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Exotic Cubic Carbon Allotropes

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ABSTRACT: Elemental carbon exists in various aesthetically pleasing architectures. These forms include a group of synthesized allotropes with cubic modifications that have taken controversial or even unidentified crystal structures, which makes determining their physical properties difficult. In this study, four novel cubic carbon polymorphs (fcc-C_{10}, fcc-C_{12}, bcc-C_{20}, and fcc-C_{32}) that exhibit lattice parameters within the same range as those of undetermined cubic carbon allotropes are proposed by employing a newly developed ab initio particle-swarm optimization methodology for crystal structure prediction. The four structures are all three-dimensional polymers consisting of unique, small C_{10}, C_{12}, C_{20}, and C_{32} cages with quite low density. Investigation of their electronic and mechanical properties illustrate that the cage-like cubic carbons are all semiconductors with excellent mechanical performance, specifically superhardness and high ductility. Moreover, we readily explain a long-standing controversial experimentally synthesized cubic carbon (viz., the so-called "superdense" carbon) using the previously proposed bcc C_6 based on the coincident lattice constant and electron diffraction data between the theoretical and experimental results.
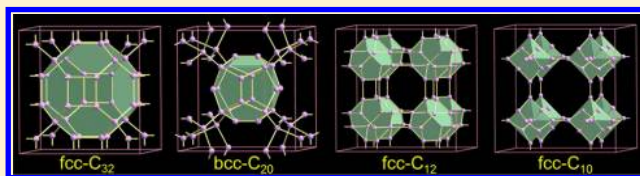
1. INTRODUCTION

Carbon forms multifarious allotropes that arise from its versatile sp, sp^2, and sp^3 bonding models, which allow it to foster graphite, lonsdaleite, diamond, fullerenes, nanotubes, and so on. Scientists have pursued new carbon allotropes in the past decades, and the recent discovery of graphene,[1,2] graphyne, and graphdiyne[3−5] has promoted carbon research to a new height. At present, it should be reminded that a class of cubic carbon polymorphs exists broadly with excellent properties, such as good thermostability,[6] blue luminescence,[7] superhardness,[8] semiconductivity, and transparency.[9] However, it is unfortunate that most of the synthesized cubic carbon phases take the disputable and even unsolved crystal structures, hindering understanding the nature of their related physical properties.

One of the most controversial cubic carbons is the body-centered cubic (bcc) "superdense" carbon, which has a lattice parameter of $a = 4.28$ Å. This carbon phase was first identified in the plasma-deposited amorphous carbon films.[10−12] Strel'nitskii et al.[11] suggested this carbon possesses a super-cubane-like structure (designated as supercubane C_8) with a calculated density of 4.1 g/cm^3, which exceeds by 15% the density of diamond (3.55 g/cm^3). Given the unusually short bond lengths in supercubane C_8, Johnston and Hoffmann[8] doubted its structural validity and proposed a new candidate, namely, BC8 carbon, which is popularly considered as an ultrahigh-pressure phase of carbon (above ∼1.0 TPa).[13−18] This "superdense" carbon was detected successively by other research groups.[19,20] Another disputant allotrope is the face-centered cubic (fcc) carbon,[21,22] which has a lattice parameter of about 3.56 Å, close to that of cubic diamond. Several independent research groups confirmed its existence through electron diffraction technology, and they denominated it separately as $γ$-carbon,[23] n-diamond,[24−27] and x-diamond.[28,29] This fcc carbon was also discovered in natural Mexican crude oil[30] and in the Younger Dryas boundary sediment layer.[31] Nevertheless, the first-principle calculations revealed that this fcc carbon has an equilibrium lattice parameter of 3.08 Å,[32−34] far less than the experimental value, and has much higher energy compared with diamond.[34] Other structural models, such as modified diamond,[35] CH_x,[36] and glitter,[37] have also been proposed to interpret this allotrope. The third controversial cubic carbon, with $a = 5.545$ Å, was obtained by experimentally compressing graphite up to 50 GPa.[6] Pokropivny et al. posited the carbon as a three-dimensional polymer of the C_{24} cages (termed as 3D-C_{24}).[38] More recently, Wang et al. proposed an alternative candidate, viz., C_3, which reportedly had a more feasible energy profile than 3D-C_{24} at high pressure.[39] Aside from the above three controversial allotropes, other cubic carbons with uncertain crystallography have also been reported in experiments. For instance, an i-carbon with $a = 4.25$ Å was first chemically synthesized[40] and was later found in shock compressed graphite;[24] a simple cubic (sc) carbon with $a = 5.14$ Å was shock-synthesized by compressing powdered carbon black and tetracyanoethylene mixture;[41] a bcc carbon with $a = 5.46$ Å was synthesized using laser ablation in liquid;[7] two fcc carbon, with respective lattice parameters of 5.45 and 11.54 Å, were obtained by heating carbon soot at a temperature of 1073 K and pressure of $10^{−3}$

Pa;[42] a transparent and superhard carbon with $a = 14.697$ Å was found in the natural Popigai impact crater.[9] These lesser-known cubic carbon allotropes stimulate our interest to prompt in-depth investigations.

