit cell, can be regarded as a three-dimensional modification of graphite, consisting of benzene linear chains connected by ethene-type planar π conjugation (see Fig. 1a). Total-energy calculations show that bco-C_{16} is comparable to solid fcc-C_{60} in energetic stability (see Fig. 1b), and its dynamic stability is verified by phonon and molecular dynamics simulations. An excellent match of simulated and measured x-ray diffraction spectra indicates the presence of bco-C_{16} in detonation and chimney soot. Electronic band structure calculations show that bco-C_{16} belongs to a new class of topological node-line semimetals. The valence and conduction bands exhibit linear dispersion near the Fermi energy and cross at the Fermi level (see Fig. 2a), and further analysis of the band structure in the full Brillouin zone indicates that the band crossing points (or nodal points) of the valence and conduction bands in bco-C_{16} form a continuous nodal ring inside a mirror plane (the shaded region in Fig. 2b), in contrary to the Dirac cone or nodal point in two-dimensional graphene. Moreover, the states near the crossing points around the nodal ring are formed by the inversion of the valence and conduction bands and protected by the coexistence of the time-reversal and inversion symmetry. When the nodal ring is projected onto the (100) surface, it produces topologically protected surface flat bands either inside or outside the ring, depending on the termination of the surface, as shown in Fig. 2 (c, d). These flat bands can be detected by photoelectron spectroscopy.

Their findings should facilitate further exploration of this class of intriguing materials. A major challenge is to find a route toward more effective synthesis of bco-C_{16} for more detailed studies. The structural identification and characterization of bco-C_{16} reported in the present work provide crucial knowledge for fundamental understanding and further exploration of this new carbon allotrope.



Calculated bulk and surface band structures of bco-C_{16} at equilibrium lattice parameters. (a) The bulk band structure along several high-symmetry directions. G_1 and G_2 indicate the irreducible representation of the two crossing bands, respectively. (b) The Brillouin zone with several high-symmetry momenta indicated. The nodal ring (red circle), formed by the band crossing points, is in the shaded mirror plane. (c) and (d) show the surface states for different zigzag-like (c) and beard-like (d) terminations of the (100) surface. The surface flat band (red line) can be outside or inside the surface projected nodal ring. (Image by IOP)

This study, entitled "Body-Centered Orthorhombic C_{16}: A Novel Topological Node-Line Semimetal", was published on *Physical Review Letters* 116, 195501 (2016).

The study was supported by the National Natural Science Foundation of China (Grant No. 11274356, No. 11274359, and No. 11422428) and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB07000000). H.W., S.N. and Z.F. acknowledge the National 973 program of China (Grant No. 2011CBA00108 and No. 2013CB921700) sponsored by the Chinese Ministry of Science and Technology. C.F.C. acknowledges support by DOE under Cooperative Agreement No. DE-NA0001982.