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o-C₈ Carbon: a New Allotrope of Superhard Carbon

Jun-ru Kou, Ai-hua Cao, Song-li Liu, Li-hua Gan*

*School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China;
College of Materials Science and Engineering, Yangtze Normal University, Chongqing 408100, China*

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An orthonormal crystal of carbon with PMMA space group (o-C₈) was found to be a stable superhard carbon allotrope by particle swarm optimization algorithm and density functional calculations. The phonon spectrum calculations demonstrate that the o-C₈ carbon phase is dynamically stable. The volume compression calculations show that it is highly incompressible, with bulk modulus of 298.6 GPa. The calculations demonstrate that it is a low-density superhard material with density of 2.993 g/cm³ and Vickers hardness of 82.4 GPa.

Key words: Carbon, Hardness, Stability, Structures**I. INTRODUCTION**

Carbon allotropes had been known to be only diamonds (sp³-hybridized) and graphite (sp²-hybridized) for millennium. Later, fullerene, carbon nanotube, and graphene with the sp² networks have been widely investigated and their important roles in various fields of modern industry have been highlighted. Carbon allotropes exhibit different properties mainly because carbon has the bonding ability to form sp, sp², and sp³ hybridized bonds. According to the bond hybridization, these carbon allotropes can be classified into sp³ carbon allotropes (such as M-carbon [1], W-carbon [2], F-carbon [3], imma-carbon [4], body-centered tetragonal carbon allotrope Bct C₈ [5], O-carbon [6], amm₂-carbon [7], P carbon [8]), and pure sp² carbon allotropes (such as graphene, Rh₆ [9], cR₆ [10], cT₈ [11], *etc.*) and those with mixed hybridization, such as sp²-sp³ hybridized tetra-carbon [12], graphdiyne [13], sp²-sp³ carbon allotrope H₁₈ [14], C₄₈ carbon [15], T-C₈ [16], *etc.* In these allotropes, sp³-bonded carbons are attracting special interest since many of them have fancy properties such as high thermal conductivity and hardness, special band structure, *etc.* Recently, a number of carbon phases with high Vickers hardness have been theoretically constructed, for instance, H-carbon and S-carbon, which were formed from cold-compressed graphite under pressure of 10.08 GPa and 5.93 GPa, respectively [17], and V-carbon [18] formed from cold-compressed C₇₀ peapods, which is a fully sp³-bonded monoclinic structure and its theoretical data agree well with experimental ones. However, only some can be experimentally synthesized [19]. New carbon phases were also formed by compressing and decompressing graphite un-

der room-temperature with synchrotron XRD [20].

Crystal structure analysis by particle swarm optimization (CALYPSO) [21] is an efficient structure prediction program, which only requires chemical compositions to predict stable or metastable structures at certain temperature and pressure and can also be used to design multi-functional materials such as superhard materials, optical materials. Here, an orthonormal carbon allotrope was predicted to be a new superhard material by the use of particle swarm optimization algorithm implemented in CALYPSO and density functional calculations. The calculations suggest that o-C₈ is a low-density superhard material with Vickers hardness of 82.4 GPa and the stability of sp³-bonded crystalline carbons would be weakened by the inserted four-membered ring in the crystal.