2. THEORETICAL METHODS

To design reasonable structures, the ab initio particle swarm optimization (PSO) algorithm implemented in Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code,[43−45] which has been successfully applied in many studies,[46−54] was employed. Structural searches were conducted up to 24 atoms/cell in the 0 to 25 GPa pressure range. We obtained thousands of carbon allotropes, from which the cubic crystals were collected to investigate their structural and physical properties further. The underlying structural relaxations were performed using the Vienna Ab-initio Simulation Package (VASP) code,[55] and further geometric optimization and property predictions were carried out using the Cambridge Serial Total Energy Package (CASTEP) code.[56] The Vanderbilt ultrasoft pseudopotential[56] was used at the chosen plane-wave cutoff energy of 310 eV. This cutoff energy is sufficient and gives reliable calculation results with relative deviation of lattice parameters less than 2‰ compared with those obtained from lager cutoff energy of 620 eV. The exchange correlation terms were treated using the Ceperley and Alder as parametrized by Perdew and Zunger (CA-PZ) form of local density approximation (LDA).[57,58] A k-point separation ($2\pi \times 0.04$ Å^{-1}) was assigned to generate a k-point grid using the Monkhorst−Pack grid parameters.[59] The linear response method[60,61] was used to calculate the phonon frequencies of the semiconducting carbons. A primitive cell was used to calculate the elastic constants C_{ij}. After applying a finite strain to the optimized structure, the elastic constants can be determined from the linear relationship (Hooke's law) between the applied strain and the resulting stress. For each distorted structure, the atomic coordinates were optimized with fixed lattice parameters in order to obtain the internal stress of crystal.

3. RESULTS AND DISCUSSION

In the structural searches, some earlier known experimental and theoretical cubic carbons, such as diamond, sc C_{20},[62] bcc C_6,[62] supercubane C_8,[11] and BC8 carbon,[9−15] were reproduced. Moreover, four exotic cubic carbons with lattice parameters within the range of the experimental and natural carbon values specified above[6,14,16,17,20−28,35,38−42] were uncovered. They are termed as fcc-C_{32}, bcc-C_{20}, fcc-C_{12}, and fcc-C_{10}, which are composed of C_{32}, C_{20}, C_{12}, and C_{10} cages, respectively (Figure 1 and Table 1). These structures are strikingly different from graphite and diamond due to distinct bonding types. The fcc-C_{10} and bcc-C_{20} have a mixed sp^2- and sp^3-hybridization, while fcc-C_{32} and fcc-C_{12} are all sp^3-hybridized with variable bond angles (109.5°, 125.3°, and 90° for fcc-C_{32}, and 135.0°, 60.0°, and 90.0° for fcc-C_{12}), which is completely different from that of diamond (with a unique bond angle of 109.5°). Specifically, the cages in bcc-C_{20}, fcc-C_{12}, and fcc-C_{10} are directly interlinked through bridge-like bonds similar to 3D-C_{60},[63−66] with eight, six, and six nearest neighbor cages, respectively. By contrast, the C_{32} cages in fcc-C_{32} are linked through both bridge-like bonds and shared faces, and each cage is surrounded by the 14 nearest ones. Thus, eight cages share the faces with it, and six residual cages are covalently bonded to it through $[2 + 2]$ cycloaddition.
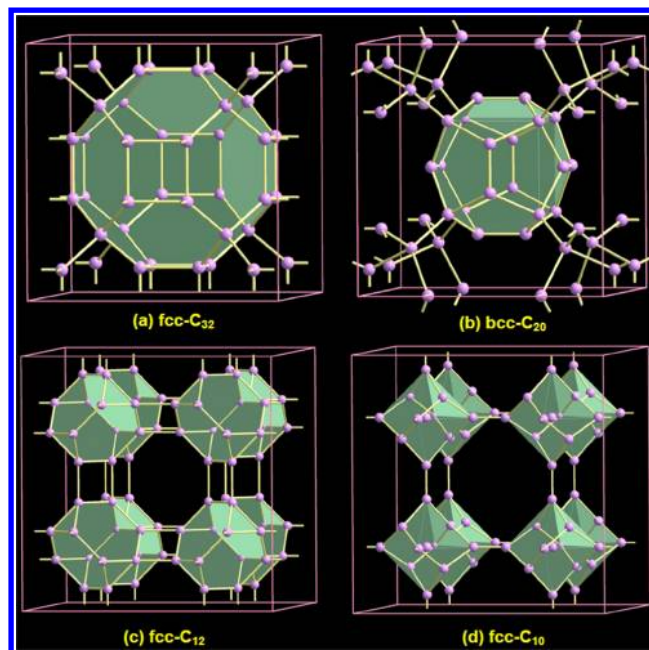

