Prediction of a novel monoclinic carbon allotrope

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Abstract

A novel allotrope of carbon with \(P2/m\) symmetry was identified during an \(ab\)-initio minima-hopping structural search which we call \(M10\)-carbon. This structure is predicted to be more stable than graphite at pressures above 14.4 GPa and consists purely of \(sp^2\) bonds. It has a high bulk modulus and is almost as hard as diamond. A comparison of the simulated X-ray diffraction pattern shows a good agreement with experimental results from cold compressed graphite.

Graphite and diamond are the thermodynamically most stable forms of carbon at ambient conditions. However, carbon can be found in a vast structural variety due to its flexibility to form \(sp^2\), \(sp^3\)- and \(sp^2\)-hybridized bonds: hexagonal diamond, nano-diamond, carbon-foams, fullerenes and nanowires are just some examples of known carbon allotropes. Experimental evidences of a novel super-hard carbon phase have been reported in literature when graphite is compressed at room temperatures. Changes in resistivity \(1\), optical transmittance \(2\, 3\), optical reflectivity \(4\), X-ray diffraction (XRD) patterns \(5\, 6\) and in the raman spectra \(7\) indicate a phase transition in the range of 10 to 25 GPa. Recently, several candidate structures have been proposed to match these experimental observations, such as \(M\)-carbon \(8\), bct-\(C_{14}\)-carbon \(10\), \(W\)-carbon \(11\) and \(Z\)-carbon \(8\, 12\). Although \(Z\)-carbon is thermodynamically the most promising structure, a final and conclusive determination has not yet been possible.

In this article we report on a novel carbon allotrope discovered with the recently developed minima hopping crystal structure prediction method (MHM) \(13\, 14\). The MHM is capable to predict the most stable and metastable structures given solely the chemical composition of a system. Short molecular dynamics simulations are used to escape from local minima, and local geometry relaxations are performed to identify stable configurations. High efficiency of the escape step is ensured by aligning the initial molecular dynamics velocities along soft mode direction, and revisiting already explored regions of the potential energy surface is avoided by a feedback mechanism. The minima hopping method has been successfully used in a wide range of applications \(8\, 13\, 15\, 19\).

During our MHM simulations, the energies and the Hellman-Feynman forces were evaluated at the density functional theory (DFT) level within the local density approximation (LDA), and the all-electron projector-augmented wave method was employed as implemented in the \textsc{abinit} code \(20\, 21\). The most promising structures were further relaxed using norm-conserving Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials \(22\). The total energy was converged within less than 1 meV per atom by a plane wave cut-off energy of 2100 eV and well converged Mankhorst-Pack \(k\)-point meshes. We reconfirmed the energy ordering with two other exchange-correlation functionals within the generalized gradient approximation, namely PBE \(23\) and PBEsol \(24\).

Several MHM simulations were carried out with cells containing up to 8 atoms at 15 GPa within an unconstrained and thorough structural search, starting from different input configurations. We identified a novel, monoclinic carbon phase with \(P2/m\) symmetry, which we call \(M10\)-carbon. It consists solely of \(sp^3\) bonds and contains 8 atoms per cell. At ambient pressure, the unit cell parameters are given by \(a = 4.080\ \text{Å}, b = 2.498\ \text{Å}, a = 4.728\ \text{Å}, \alpha = \gamma = 90^\circ\) and \(\beta = 73.96^\circ\). Two carbon atoms each occupy the crystallographic \(2n\) sites at \((-0.1, 0.5, -0.113)\) and \((-0.132, 0.5, 0.421)\), and the \(2m\) sites at \((-0.333, 0, -0.466)\) and \((-0.325, 0, -0.117)\). The overall structure is closely related to \(M\)-carbon, also consisting of 5- and 7-membered rings along the \(b\)-axis, while 6-membered rings are formed along the \(c\)-axis.
contrast to \( M \)-carbon, the 5-rings share the long edge, whereas in \( M\)-10-carbon they share the short edge. The structure is illustrated in Fig. 1.

The dynamical stability was investigated by analyzing the phonon dispersion within the whole Brillouin zone. The density-functional perturbation theory \[25\] as implemented in \textsc{abinit} was employed with a 12x12x12 \( k \)-point sampling and a 4x4x4 \( q \)-point mesh. No imaginary phonon frequencies were found, confirming the lattice stability of the phase. The thermodynamical stability of \( M\)-10-carbon was investigated by computing its enthalpy within a wide pressure range. In Fig. 2 the enthalpies of all proposed candidates for cold graphite are plotted with respect to graphite as a function of pressure. We neglected the zero-point vibrational energies in our calculations. \( M\)-10-carbon becomes enthalpically favorable over graphite above a pressure of 14.4 GPa. As expected from the structural similarities with \( M \)-carbon, both \( M\)-10- and \( M \)-carbon are very close in enthalpy throughout the whole pressure range.

In Table I we compare the structural properties of \( M\)-10-carbon with other carbon allotropes. The bulk moduli \( B_0 \) were computed using the Murnaghan equation, and the Vicker’s hardnesses \( H_v \) were estimated with the method of Gao et al. \[26\]. Like all of the investigated structures, \( M\)-10-carbon is nearly as hard as diamond and has a very high bulk modulus, which could well account for ring cracks in diamond anvil cells \[7\]. Furthermore, an analysis of the electronic bandstructure was carried out, showing that \( M\)-10-carbon is a wide band-gap semiconductor with an indirect DFT gap of 4.4 eV at 0 GPa.

Finally, we compare the XRD pattern of \( M\)-10-carbon to experimental measurements from Ref. \[7\], as illustrated in Fig. 3. The simulated pattern gives a good match to the experimental spectrum and could well explain the observed changes. It can therefore be expected that \( M\)-10-carbon is present in samples of cold compressed graphite above 14.4 GPa. However, other carbon allotropes show a similarly good agreement and thus the XRD pattern alone is by no way a conclusive evidence.