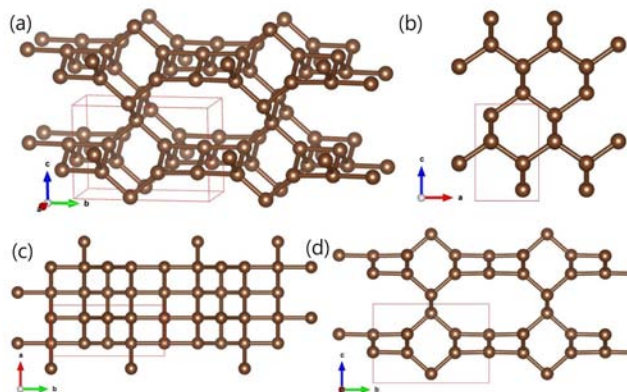
II. MODELS AND CALCULATION METHODS

The structure prediction of carbon allotrope with simulation cell sizes up to 8 atoms through CALYPSO code was performed and some 3D crystal structures were obtained. The structures with energy per atom lower than -6 eV and hardness higher than 40 GPa were selected for optimization, including c-diamond, hl-diamond, Bct-C₄ [22], o-C₁₆-II [23] (named Z-carbon [24] or Cco-C₈ [25]), P4122-C (labeled as G114 in the Samara Carbon Allotrope Database (SACADA) [26]) and a new structure. The new crystal structure is a low-energy stable orthorhombic crystal containing 8 carbon atoms in a cell, named o-C₈ hereafter. The generalized gradient approximation (GGA) developed by Perdew-Burke-Ernzerhof (PBE) [27], combined with the projector augmented wave (PAW) method [28], implemented in VASP code [29] were used to optimize o-C₈. The electronic wave functions are expanded using a plane-wave basis set with a cutoff energy of 500 eV, and the reciprocal space is scattered by a Monkhorst-Pack *k*-point

* Author to whom correspondence should be addressed. E-mail: ganlh@swu.edu.cn

TABLE I Space groups, lattice parameters, and density of the considered crystals calculated at the GGA/PBE level.

Systems	Space group	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/(\text{^\circ})$	$\beta/(\text{^\circ})$	$\gamma/(\text{^\circ})$	$\rho/(\text{g/cm}^3)$
Diamond	Fd-3m	3.574	-	-	90.0	90.0	90.0	3.52
o-C ₈	PMMA	2.508	5.606	3.814	90.0	90.0	90.0	2.99
D-carbon	PMMA	2.524	3.912	3.816	90.0	90.0	90.0	3.20
o-C ₁₆ -II	CMMM	8.772	4.256	2.515	90.0	90.0	90.0	3.42
o-C ₃₂	CMMM	17.482	4.217	2.514	90.0	90.0	90.0	3.47

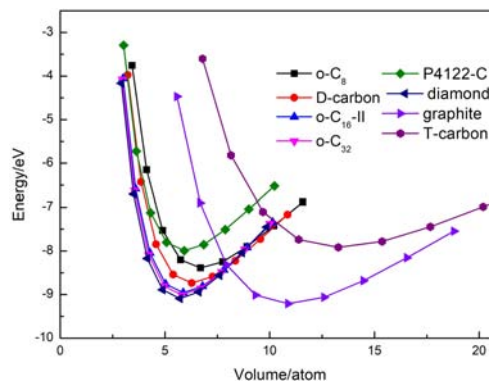
FIG. 1 The optimized ($2\times 2\times 2$) supercell crystal structure of o-C₈ carbon (a) perspective view, and along [010] direction (b), [001] direction (c), and [100] direction (d), respectively.

mesh of $10\times 10\times 10$. The convergence tolerance of force is 0.01 eV/\AA and the energy tolerance is 10^{-6} eV . The electronic band structure and elastic constant are calculated by the use of the Cambridge Serial Total Energy Package (CASTEP) code [30]. The phonon frequencies [31] were performed by using PHONON software with the forces obtained from VASP. For comparison, diamond and other four carbon allotropes containing four-membered ring in their structures are also considered.

III. RESULTS AND DISCUSSION

A. Lattice parameters

The as-searched allotrope (o-C₈) is shown in FIG. 1. The conventional cell contains eight carbon atoms buckled through sp^3 -hybridized bonds. The space groups, lattice parameters and density of o-C₈, diamond and other fully sp^3 -bonded orthorhombic carbon crystals (D-carbon [32], o-C₃₂ [33], o-C₁₆-II) are all shown in Table I. The space group of o-C₈ carbon is PMMA and lattice parameters $a=2.5080\text{ \AA}$, $b=5.6058\text{ \AA}$, and $c=3.8142\text{ \AA}$. There are three nonequivalent atomic Wyckoff positions occupying 4k ($1/4, 0.707, 0.618$), 2f ($1/4, 1/2, 0.884$) and 2e ($3/4, 0, 0.391$) and five distinct carbon-carbon bonds in o-C₈.