Figure 1. Crystal structures of (a) fcc-C_{32}, (b) bcc-C_{20}, (c) fcc-C_{12}, and (d) fcc-C_{10}, respectively. They consist of identical C_{32}, C_{20}, C_{12}, and C_{10} cages, respectively. Notably, a central atom in the C_{10} cage bonds to the nearest four atoms.

Such cage-like structures spontaneously reduce the densities, much lower than that of diamond (Table 1). The fcc-C_{10} has the lowest density (1.65 g/cm^3), which is close to that of C_{60}, and the densest is fcc-C_{32} at 2.75 g/cm^3, which just matches that of graphite. Evidently, the cage-like configurations readily accommodate small atoms or molecules such as alkali metal ions, hydrogen, and argon.

The mechanical and dynamic stabilities were studied to confirm their structural validity. To guarantee the mechanical stability of a structure, the corresponding elastic constants should satisfy the elastic stability criteria. For a stable cubic structure, its three independent elastic constants (C_{11}, C_{44}, and C_{12}) should satisfy the following generalized Born stability criteria:[67] $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, and $C_{11} + 2C_{12} > 0$. Clearly, the calculated elastic constants C_{ij} of four structures meet the mechanical stability criteria, suggesting they are mechanically stable at ambient pressure (Table 2). Moreover, phonon calculations provide a criterion for examining the dynamic stability of the crystal, which is very important for the lattice because the appearance of soft phonon modes may result in distortion of the crystal. As presented in Figure 2, the phonon dispersion curves at ambient pressure are explicitly calculated. No imaginary phonon frequency was observed throughout the whole Brillouin zone, which demonstrates the dynamical stability of these carbons. Enthalpy versus pressure calculations indicate that these four carbon phases have higher enthalpies than that of graphite in the pressure range of 0−100 GPa. Therefore, they might not be achieved through a high-pressure approach. Considering many cubic carbons can be synthesized by different experimental technologies, such as pulsed-laser induced liquid−solid interface reaction (PLIIR),[19] laser ablation,[22] chemical vapor deposition (CVD),[28,29] and plasma deposition,[11] the proposed cubic carbon allotropes are also expected to be synthesized through similar experimental treatments.

Table 1. Space Group (S.G.), Density (g/cm³), Cell Parameter (Å), and Atomic Wyckoff Positions of the Four Novel Carbon Allotropes

structure	S.G.	density	a	atomic positions
diamond	$Fd\bar{3}m$ (227)	3.63	3.53	8b (−1/2, 1/2, 1/2)
fcc-C_{32}	$Fm\bar{3}m$ (225)	2.75	6.62	32f (−0.118, 0.118, 0.118); 8c (−1/4, 1/4, 1/4)
bcc-C_{20}	$Im\bar{3}$ (204)	2.47	6.86	24g (0, −0.098, −0.731); 16f (0.186, −0.186, −0.186)
fcc-C_{12}	$Fm\bar{3}m$ (225)	2.34	9.36	96k (−0.693, −0.420, 0.307)
fcc-C_{10}	$Fm\bar{3}m$ (225)	1.65	10.20	32f (−0.669, −0.669, −0.669); 48g (−3/4, −0.935, −3/4); 8c (−1/4, −1/4, −1/4)

Table 2. Elastic Constants C_{ij} (GPa), Bulk Modulus B (GPa), Shear Modulus G (GPa), B/G Value, and Poisson'S Ratio v of the Four Novel Carbon Allotropes and Diamond at Ambient Pressure

