New Superhard Carbon Phases Between Graphite and Diamond

Chaoyu He, L. Z. Sun, C. X. Zhang, K. W. Zhang, Xiangyang Peng, and Jianxin Zhong

Institute for Quantum Engineering and Micro-Nano Energy Technology, Xiangtan University, Xiangtan 411105, China

(Dated: October 29, 2018)

Two new carbon allotropes (H-carbon and S-carbon) are proposed, as possible candidates for the intermediate superhard phases between graphite and diamond obtained in the process of cold compressing graphite, based on the results of first-principles calculations. Both H-carbon and S-carbon are more stable than previously proposed M-carbon and W-carbon and their bulk modulus are comparable to that of diamond. H-carbon is an indirect-band-gap semiconductor with a gap of 4.450 eV and S-carbon is a direct-band-gap semiconductor with a gap of 4.343 eV. The transition pressure from cold compressing graphite is 10.08 GPa and 5.93 Gpa for H-carbon and S-carbon, respectively, which is consistent with the recent experimental report.

PACS numbers: 61.50.Ks, 61.66.Bi, 62.50. -p, 63.20. D-

INTRODUCTION

Carbon is considered as the most active element in the periodic table due to its broad sp, sp² and sp³ hybridizing ability. Besides the four best-known carbon allotropes, graphite, cubic-diamond, hexagonal diamond and amorphous carbon, an unknown superhard phase of carbon has been reported in experiment along with the structural phase transition in cold pressed graphite. Several structures have been proposed as the candidates for this superhard phase, such as the monoclinic M-carbon, cubic body center C4 carbon (bct-C4) and the orthorhombic W-carbon. The cohesive energy of the most stable W-carbon is about 160 meV per atom higher than that of diamond, indicating that other more stable carbon phases may exist.

Very recently, another new carbon allotrope, named as Z-carbon, was proposed and investigated at almost the same time by three independent research groups. Z-carbon is more stable (its cohesive energy is about 129 meV per atom larger than that of diamond) and harder than W-carbon. Moreover, its transition pressure is around 10 Gpa which is lower than that of W-carbon.

Thus, it is believed that the formation in the process of the cold compressing graphite prefers Z-carbon rather than W-carbon. Although none of them can fit the experimental results satisfactorily, these theoretically proposed phases are significant in understanding the experimental process of cold compressing graphite.

The formation of the new carbon phase needs large lattice distortions, such as buckling between adjacent carbon layers of graphite. Therefore, the phase transition depends not only on the particular nucleation history but also on the structure of the starting graphitic material. Intuitively, such buckling between carbon layers will start from the natural AB stacking graphite rather than the AA stacking graphite chosen in previous theoretical studies. From this hypothesis, we propose two new superhard crystals, namely H-carbon and S-carbon, as potential candidates for the experimentally observed intermediate state of carbon, which can be formed from compressing AB stacking graphite. Our first-principles calculations based on density functional theory show that both the allotropes are transparent wide band gap insulators and their hardness are comparable to that of diamond.

S-carbon has the lowest enthalpy compared with bct-C4 carbon, M-carbon, W-carbon, and Z-carbon and is the most stable new carbon phase theoretically proposed until now. H-carbon is always more stable than W-carbon and M-carbon. When the pressure is above 5.93 Gpa (10.08 Gpa), S-carbon (H-carbon) is more favorable than graphite.

FIG. 1: Crystal structure of H-carbon(a), initial AB stacking graphite supercell for H-carbon (b) and side view containing five and seven carbon rings of H-carbon (c). Crystal structure of S-carbon (d), initial AB stacking graphite supercell for S-carbon (e) and side view containing five and seven carbon rings of S-carbon (f).
MODELS AND METHODS

H-carbon and S-carbon belong to the orthorhombic lattice and they can be obtained from cold compressing AB stacking graphite. Crystal structures of H-carbon and S-carbon are shown in Fig. 1 (a) and (d), and their corresponding initial graphite structures are shown in Fig. 1 (b) and (e), respectively. H-carbon with the Pbam symmetry containing 16 carbon atoms per crystal cell is obtained by reorganizing C atoms to form sp^3 bonds through compressing an AB stacking graphite supercell with 16 atoms. While, S-carbon with Cmcm symmetry containing 24 carbon atoms per crystal cell is obtained from larger AB stacking graphite supercell with 24 atoms. All calculations are carried out using the density functional theory within both local density approximation (LDA) [14, 15] and general gradient approximation (GGA) [16] as implemented in Vienna ab initio simulation package (VASP) [17, 18]. In evaluating of the transition pressure from graphite to each superhard phases, it is known that LDA is a better choice because LDA can give reasonable interlayer distances, mechanical properties of graphite sheets due to a delicate error cancellation between exchange and correlation in comparison with that of semi-local generalized gradient approximation (GGA). The interactions between nucleus and the 2s^2p^2 valence electrons of carbon are described by the projector augmented wave (PAW) method [19, 20]. A plane-wave basis with a cutoff energy of 500 eV is used to expand the wave functions. The Brillouin Zone (BZ) sample meshes are set to be dense enough to ensure the accuracy of our calculations [21]. Crystal lattices and atom positions of graphite, diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon are fully optimized up to the residual force on every atom less than 0.005 eV/Å through the conjugate-gradient algorithm. Vibration properties are calculated by using the phonon package [22] with the forces calculated from VASP.

