# Orthorhombic Carbon Allotrope of Compressed Graphite

*We identify by ab initio calculations an orthorhombic carbon (O-carbon) in Pbam symmetry for compressed graphite in AA stacking, which is formed via a distinct one-layer by one-layer slip and buckling mechanism along the [210] direction. The O-carbon is comparable to diamond in ultralow compressibility, has a band gap wider than that of diamond, and is compatible with experimental x-ray diffraction data.*

Experimentally, an unquenchable transparent and hard phase has long been observed during the cold-compression (at room temperature) stage of the synthesis. Recent studies have identified several structural forms for cold-compressed graphite, including a monoclinic M-carbon and an orthorhombic W-carbon, which provide a critical link for the graphite-to-diamond transformation [1]. In this Report, we identify by *ab initio* calculations an O-carbon allotrope in Pbam symmetry, which is formed via a one-layer by one-layer slip and buckling along the [210] direction [2]. This transformation mechanism is distinct from mechanisms previously proposed for M- and W-carbon that occur along the [100] direction [3]. Its simulated x-ray diffraction pattern matches well the experimental data on compressed graphite. The O-carbon has a band gap wider than that of diamond and a bulk modulus comparable to that of diamond. It is more stable than W- and M-carbon energetically. These results broaden our understanding of the complex structural landscape of compressed graphite and provide insights into the relations among the rich variety of carbon allotropes.

The crystal structure of O-carbon with the space group Pbam is shown in Fig. 1(a). It can be considered as distorted graphite in an AA stacking. At zero pressure, the equilibrium lattice parameters are a = 4.755 Å, b = 7.786 Å, and c = 2.494 Å with four inequivalent crystallographic sites, occupying the 4h (0.1072, 0.0706, 0.5), 4h (0.3614, 0.9546, 0.5), 4g (0.9632, 0.8267, 0.0), and 4g (0.3090, 0.8436, 0.0) positions, respectively. At high pressures, O-carbon becomes stable relative to graphite above 11.15 GPa [Fig. 1(b)], and it is more stable (i.e., lower in enthalpy) than both M-carbon and W-carbon.

Figure 1(c) shows the calculated band structure of O-carbon at 15 GPa using the hybrid functional (LDA-HSE06) that produce the band gap in good agreement with experimental data for diamond. The valence band top and the conduction band bottom of O-carbon are both at the point; the calculated band gap is 5.87-6.04 eV over a wide pressure range of 0-25 GPa, which is close to 5.69 eV for W-carbon, but markedly larger than 4.78 eV for M-carbon; it is even appreciably larger than the gap (5.43 eV) for diamond [2]. Therefore, O-carbon is expected to be optically transparent like M-carbon and W-carbon. We have also calculated its phonon dispersion curves over a wide pressure range up to 60 GPa. No imaginary frequencies were observed throughout the entire Brillioun zone [see Fig. 1(d)], confirming the dynamical stability of the O-carbon phase.
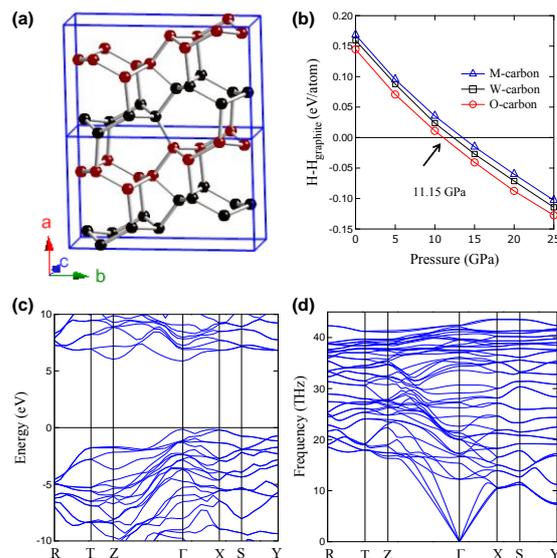


Fig. 1 The orthorhombic O-carbon in Pbam symmetry. (a) A polyhedral view of the crystal structure. (b) The enthalpy per atom (relative to that of graphite) for M-carbon, W-carbon, and O-carbon versus pressure. (c) Calculated electronic band structure of O-carbon at 15 GPa; (d) Calculated phonon dispersion curves of O-carbon at 15 GPa.

**References**

[1] J. T. Wang, C. F. Chen, and Y. Kawazoe, Phys. Rev. B 84, 012102 (2011).

[2] J. T. Wang, C. F. Chen, and Y. Kawazoe, Phys. Rev. B 85, 033410 (2012).

[3] J. T. Wang, C. F. Chen, and Y. Kawazoe, Phys. Rev. Lett. 106, 075501 (2011).

**Contact to**

Jian-Tao Wang (Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China)

E-mail: wjt@aphy.iphy.ac.cn

http://js.caseducation.cn/JS/~wjt