FIG. 2 The calculated energy per atom versus volume per atom at the GGA/PBE level for o-C₈, D-carbon, o-C₁₆-II, o-C₃₂, P4122-C, diamond, graphite, and T-carbon.

B. Thermodynamic stability

FIG. 2 gives the total energy of considered allotropes as a function of volume per atom. It shows that o-C₈ carbon has a single minimum (-8.388 eV), and it is evidently higher than that of diamond and a little lower than that of P4122-C at the same level of theory. These results suggest that o-C₈ carbon is meta-stable.

In terms of crystal structures, o-C₈, D-carbon, o-C₁₆-II and o-C₃₂ all contain four-membered ring, the $\angle\text{CCC}$ in the four-membered ring is 90° , instead of normal 109.5° . Actually all of the four crystal structures are of higher energy than diamond. The ratio of four-membered ring in them decreases in turn and their energy per atom decreases also. These results suggest that σ - σ repulsion [34] between the adjacent bonds in the four-membered ring plays a dormonting role in their stability.

The enthalpy per atom for o-C₈ and for other well-known carbon allotropes versus pressure relative to graphite from GGA calculations are shown in FIG. 3. Under the pressure of 0 GPa, o-C₈ carbon is less stable than graphite and diamond but more favorable than T-carbon [35] and K₆ containing 3-membered rings [36]. Its enthalpy decreases with increasing pressure, but is higher than that of graphite within 100 GPa, similar to the cases of P4122-C [26]. Therefore, these phases may

TABLE II The calculated elastic constants of considered carbon phases at the GGA/PBE level.

Crystal	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Diamond	1050.9	—	—	559.5	—	—	126.3	—	—
o-C ₈	1001.3	835.9	516.8	381.6	128.2	282.7	10.8	30.3	158.0
D-carbon	1032.4	866.6	732.3	369.8	287.1	412.9	59.8	48.5	236.1
o-C ₁₆ -II	1068.6	1098.6	1180.7	363.6	452.2	500.4	75.7	88.5	29.5
o-C ₃₂	1125.4	1188.5	1183.8	397.7	454.4	521.2	47.5	92.4	22.5

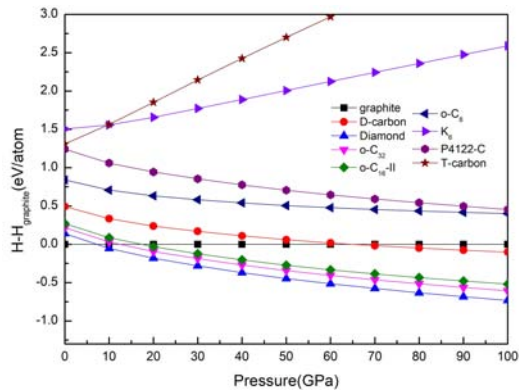


FIG. 3 The relative enthalpies of considered carbon phases with respect to graphite against pressure.

not be obtained from graphite under cold compression.

C. Mechanical stability

Just like D-carbon, o-C₈ carbon is also an orthorhombic crystal which contains nine independent elastic constants, C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} and C_{23} . The elastic constants of them are listed in Table II. For orthorhombic crystals, the criteria for mechanical stability [37] are given by:

$$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0 \quad (1)$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0 \quad (2)$$

$$(C_{11} + C_{22} - 2C_{12}) > 0 \quad (3)$$

$$(C_{11} + C_{33} - 2C_{13}) > 0 \quad (4)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0 \quad (5)$$

According to the elastic constants listed in Table II, all of the inequations are satisfied, in other words, o-C₈ carbon is mechanical stable.