RESULTS AND DISCUSSION

Similar to M-carbon and W-carbon, H-carbon and S-carbon contain distorted five and seven carbon rings, as shown in Fig. 1 (c) and (f). Their difference from Z-carbon and bct-C4 carbon is the absence of four and eight carbon rings. The crystal structure of H-carbon belongs to the Pbam space group. At zero pressure, the GGA calculated equilibrium lattice constants are a=7.872 Å, b=4.807 Å and c=4.899 Å. Four inequivalent atoms in S-carbon locate at positions of (0.500, 0.778, 0.250), (0.500, 0.132, 0.518) and (0.000, 0.300, 0.750). Recently proposed Z-carbon contains even number carbon rings and hold Cmmm symmetry, with equilibrium lattice parameters a=8.772 Å, b=4.256 Å and c=2.514 Å. There are only two inequivalent atoms in Z-carbon located at (0.089, 0.316, 0.500) and (0.167, 0.185, 0.000). All the results of the lattice constants of diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon derived from both GGA and LDA calculations are listed in Tab. 1. The LDA calculations tend to give smaller lattice constants for all structures considered here, but the conclusions derived from LDA and GGA are consistent.

The relative stability of diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon is evaluated through comparing their cohesive energy per atom. The energy of H-carbon is about 15 meV lower than that of W-carbon, about 25 meV lower than that of M-carbon, and 10 meV higher than that of Z-carbon at both LDA and GGA level. Namely, H-carbon is more stable than M-carbon and W-carbon but less stable than Z-carbon. Among these allotropes, S-carbon is the most stable one whose cohesive energy is about 30 meV lower than that of Z-carbon. From the cohesive energy, S-carbon is the most stable carbon allotrope theoretically proposed until now. The enthalpy per atom for cubic diamond, hexagonal diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon as a function of pressure as shown in Fig. 2. The results indicate that H-carbon is more stable than graphite when the external pressure is larger than 10.08 GPa. H-carbon is always favorable than M-carbon and W-carbon at the pressure range from 0 to 25 GPa.
TABLE I: Space group, exchange-correlation functional (EXC), lattice parameters (LP), density (g/cm$^3$), band gap (E$_g$: eV), cohesive energy (E$_{coh}$: eV) and bulk modulus (B$_0$: GPa) for diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon.

| Systems  | Space group | EXC   | LP               | Density | E$_{coh}$ | E$_g$ | B$_0$ |
|----------|-------------|-------|------------------|---------|----------|-------|-------|
| diamond  | Fd-3m       | LDA   | a=b=c=3.536Å     | 3.611   | 4.648    | -8.997| 514.08|
| diamond  | Fd-3m       | GGA   | a=b=c=3.574Å     | 3.491   | 4.635    | -7.693| 478.96|
| M-carbon | C2/m        | LDA   | a=9.093Å, b=2.498Å, c=4.108Å, beta=96.96$^\circ$ | 3.443   | 3.532    | -8.821| 447.33|
| M-carbon | C2/m        | GGA   | a=9.194Å, b=2.525Å, c=4.151Å, beta=97.03$^\circ$ | 3.333   | 3.493    | -7.531| 431.44|
| W-carbon | Pnma        | LDA   | a=8.984Å, b=4.116Å, c=2.498Å | 3.455   | 4.325    | -8.830| 468.12|
| W-carbon | Pnma        | GGA   | a=9.086Å, b=4.156Å, c=2.525Å | 3.345   | 4.281    | -7.539| 447.03|
| Z-carbon | Cmmm        | LDA   | a=8.677Å, b=4.211Å, c=2.489Å | 3.507   | 3.414    | -8.857| 497.87|
| Z-carbon | Cmmm        | GGA   | a=8.772Å, b=4.256Å, c=2.514Å | 3.394   | 3.273    | -7.564| 464.13|
| H-carbon | Pham        | LDA   | a=7.792Å, b=4.757Å, c=2.497Å | 3.440   | 4.512    | -8.845| 466.92|
| H-carbon | Pham        | GGA   | a=8.747Å, b=4.807Å, c=2.524Å | 3.339   | 4.459    | -7.554| 445.88|
| S-carbon | Cmcm        | LDA   | a=2.496Å, b=11.293Å, c=4.857Å | 3.489   | 4.451    | -8.896| 486.29|
| S-carbon | Cmcm        | GGA   | a=2.523Å, b=11.385Å, c=4.899Å | 3.399   | 4.342    | -7.593| 468.45|