structure	C_{11}	C_{44}	C_{12}	B	G	B/G	v
diamond	1092.35	595.57	135.62	454.53	545.55	0.83	0.07
fcc-C_{32}	590.45	334.64	165.85	307.38	278.83	1.10	0.15
bcc-C_{20}	389.51	167.70	105.34	200.06	156.94	1.27	0.19
fcc-C_{12}	546.67	136.81	115.75	259.39	164.24	1.58	0.24
fcc-C_{10}	218.79	26.62	51.30	107.13	43.04	2.49	0.32
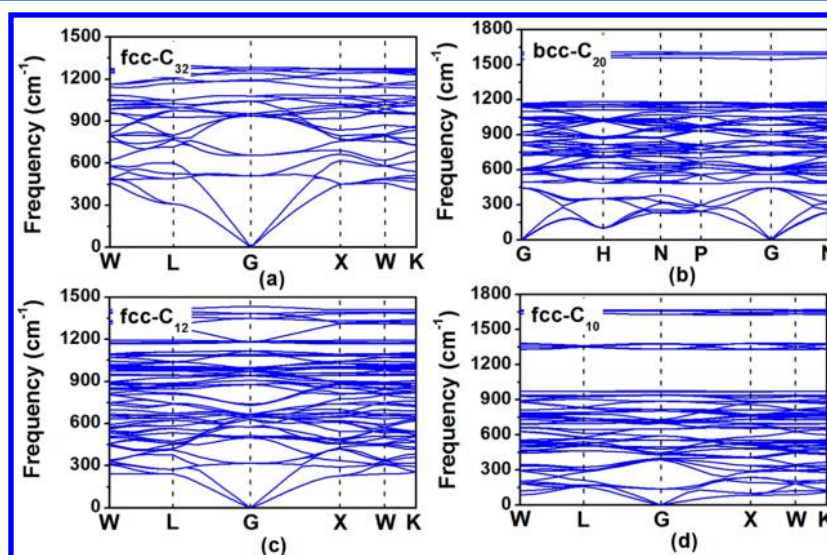
Figure 2. Phonon dispersion curves of (a) fcc-C_{32}, (b) bcc-C_{20}, (c) fcc-C_{12}, and (d) fcc-C_{10} at ambient pressure.

Electronic band structures show the tops of the valence bands of fcc-C_{32}, bcc-C_{20}, fcc-C_{12}, and fcc-C_{10} are along the G, P, G, and W symmetry points, respectively. In addition, the bottoms of the conduction bands are located at the L, between the H and N, W, and L points, respectively (Figure 3). As shown in the figure, fcc-C_{32}, bcc-C_{20}, fcc-C_{12}, and fcc-C_{10} are all semiconductors with indirect band gaps of 2.00, 2.26, 2.75, and 1.85 eV, respectively, which are all much smaller than that of diamond (4.20 eV). Larger band gaps are expected because density functional theory (DFT) tends to underestimate the band gap systematically by about 30 to 40%. Both fcc-C_{32} and fcc-C_{12} are entirely composed of sp³ hybridized atoms with all valence electrons localized to form σ bonds. The semiconducting properties of fcc-C_{32} and fcc-C_{12} are thus expectable. However, it is interesting to find that the sp² + sp³ bonded fcc-C_{10} and bcc-C_{20} are also semiconductors. In order to understand the nature, electron orbitals of top valence band (the gray bands in Figure 3) and bottom conduction band (the magenta bands in Figure 3) are calculated (Figure 4). It is known that each energy band is defined by the position of its eigenvalue with ordered electronic energy at each k-point, and the corresponding electron orbital is the square of the absolute

value of the wave function for this given electronic band, summed over all k-points.[47] For fcc-C_{10}, the electron orbitals of top valence band and bottom conduction band distribute at different positions (Figure 4a,b), which is responsible for the band gap. To conquer the gap, an electron transfer from σ bond state (top valence bond) to π bond state (bottom conduction band) is necessary. For bcc-C_{20} (Figure 4c,d), the electron orbitals of top valence band and bottom conduction band are both composed of π bond state but take different energy states. Exciting the transfer from lower to higher π bond state can result in conductivity.