The lattice constants and volume calculations were performed to examine the stability of o-C₈ carbon under hydrostatic pressure [38], the ratio of the lattice constants (a/a_0 , b/b_0 , c/c_0) as a function of pressure and the corresponding pressure-volume relationships are shown in FIG. 4. It can be seen from FIG. 4 (a), (b), and (c) that the ratios tend to decrease as the

pressure increases, and the change ratio of the three directions are different. o-C₈ carbon has a stronger and weaker incompressibility along b direction and a or c direction compared to D-carbon, o-C₃₂, o-C₁₆-II, and diamond, suggesting that the properties of o-C₈ is evidently different from other considered crystals. The volume decreases with pressure for all the considered systems, however o-C₈ carbon has a lower ratio at the same pressure, indicating that it has a lower incompressibility compared to diamond, o-C₃₂, o-C₁₆-II, and D-carbon.

The stress was obtained by applying a given homogeneous deformation (strain) via CASTEP. The stress-strain curves of o-C₈ carbon under tensile loading in the Cartesian axes x , y , and z directions are presented in FIG. 5. It can be seen that o-C₈ carbon has strong stress responses in the [100] and [001] directions with the peak tensile stresses of 89.68 and 84.49 GPa, respectively, which are smaller than that of diamond [39]. The weakest tensile strength for the o-C₈ carbon phase is found to be 57.25 GPa in the [010] direction. It shows that the structure has resistance to deformation and is anisotropic.

D. Dynamics stability

In order to confirm the dynamical stability of o-C₈ carbon phases, we calculated phonon dispersion curve of the optimized crystal ($2 \times 2 \times 2$ supercell) within the constraints imposed by the crystallization space group. The calculations show that there is no imaginary frequency in the whole Brillouin zone, as shown in FIG. 6. The highest phonon frequency of o-C₈ carbon (FIG. 6(a)) is about 39 THz, comparable with that of diamond under the same conditions (FIG. 6(b)) (also closed to the value reported in Ref.[40]). These results demonstrate that o-C₈ carbon phase is dynamically stable.

E. Elastic anisotropy

Elastic anisotropy plays an important role in many applications, such as phase transitions and polarization kinetics, crack behavior [41], and so on. In crystal system, the arrangement of atoms has directivity, so the elastic properties of single crystals may have a large