FIG. 3: Phonon band structure and density of state for H-carbon (a) and S-carbon (b). Electronic band structure and density of state for H-carbon (c) and S-carbon (d).

can be formed by cold compressing graphite and their densities and bulk modulus are close to that of diamond. The density of H-carbon and S-carbon derived from GGA is 3.339 g/cm$^3$ and 3.399 g/cm$^3$, respectively, which is similar to that of M-carbon (3.333 g/cm$^3$), W-carbon (3.345 g/cm$^3$) and Z-carbon (3.394 g/cm$^3$) derived from the same method. The bulk modulus of H-carbon is 445.88 GPa which is almost the same as that of W-carbon (447.03 GPa) and slightly larger than that of M-carbon (431.44 GPa). The bulk modulus of S-carbon is 468.45 GPa which is close to that of Z-carbon (466.13 GPa). The values of the bulk modulus indicate that H-carbon and S-carbon are superhard materials which are comparable to diamond (478.96 GPa).

Electronic properties of diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon are also investigated under both GGA and LDA calculations. All these superhard carbon allotropes are indirect wide band gap semiconductors except for S-carbon. The GGA results show that H-carbon holds an indirect wide gap of 4.531 eV which is larger than that of M-carbon (3.523 eV), W-carbon (4.325 eV) and Z-carbon (3.273 eV), and smaller than that of diamond (4.635 eV). Different from other previously proposed superhard carbon allotropes, S-carbon is a direct-band-gap semiconductor with a gap of 4.342 eV. The wide band gap indicates that both H-carbon and S-carbon are transparent carbon allotropes. Fig. 3(c) and (d) show the electronic band structures and densities of states of H-carbon and S-carbon derived from GGA. The densities of states indicate that the valence band maximum for both H-carbon and S-carbon is mainly contributed from the 2p states of carbon, whereas the conduction band minimum comes from the sp hybridized states.

The simulated X-ray diffraction (XRD) patterns for graphite, Z-carbon, H-carbon and S-carbon at the pressure of 23.9 GPa are shown in Fig. 4 to compare all of the previously proposed carbon allotropes. To further confirm the dynamic stabilities of H-carbon and S-carbon, we calculate their phonon band structures and phonon densities of state as shown in Fig. 3. Both LDA and GGA calculations indicate that there is no negative frequency for both structures confirming that H-carbon and S-carbon are dynamic stable phases of carbon.

Space group, density, band gap, cohesive energy and bulk modulus of diamond, M-carbon, W-carbon, Z-carbon, H-carbon, and S-carbon are also summarized in Tab. I The results indicate that, as superhard intermediate phases between graphite and diamond, M-carbon, W-carbon, Z-carbon, H-carbon, and S-carbon
with the experimental data from reference [5]. The experimental data under high pressure can be explained by H-carbon and S-carbon to some extent. The main XRD peaks located in the region between 8.5° - 11° and 15° - 17° for H-carbon and S-carbon agree well with the experimental observations. As indicated by Amsler et al. [11] that sole comparison between experimental and theoretical XRD can not directly clarify the new carbon phase. In view of the cohesive energy, dynamical stability, electronic structure, bulk modulus, lowest phase transition pressure point, and especially the natural transition from AB stacking graphite, H-carbon and S-carbon are excellent candidates for the new superhard carbon phase.

Note. added During the course of our submission, we became aware of several recent papers [23–30] reporting the new superhard carbon phases similar to our H-carbon [23, 26] and S-carbon [24, 26].