Diamond is superhard but brittle, while graphite is soft but ductile. A material combined high hardness and ductility is highly anticipated. Usually, high-density carbons exhibit high hardness. The Vickers hardness of the densest carbon, fcc-C_{32}, was estimated using our semiempirical hardness model.[68−71] The calculated hardness of fcc-C_{32} is 79.9 GPa (Table 3), which illustrates its superhard nature. Proverbially, bulk modulus (B) represents the resistance to material fracture, whereas the shear modulus (G) represents the resistance to plastic deformation of a material. Hence, the B/G ratio is defined as a quantitative index for assessing the brittle or ductile behavior of crystals.
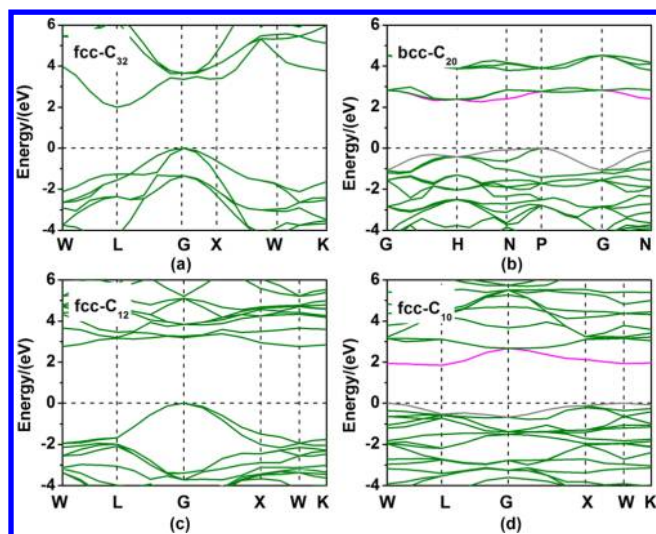
Figure 3. Electronic band structures of (a) fcc-C_{32}, (b) bcc-C_{20}, (c) fcc-C_{12}, and (d) fcc-C_{10} at ambient pressure. The gray curves represent the valence band top, and the magenta curves represent the conduction band bottom.
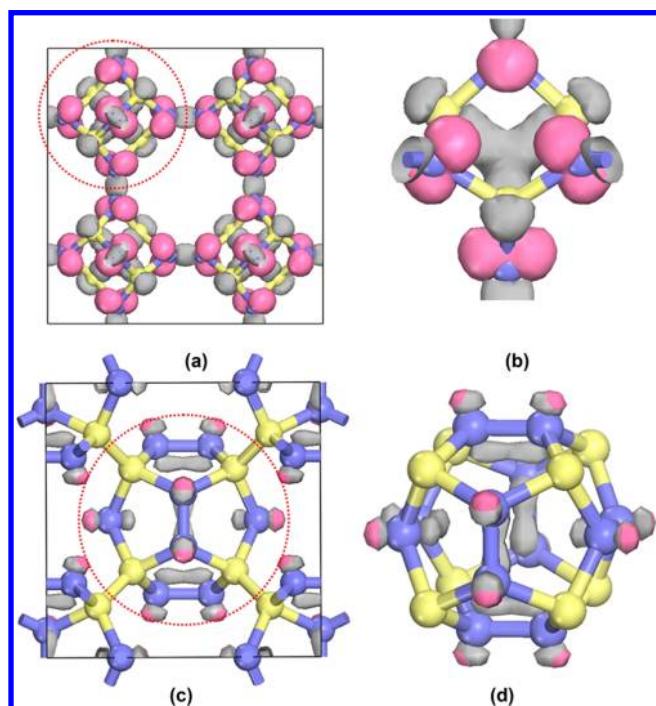

Figure 4. Calculated electron orbitals of fcc-C_{10} (a,b) and bcc-C_{20} (c,d). Panels b and d show the local fragments marked by red circles in panels a and c, respectively. The yellow atoms are sp^3 hybridized, and the purple atoms are sp^2 hybridized. The gray parts represent the electron orbitals of valence band top, and the magenta parts represent the electron orbitals of conduction band bottom, which correspond to the gray and magenta bands in Figure 3.

Paugh[72] proposed that a high (low) B/G value is often associated with ductility (brittleness) and that the critical value that differentiates ductile and brittle materials is about 1.75. The B/G ratios of fcc-C_{10}, fcc-C_{12}, bcc-C_{20}, and fcc-C_{32} are 2.49, 1.58, 1.27, and 1.10, respectively, which are all higher than that of diamond (0.83), implying their very ductile nature. The fcc-C_{10} is a ductile material with a B/G value almost triple that of brittle diamond. For conviction, the brittleness/ductility

Table 3. Bond Parameters and Theoretical Vickers Hardness of fcc-C_{32}: the Number of Bonds n, the Bond Length d (Å), the Valence Electron Density N_e (electron·Å^{-3}), the Bond Hardness H_v (GPa), and the Calculated Crystal Vickers Hardness H_{vcal} (GPa)

band type	n	d	N_e	H_v	H_{vcal}
C−C	32	1.516	0.581	86.11	79.9
C−C	48	1.559	0.534	75.93	

were also estimated by Frantsevich rule adopting the Poisson's ratio of a material.[73] A high (low) Poisson's ratio value usually suggests ductility (brittleness), and the critical value is 1/3. The Poisson's ratios of fcc-C_{10}, fcc-C_{12}, bcc-C_{20}, and fcc-C_{32} are, respectively, 0.32, 0.24, 0.19, and 0.15, which also indicate that the four are more ductile than diamond (0.07). This agrees well with the estimation from the B/G relationship. The four cubic carbons possess multiple mechanical performances, making them act as cutting tools, coatings, and so on.