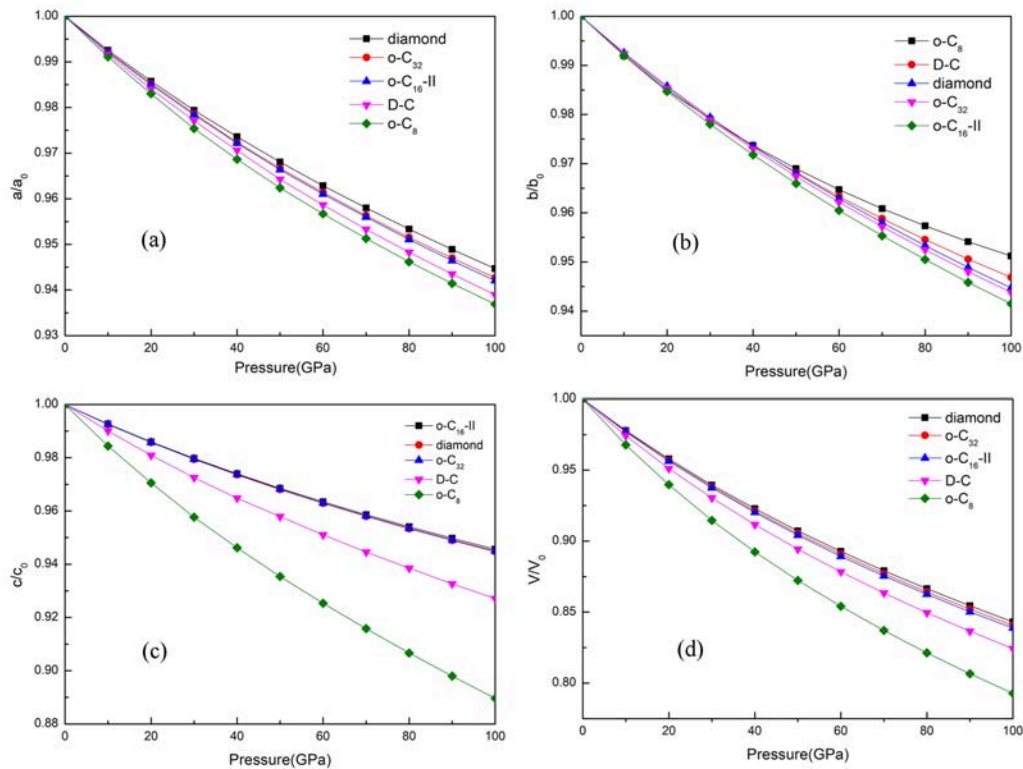


FIG. 4 The ratio of lattice constants (a) a/a_0 , (b) b/b_0 , (c) c/c_0 , and (d) volume as a function of pressure for the considered carbon crystals.

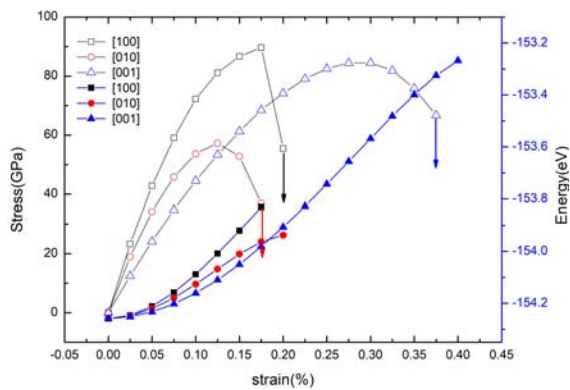


FIG. 5 The calculated stress and total energy per atom of $o\text{-C}_8$ as a function of the tensile strain for the [100], [010], and [001] direction.

difference along different directions. In other words, the elastic response of a single crystal is most-likely anisotropic. Since anisotropy is different for different crystals, a universal elastic anisotropy index A^U [42] is usually employed to quantify their extent, which can be calculated by the formula:

$$A^U = 5(G_V/G_R) + (B_V/B_R) - 6 \geq 0 \quad (6)$$

where G_V and G_R are the shear modulus, B_V and B_R are the bulk modulus from the Voigt-Reuss-Hill (VRH) [43] approximations. They can be calculated according to the equation shown below [44]:

$$B_V = \frac{1}{9} [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] \quad (7)$$

$$G_V = \frac{1}{15} [C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})] \quad (8)$$

$$B_R = m [C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12}(2C_{23} - C_{12}) + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})]^{-1} \quad (9)$$

$$G_R = 15 \{ 4[C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12} - C_{12}(C_{23} + C_{12}) - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})] / m + 3[(1/C_{44}) + (1/C_{55}) + (1/C_{66})] \}^{-1} \quad (10)$$

$$m = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{12} - C_{12}^2) \quad (11)$$

When the crystal is locally isotropic, the A^U is equal to zero. The magnitude of the A^U value indicates the degree of single crystal anisotropy, and an increment of the shear modulus ratio (G_V/G_R) influences the anisotropy much more than an identical increment of the bulk modulus ratio (B_V/B_R).

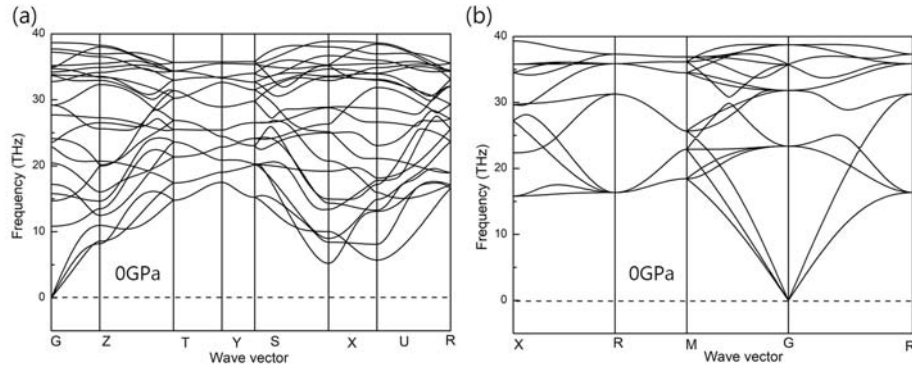


FIG. 6 The phonon band structures of o-C₈ carbon (a) and diamond (b) at ambient pressure.