CONCLUSION

In summary, we propose two new superhard carbon phases, H-carbon and S-carbon, as the possible candidates for the intermediate phase of cold compressing graphite. Both H-carbon and S-carbon with sp³ carbon bonds are optical transparent superhard carbon phases. They are more stable than M-carbon and W-carbon, and S-carbon is the most table carbon phase theoretically proposed until now. Moreover, when the pressure is above 5.93 Gpa (10.08 Gpa), S-carbon (H-carbon) is more favorable than graphite. These two new members together with the previous proposed M-carbon, bct-C4, W-carbon and Z-carbon will enrich the theoretical evidence for understanding the experimental observation.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant Nos. 11074211, 10874143 and 10974166), the Cultivation Fund of the Key Scientific and Technical Innovation Project, the Program for New Century Excellent Talents in University (Grant No. NCET-10-0169), and the Scientific Research Fund of Hunan Provincial Education Department (Grant Nos. 10K065, 10A118, 09K033)

* Electronic address: lzsuni@xtu.edu.cn
† Electronic address: zhong_xtu@gmail.com

[1] F. P. Bundy, J. Chem. Phys. 46, 3437 (1967).
[2] A. F. Goncharov, I. N. Makarenko, and S. M. Stishov, Sov. Phys. JETP 69, 380 (1989).
[3] M. Hanfland, H. Beister, and K. Syassen, Phys. Rev. B 39, 12508 (1989).
[4] W. Utsunomi and T. Yagi, Science 252, 1542 (1991).
[5] W. L. Mao, H. Mao, P. J. Eng, T. P. Trainor, M. Newville, C. C. Kao, D. L. Heinz, J. F. Shu, Y. Eng and R. J. Hemley, Science 302, 425 (2003).
[6] A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006).
[7] Q. Li, Y. M. Ma, A. R. Oganov, H. B. Wang, H. Wang, Y. Xu, T. Cui, H. K. Mao, and G. T. Zou, Phys. Rev. Lett. 102, 175506 (2009).
[8] K. Umemoto, R. M. Wentzcovitch, S. Saito, and T. Miyake, Phys. Rev. Lett. 104, 125504 (2010).
[9] J. T. Wang, C. F. Chen and Y. Kawazoe, Phys. Rev. Lett. 106, 075501 (2011).
[10] D. Selli, I. A. Baburin, R. Martoànik and S. Leoni, Phys. Rev. B 84, 161411(R) (2011).
[11] M. Amsler, J. A. Flores-Livas, L. Lehtovaara, F. Balima, S. A. Ghasemi, D. Machon, S. Pailhès, A. Willand, D. Caliste, S. Botti, A. S. Miguel, S. Goedecker and M. A. Marques, Phys. Rev. Lett. 108, 065501 (2012).
[12] Z. S. Zhao, B. Xu, X. F. Zhou, L. M. Wang, B. Wen, J. L. He, Z. Y. Liu, H. T. Wang and Y. J. Tian, Phys. Rev. Lett. 107, 215502 (2011).
[13] R. Z. Khaliullin, H. Eshet, T. D. Kühne, J. Behler and M. Parrinello, Nat. Mater. textbf10, 693 (2011).
[14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
[15] J. P. Perdew and A. Zunger, Phys. Rev. B 33, 5048 (1981).
[16] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[17] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[18] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).

[19] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).

[20] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

[21] $13 \times 13 \times 13$, $5 \times 15 \times 11$, $5 \times 11 \times 15$, $5 \times 11 \times 15$, $15 \times 11 \times 11$ and $15 \times 5 \times 11$ for diamond, M-carbon, W-carbon, Z-carbon, H-carbon and S-carbon, respectively.

[22] K. Parlinski, Z.-Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997).

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

[24] D. Li, K. Bao, F. B. Tian, Z. W. Zeng, Z. He, B. B. Liu and T. Cui, Phys. Chem. Chem. Phys. 14, 4347 (2012).

[25] F. Tian, X. Dong, Z. S. Zhao, J. L. He and H. T. Wang, J. Phys: Condens. Matter. 24, 165504 (2012).

[26] H. Y. Niu, X. Q. Chen, S. B. Wang, D. Z. Li, W. L. Mao and Y. Y. Li, Phys. Rev. Lett. 108, 135501 (2012).

[27] R. L. Zhou and X. C. Zeng, J. Am. Chem. Soc. 134, 7530 (2012).

[28] M. Amsler, J. A. Flores-Livas, S. Botti, M. A. L Marques and S Geodecker, arXiv:1202.6030v1.

[29] Q. Zhu, Q. Zeng and A. R. Oganov. Phys. Rev. B 85, 201407 (2012).

[30] C. Y. He, L. Z. Sun, C. X. Zhang, X. Y. Peng, K. W. Zhang and J. X. Zhong, Phys. Chem. Chem. Phys. 14, 8410 (2012).