Moreover, we accidentally discovered that the recently proposed cage-like bcc C_6[62] better exemplifies the experimental "superdense" carbon, which has a structure remained debatable for decades, than the previously proposed supercubane C_8 and BC8 carbon allotropes.[8,10−12,15,16] Our argument confirms this in three aspects. First, the lattice parameter a = 4.33 Å of bcc C_6 agrees well with the experimentally identified 4.28 Å.[10−12] However, the lattice parameters of BC8 and supercubane C_8 (4.42 and 4.82 Å, respectively) are much higher when fully optimized at ambient pressure. Second, the simulated d-spacing (d_{cal}) of bcc C_6 agree better with the experimental d_{exp} values[11,19] than those of BC8 and supercubane C_8 (Table 4).

Table 4. Experimental d-Spacing (d_{exp}, Å) of the Superdense Carbon Compared with the Simulated d-Spacings (d_{cal}, Å) of bcc-C_6, Supercubane C_8, and BC8

index	d_{exp}^{a}	d_{exp}^{b}	d_{cal} bcc-C_6	d_{cal} supercubane C_8	d_{cal} BC8
(011)	3.02	2.97	3.063	3.407	
(002)	2.13	2.11	2.166	2.409	2.209
(112)	1.74		1.769	1.967	1.803
(022)	1.52	1.48	1.532	1.704	1.562
(013)	1.352	1.33	1.370	1.524	
		1.32			
(222)	1.234		1.251	1.391	1.275
(040)		1.06	1.083	1.205	1.104
(330)		0.99	1.021	1.136	
(510)		0.83	0.850	0.945	

^{a}Reference 11. ^{b}Reference 19.

Third, bcc C_6 is more thermodynamically stable and has ground-state enthalpies of 0.26 and 0.24 eV/atom lower than those of supercubane C_8 and BC8 carbon, respectively. Furthermore, because bcc C_6 has a density of just 2.94 g/cm^3, which is 17.2% lower than that of diamond, the "superdense" carbon would not be superdense beyond the understanding of pioneers.

4. CONCLUSIONS

In summary, four cage-like cubic carbons (fcc-C_{32}, bcc-C_{20}, fcc-C_{12}, and fcc-C_{10}) with lattice parameters within the range of the experimentally synthesized and naturally existing cubic carbons have been predicted using first-principles calculations. In each

of the structures, the identical cages are linked through intercage bridge-like bonds and/or shared faces, which lead to low crystal densities. Among them, the lightest fcc-C_{10} has a comparable density to C_{60}, and the densest fcc-C_{32} has a slightly higher density than graphite. The four cubic carbons are all semiconducting with indirect band gaps and excellent mechanical performances. The fcc-C_{32} allotrope is a superhard carbon material with a hardness of 79.9 GPa, and fcc-C_{10} is a ductile material. Therefore, such excellent properties enable these cubic carbon materials to have wide potential applications as molecular sieves, shape-selective catalysts, absorbents, cutting tools, coatings, and so on. Ultimately, we satisfactorily explained the so-called "superdense" carbon via the recently proposed bcc C_6, which more favorably matches the experimental data than the previously identified supercubane C_8 and BC8 carbon.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666−669.

(2) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. *Nature* **2005**, *438*, 197−200.

(3) Diederich, F.; Kivala, M. *Adv. Mater.* **2010**, *22*, 803−812.

(4) Li, G.; Li, Y.; Liu, H.; Guo, Y.; Zhu, D. *Chem. Commun.* **2010**, *46*, 3256−3258.

(5) Malko, D.; Neiss, C.; Viñes, F.; Görling, A. *Phys. Rev. Lett.* **2012**, *108*, 086804.

(6) Aust, R. B.; Drickamer, H. G. *Science* **1963**, *140*, 817−819.

(7) Liu, P.; Cao, Y. L.; Wang, C. X.; Chen, X. Y.; Yang, G. W. *Nano Lett.* **2008**, *8*, 2570−2575.

(8) Johnston, R. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1989**, *111*, 810−819.

(9) El Goresy, A.; Dubrovinsky, L. S.; Gillet, P.; Mostefaoui, S.; Graup, G.; Drakopoulos, M.; Simionovici, A. S.; Swamy, V.; Masaitis, V. L. *C. R. Geosci.* **2003**, *335*, 889−898.

(10) Strel'nitskii, V. E.; Padalka, V. G.; Vakula, S. I. *Zh. Tekh. Fiz.* **1978**, *48*, 377; *Sov. Phys. Tech. Phys.* **1978**, *23*, 222.

(11) Matyushenko, N. N.; Strel'nitskii, V. E.; Pis'ma, V. A. *Zh. Eksp. Teor. Fiz.* **1979**, *30*, 218−221.

(12) Bakai, A. S.; Strel'nitskii, V. E. *Zh. Tekh. Fiz.* **1981**, *51*, 2414; *Sov. Phys. Tech. Phys.* **1981**, *26*, 1425.