TABLE III The calculated bulk modulus B_V , B_R (in GPa), shear modulus G_V , G_R (in GPa) of VRH approximations, the percentage of anisotropy in the compression and shear A_B and A_G , and universal elastic anisotropy index A^U .

Crystal	B_V	B_R	G_V	G_R	A^U	A_B	A_G
Diamond	434.5	434.5	520.6	516.1	0.04	0.000	0.004
o-C ₈	305.8	291.5	302.1	246.0	1.19	0.024	0.102
D-carbon	368.9	366.6	366.4	350.3	0.24	0.003	0.022
o-C ₁₆ -II	415.0	414.5	473.5	463.9	0.11	0.001	0.010
o-C ₃₂	424.7	424.6	497.0	488.2	0.09	0.000	0.009

The calculated bulk modulus B_V , B_R , shear modulus G_V , G_R and universal elastic anisotropy index A^U are listed in Table III. The anisotropy index A^U of the o-C₈ system is calculated to be 1.19, which is greater than zero and that of diamond, indicating that it is evidently elastic anisotropic.

In addition, the fractional anisotropy ratio of bulk modulus and shear modulus proposed by Chung and Buessem also can be used to measure the elastic anisotropy of materials [45]. It is defined below:

$$A_G = \frac{G_V - G_R}{G_V + G_R} \quad (12)$$

$$A_B = \frac{B_V - B_R}{B_V + B_R} \quad (13)$$

Only when A_B , A_G is equal to 0 simultaneously, the crystal is elastic isotropic, otherwise, the system is elastic anisotropy as a whole. But when A_B is 0, it means that the bulk modulus of the system is isotropic, and similarly, when A_G is 0, it means that the shear modulus of the system is isotropic.

The calculated results are also given in Table III. The calculated A_B and A_G are 0.024 and 0.102 for o-C₈, indicating it is anisotropic.

F. Brittleness or ductility

The calculated bulk modulus B , shear modulus G , Poisson's ratio ν , and Young's modulus E are given in Table IV.

Using the VRH method, the bulk modulus and shear modulus are estimated according to Eq.(14) and Eq.(15) [46].

$$B = \frac{1}{2}(B_V + B_R) \quad (14)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (15)$$

Where G_V and G_R are the shear modulus calculated according to Eq.(8) and Eq.(10), respectively, B_V and B_R are the bulk modulus calculated according to Eq.(7) and Eq.(9), respectively.

Using Eq.(16) we obtain Young's modulus (E).

$$E = \frac{9BG}{3B + G} \quad (16)$$

The high shear modulus and the Young's modulus indicate that superhard materials may lead to minimum of plastic deformation. Here, the calculated shear modulus and Young's modulus of o-C₈ carbon are 274.1 GPa and 629.6 GPa, respectively, smaller than those of the considered crystals; thus, o-C₈ carbon is a little easier to deform compared to them.

The magnitude of the Pugh's modulus ratio (G/B) [41] determines the brittleness and ductility of materials, when the value of G/B is large, the material appears brittle, and the larger the value of G/B is, the more brittle. As shown in Table IV, the calculated Pugh's modulus ratio for o-C₈ carbon is 0.92, smaller than 1.19 of diamond and thus suggests its higher ductility than diamond.

Using Eq.(17) we obtain Poisson's ratio (ν) [47].

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (17)$$

TABLE IV The calculated bulk modulus B , shear modulus G , Poisson's ratio ν , and Young's modulus E .