In conclusion we present a novel carbon allotrope that we call \( M\)-10-carbon. It is a transparent, superhard material which becomes enthalpically favorable over graphite at pressures above 14.4 GPa. Both the structural and enthalpical properties are very similar to the

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\begin{array}{|c|c|c|c|}
\hline
\text{Structure} & \text{Method} & B_0(\text{GPa}) & H_v(\text{GPa}) & V_0(\text{Å}) \\
\hline
\text{bct-C}_4 & \text{this work} & 428.2 & 93.5 & 5.82 \\
 & \text{LDA} \[11\] & 433.7 & 5.83 \\
\hline
\text{M-carbon} & \text{this work} & 428.4 & 93.9 & 5.77 \\
 & \text{LDA} \[11\] & 431.2 & 83.1 & 5.78 \\
\hline
\text{W-carbon} & \text{this work} & 427.5 & 94.2 & 5.75 \\
 & \text{LDA} \[11\] & 444.5 & 5.76 \\
\hline
\text{Cub-Diamond} & \text{this work} & 463.0 & 97.8 & 5.51 \\
 & \text{LDA} \[11\] & 466.3 & 5.52 \\
 & \text{Expt.} & 446[a] & 60-120[b] & 5.67 \\
\hline
\text{Z-carbon} & \text{LDA} \[8\] & 441.5 & 95.4 & 5.66 \\
\hline
\text{M10-carbon} & \text{this work} & 423.7 & 93.5 & 5.79 \\
\hline
\end{array}
\]

[a] Reference \[27\]  
[b] Reference \[28\]
previously proposed $M$-carbon [9]. The XRD pattern is in good agreement with experimental measurements, and although other carbon allotropes are enthalpically preferred at lower pressures, it could well be synthesized in samples of cold compressed graphite.

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[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, 12598 (1989).
[4] W. Utsumi and T. Yagi, Science 252, 1542 (1991).
[5] Y. X. Zhao and I. L. Spaiñ, Phys. Rev. B 40, 993 (1989).
[6] T. Yagi, W. Utsumi, M.-a. Yamakata, T. Kikegawa, and O. Shimomura, Phys. Rev. B 46, 6031 (1992).
[7] W. L. Mao, H.-k. Mao, P. J. Eng, T. P. Trainor, M. Newville, C.-c. Kao, D. L. Heinz, J. Shu, Y. Meng, and R. J. Hemley, Science 302, 425 (2003).
[8] M. Amsler, J. A. Flores-Livas, L. Lehtovaara, F. Balima, S. A. Ghasemi, D. Machon, S. Pailhs, A. Willand, D. Caliste, S. Botti, A. San Miguel, S. Goedecker, and M. A. L. Marques, Phys. Rev. Lett. 108, 065501 (2012).
[9] Q. Li, Y. Ma, A. R. Oganov, H. Wang, H. Wang, Y. Xu, T. Cui, H. K. Mao, and G. Zou, Phys. Rev. Lett. 102, 175506 (2009).
[10] K. Umemoto, R. M. Wentzcovitch, S. Saito, and T. Miyake, Phys. Rev. Lett. 104, 125504 (2010).
[11] J. T. Wang, C. Chen, and Y. Kawazoe, Phys. Rev. Lett. 106, 075501 (2011).
[12] Z. Zhao, B. Xu, X. Zhou, L. Wang, B. Wen, J. He, Z. Liu, H. Wang, and Y. Tian, Phys. Rev. Lett. 107, 215502 (2011).
[13] S. Goedecker, J. Chem. Phys. 120, 9911 (2004).
[14] M. Amsler and S. Goedecker, J. Chem. Phys. 133, 224104 (2010).
[15] W. Hellmann, R. G. Hennig, S. Goedecker, C. J. Umrigar, B. Delley, and T. Lenosky, Phys. Rev. B 75, 085411 (2007).
[16] S. Roy, S. Goedecker, M. J. Field, and E. Penev, J. Phys. Chem. B 113, 7315 (2009).
[17] K. Bao, S. Goedecker, K. Koga, F. Lançon, and A. Neelov, Phys. Rev. B 79, 041405 (2009).
[18] A. Willand, M. Gramzow, S. A. Ghasemi, L. Genovese, T. Deutsch, K. Reuter, and S. Goedecker, Phys. Rev. B 81, 201405 (2010).
[19] S. De, A. Willand, M. Amsler, P. Pochet, L. Genovese, and S. Goedecker, Phys. Rev. Lett. 106, 225502 (2011).
[20] X. Gonze, G. Rignanese, M. Verstraete, J. Benken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, P. Ghosez, M. Veithen, J. Raty, V. Olevano, F. Bruneval, L. Reining, R. Godby, G. Onida, D. Harman, and D. Allan, Z. Kristallogr. 220, 558 (2005).
[21] F. Bottin, S. Leroux, A. Knyazev, and G. Zrah, Comp. Mater. Sci. 42, 329 (2008).
[22] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B 58, 3641 (1998).
[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[24] J. P. Perdew, A. Ruzinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
[25] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
[26] F. Gao, J. He, E. Wu, S. Liu, D. Yu, D. Li, S. Zhang, and Y. Tian, Phys. Rev. Lett. 91, 015502 (2003).
[27] F. Occelli, P. Loubeyre, and R. LeToullec, Nat. Mater. 2, 151 (2003).
[28] V. Brazhkin, N. Dubrovinskaia, M. Nicol, N. Novikov, R. Riedel, V. Solozhenko, and Y. Zhao, Nat. Mater. 3, 576 (2004).