(13) Yin, M. T. *Phys. Rev. B* **1984**, *30*, 1773−1776.

(14) Biswas, R.; Martin, R.; Needs, R.; Nielsen, O. *Phys. Rev. B* **1984**, *30*, 3210−3213.

(15) Biswas, R.; Martin, R.; Needs, R.; Nielsen, O. *Phys. Rev. B* **1987**, *35*, 9559−9568.

(16) Correa, A. A.; Bonev, S. A.; Galli, G. *Proc. Natl. Acad. Sci.* **2006**, *103*, 1204−1208.

(17) Knudson, M. D.; Desjarlais, M. P.; Dolan, D. H. *Science* **2008**, *322*, 1822−1825.

(18) Sun, J.; Klug, D. D.; Martonak, R. *J. Chem. Phys.* **2009**, *130*, 194512.

(19) Liu, P.; Cui, H.; Yang, G. W. *Cryst. Growth Des.* **2008**, *8*, 581−586.

(20) Basharin, A.; Dozhdikov, V.; Dubinchuk, V.; Kirillin, A.; Lysenko, I.; Turchaninov, M. *Tech. Phys. Lett.* **2009**, *35*, 428−431.

(21) Konyashin, I.; Zern, A.; Mayer, J.; Aldinger, F.; Babaev, V.; Khvostov, V.; Guseva, M. *Diamond Relat. Mater.* **2001**, *10*, 99−102.

(22) Konyashin, I.; Khvostov, V.; Babaev, V.; Guseva, M.; Mayer, J.; Sirenko, A. *Int. J. Refract. Met. Hard Mater.* **2006**, *24*, 17−23.

(23) Palatnik, L. S.; Guseva, M. B.; Babaev, V. G.; Savchenko, N. F.; Falko, I. I. *Zh. Eksp. Teor. Fiz.* **1984**, *87*, 914−917.

(24) Hirai, H.; Kondo, K.-I. *Science* **1991**, *253*, 772−774.

(25) Yoo, C. S.; Nellis, W. J.; Sattler, M. L.; Musket, R. G. *Appl. Phys. Lett.* **1992**, *61*, 273−275.

(26) Endo, S.; Idani, N.; Oshima, R.; Takano, K.; Wakatsuki, M. *Phys. Rev. B* **1994**, *49*, 22−27.

(27) Yamada, K.; Sawaoka, A. *Carbon* **1994**, *32*, 665−673.

(28) Rossi, M.; Vitali, G.; Terranova, M. L.; Sessa, V. *Appl. Phys. Lett.* **1993**, *63*, 2765−2767.

(29) Terranova, M. L.; Rossi, M.; Sessa, V.; Vitali, G. *Solid State Commun.* **1994**, *91*, 55−58.

(30) Santiago, P.; Camacho-Bragado, G. A.; Marin-Almazo, M.; Murgich, J.; José-Yacaman, M. *Energy Fuels* **2004**, *18*, 390−395.

(31) Kennett, D. J.; Kennett, J. P.; West, A.; Mercer, C.; Hee, S. S. Q.; Bement, L.; Bunch, T. E.; Sellers, M.; Wolbach, W. S. *Science* **2009**, *323*, 94.

(32) Murrieta, G.; Tapia, A.; de Coss, R. *Carbon* **2004**, *42*, 771−774.

(33) Dadsetani, M.; Titantah, J. T.; Lamoen, D. *Diamond Relat. Mater.* **2010**, *19*, 73−77.

(34) Pickard, C. J.; Milman, V.; Winkler, B. *Diamond Relat. Mater.* **2001**, *10*, 2225−2227.

(35) Hirai, H.; Kondo, K.-I.; Sugiura, H. *Appl. Phys. Lett.* **1992**, *61*, 414−416.

(36) Singh, T.; Behr, M. J.; Aydil, E. S.; Maroudas, D. *Chem. Phys. Lett.* **2009**, *474*, 168−174.

(37) Bucknum, M.; Castro, E. *J. Math. Chem.* **2012**, *50*, 1034−1038.

(38) Pokropivny, V.; Pokropivny, A. *Phys. Solid State* **2004**, *46*, 392−394.

(39) Wang, J.-T.; Chen, C.; Kawazoe, Y. *Phys. Rev. B* **2012**, *85*, 214104.

(40) Vora, H.; Moravec, T. J. *J. Appl. Phys.* **1981**, *52*, 6151−6157.

(41) Yamada, K. *Carbon* **2003**, *41*, 1309−1313.

(42) Miki-Yoshida, M.; Rendon, L.; Jose-Yacaman, M. *Carbon* **1993**, *31*, 843−846.

(43) Zhu, L.; Ma, Y.; Wang, Y.; Lv, J. *Calypso*, 2012; see http://mym.calypso.cn/.