Crystal	B/GPa	G/GPa	G/B	ν	E/GPa
Diamond	434.5	518.3	1.19	0.07	1112.6
o-C ₈	298.6	274.1	0.92	0.15	629.6
D-carbon	367.7	358.4	0.97	0.13	811.5
o-C ₁₆ -II	414.8	468.7	1.13	0.09	1021.4
o-C ₃₂	424.7	492.6	1.16	0.08	1065.7

Poisson's ratio also can be used to estimate the brittleness/ductility of a material. The calculated Poisson's ratio of o-C₈ carbon (0.15) is evidently higher than that of diamond (0.07), indicating that its brittleness is weaker than diamond. This is in agreement with the result judged from B/G ratio.

G. Hardness

The Vickers hardness of complex crystals composed by the μ -type bond can be integrated as [48]:

$$H_v^\mu = 556 \frac{N_a^\mu e^{-1.191f_i}}{(d^\mu)^{2.5}} = 350 \frac{(N_e^\mu)^{2/3} e^{-1.191f_i}}{(d^\mu)^{2.5}} \quad (18)$$

According to Eq.(18), the hardness of complex crystals depends on the effective valence electron densities (N_e^μ), the bond length (d^μ), and the Phillips ionicity of the μ -type bond (f_i).

The N_e^μ of complex crystals can be expressed as:

$$N_e^\mu = \left(\frac{Z_X^\mu}{N_X} + \frac{Z_Y^\mu}{N_Y} \right) \left[\frac{\sum n^\mu (d^\mu)^3}{V (d^\mu)^3} \right] \quad (19)$$

Where Z_X^μ (Z_Y^μ) is the effective valence electron number of the X (Y) atom forming the bond of type μ , N_X (N_Y) is the coordination number of the X (Y) atom, n^μ is the number of the μ -type bond composing the actual complex crystal, d^μ represents the length of the μ -type bond (\AA) and V is the volume of the unit cell (\AA^3). For pure covalent crystals, the ionicity of the same type of chemical bond of the carbon allotrope can be approximately thought to be zero since $f_i = (1 - e^{-|P_C - P|/P})^{0.735}$ [49]; of course, it should be noted that this approximate treatment will obtain an overestimated hardness except for diamond.

The geometric average of Vickers hardness for the hypothetical binary compound is calculated:

$$H_v = \left[\prod^\mu (H_v^\mu)^{n^\mu} \right]^{1/\sum n^\mu} \quad (20)$$

TABLE V The volume in a cell unit V , number of bonds n and bond length d^μ , and the calculated effective valence electron densities N_e^μ , Vickers hardness H_v^μ and the geometric average of hardness H_v of complex crystals.

Crystal	$V/\text{\AA}^3$	n	$d^\mu/\text{\AA}$	$N_e^\mu/\text{\AA}^{-3}$	H_v^μ/GPa	H_v/GPa	
Diamond	45.35	16	1.544	0.706	93.63	93.6	
o-C ₈	53.31	2	1.502	0.515	81.39	82.4	
		2	1.530	0.487	74.86		
		4	1.540	0.479	72.87		
		4	1.540	0.478	72.81		
		4	1.641	0.395	54.65		
		4	1.535	0.498	75.42		87.2
D-carbon	37.44	2	1.535	0.498	75.42	87.2	
		4	1.539	0.494	74.51		
		4	1.542	0.491	73.71		
		2	1.600	0.440	62.56		
		16	1.530	0.539	80.15		91.5
		4	1.560	0.508	73.25		
o-C ₁₆ -II	93.27	4	1.560	0.508	73.25	91.5	
		4	1.560	0.508	73.27		
		4	1.567	0.502	71.89		
		4	1.574	0.495	70.54		
		16	1.528	0.545	80.89		92.4
		16	1.541	0.531	77.91		
o-C ₃₂	184.19	4	1.543	0.529	77.41	92.4	
		8	1.548	0.524	76.24		
		4	1.557	0.515	74.33		
		4	1.557	0.515	74.38		
		4	1.561	0.511	73.45		
		4	1.577	0.496	70.26		
		4	1.579	0.494	69.87		

The calculated H_v^μ , N_e^μ and H_v of complex crystals are listed in Table V.