(44) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. *Phys. Rev. B* **2010**, *82*, 094116.

(45) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. *Comput. Phys. Commun.* **2012**, *183*, 2063−2070.

(46) Li, P.; Gao, G.; Wang, Y.; Ma, Y. *J. Phys. Chem. C* **2010**, *114*, 21745−21749.

(47) Zhao, Z.; Xu, B.; Wang, L.-M.; Zhou, X.-F.; He, J.; Liu, Z.; Wang, H.-T.; Tian, Y. *ACS Nano* **2011**, *5*, 7226−7234.

(48) Zhao, Z.; Xu, B.; Zhou, X.-F.; Wang, L.-M.; Wen, B.; He, J.; Liu, Z.; Wang, H.-T.; Tian, Y. *Phys. Rev. Lett.* **2011**, *107*, 215502.

(49) Lv, J.; Wang, Y.; Zhu, L.; Ma, Y. *Phys. Rev. Lett.* **2011**, *106*, 015503.

(50) Wang, Y.; Liu, H.; Lv, J.; Zhu, L.; Wang, H.; Ma, Y. *Nat. Commun.* **2011**, *2*, 563.

(51) Zhu, L.; Wang, H.; Wang, Y.; Lv, J.; Ma, Y.; Cui, Q.; Ma, Y.; Zou, G. *Phys. Rev. Lett.* **2011**, *106*, 145501.

(52) Luo, X.; Yang, J.; Liu, H.; Wu, X.; Wang, Y.; Ma, Y.; Wei, S.-H.; Gong, X.; Xiang, H. *J. Am. Chem. Soc.* **2011**, *133*, 16285−16290.

(53) Tian, F.; Dong, X.; Zhao, Z.; He, J.; Wang, H. T. *J. Phys.: Condens. Matter* **2012**, *24*, 165504.

(54) Wang, H.; Tse, J. S.; Tanaka, K.; Iitaka, T.; Ma, Y. *Proc. Natl. Acad. Sci.* **2012**, *109*, 6463−6466.

(55) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169−11186.

(56) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. *Z. Kristallogr.* **2005**, *220*, 567−570.

(57) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 566−569.

(58) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048−5079.

(59) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188−5192.

(60) Baroni, S.; Giannozzi, P.; Testa, A. *Phys. Rev. Lett.* **1987**, *58*, 1861−1864.

(61) Giannozzi, P.; de Gironcoli, S.; Pavone, P.; Baroni, S. *Phys. Rev. B* **1991**, *43*, 7231−7242.

(62) Ribeiro, F.; Tangney, P.; Louie, S.; Cohen, M. *Phys. Rev. B* **2006**, *74*, 172101.

(63) Blank, V. D.; Buga, S. G.; Dubitsky, G. A.; Serebryanaya, N. R.; Popov, M. Y.; Sundqvist, B. *Carbon* **1998**, *36*, 319−343.

(64) Yamanaka, S.; Kubo, A.; Inumaru, K.; Komaguchi, K.; Kini, N.; Inoue, T.; Irifune, T. *Phys. Rev. Lett.* **2006**, *96*, 076602.

(65) Yamanaka, S.; Kini, N. S.; Kubo, A.; Jida, S.; Kuramoto, H. *J. Am. Chem. Soc.* **2008**, *130*, 4303−4309.

(66) Tonkov, E. Y.; Ponyatovsky, E. G. *Phase Transformations of Elements under High Pressure*; CRC Press: Boca Raton, FL, 2005.

(67) Nye, J. F. *Physical Properties of Crystals*; Oxford University Press: Oxford, U.K., 1985.

(68) Gao, F.; He, J.; Wu, E.; Liu, S.; Yu, D.; Li, D.; Zhang, S.; Tian, Y. *Phys. Rev. Lett.* **2003**, *91*, 015502.

(69) He, J.; Wu, E.; Wang, H.; Liu, R.; Tian, Y. *Phys. Rev. Lett.* **2005**, *94*, 15504.

(70) Guo, X.; Li, L.; Liu, Z.; Yu, D.; He, J.; Liu, R.; Xu, B.; Tian, Y.; Wang, H.-T. *J. Appl. Phys.* **2008**, *104*, 023503.

(71) Tian, Y.; Xu, B.; Zhao, Z. *Int. J. Refract. Met. Hard Mater.* **2012**, *33*, 93−106.

(72) Pugh, S. F. *Philos. Mag.* **1954**, *45*, 823−843.

(73) Frantsevich, I. N.; Voronov, F. F.; Bokuta, S. A. *Elastic Constants and Elastic Moduli of Metals and Insulators*; Naukova Dumka: Kiev, Ukraine, 1983.