The Vickers hardness of o-C₈ carbon was calculated to be 82.43 GPa, softer than diamond with theoretical 93.6 GPa at the same level of theory and experimental (96±5) GPa [50], but harder than 65.6 GPa of c-BN at the same level of theory. Therefore o-C₈ carbon is a superhard material.

H. Electronic structure

The calculated electronic band structure and density of states (DOS) of o-C₈ carbon are shown in FIG. 7. It is shown that o-C₈ carbon is a semiconductor with the indirect band gap of 2.267 eV, smaller than that of diamond (4.461 eV). The electronic band structure of o-C₈ is similar to that of o-C₁₆-II and o-C₃₂. It can be seen from FIG. 7(a) that the DOS are mainly contributed by the C_{2s} states from about -22 eV to -17 eV, and are mainly from C_{2s} states and C_{2p} states in the range of -17 eV to -13 eV, and the total and partial density of states of o-C₈ carbon suggest all the atoms in it is sp³-

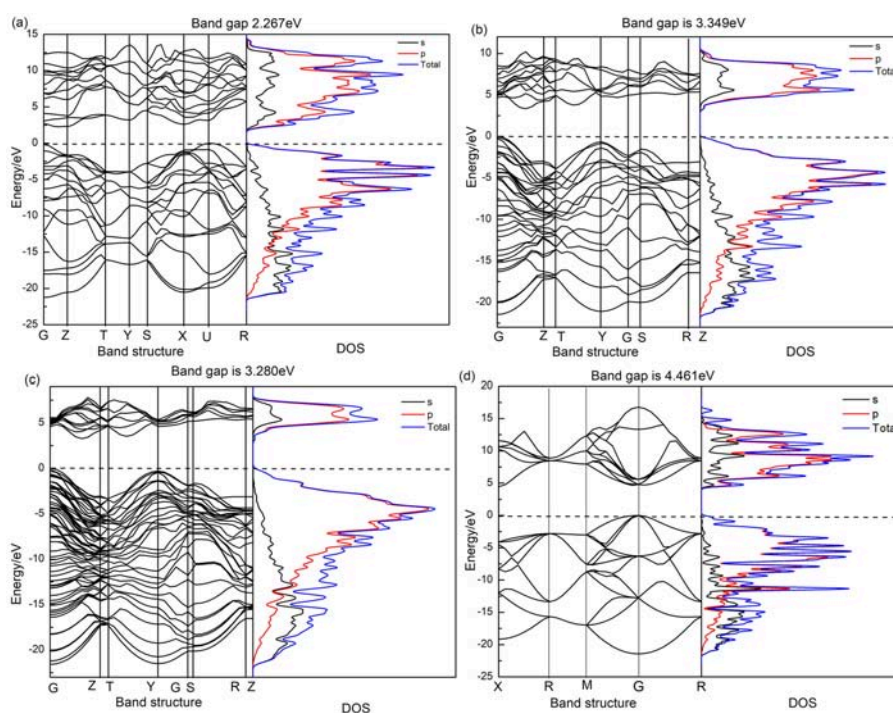


FIG. 7 Electronic band structure and density of states of (a) o-C₈ carbon, (b) o-C_{16-II}, (c) o-C₃₂, (d) diamond.

hybridized, similar to the case in o-C_{16-II}, o-C₃₂ and diamond. It thus can be concluded that it is the same sp³-bonding that makes o-C₈ a superhard material.

IV. CONCLUSION

A superhard material o-C₈ carbon was predicted theoretically using particle swarm optimization algorithm and density functional calculations. The calculations show that o-C₈ carbon is a stable semiconductor at ambient pressure and its Vickers hardness is 82.4 GPa. Structural analysis suggests that it is the strained four-membered ring that determines the stability of carbon crystals.

V. ACKNOWLEDGEMENTS

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