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Investigation of new superhard carbon allotropes with promising electronic properties

Yulia A. Kvashnina,^{1,2} Alexander G. Kvashnin,^{1,2} and Pavel B. Sorokin^{1,2,3,a)}

¹*Technological Institute for Superhard and Novel Carbon Materials, 7a Centralnaya Street, Troitsk, Moscow 142190, Russian Federation*

²*Moscow Institute of Physics and Technology, 9 Institutsky Lane, 141700 Dolgoprudny, Russian Federation*

³*Emanuel Institute of Biochemical Physics of RAS, 4 Kosigina St., Moscow 119334, Russian Federation*

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During the systematic search for a new superhard carbon allotrope, we predicted three structures with promising physical properties. Our electronic structure calculations show that these materials have a semiconducting band gap and a high carrier mobility comparable with diamond. The simulated x-ray diffraction patterns of the proposed materials are in a good agreement with the experimental X-ray spectra. Evaluated phase transition pressures from graphite to the new proposed carbon phases are smaller than 25 GPa and close to the experimental values. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829002>]

I. INTRODUCTION

Carbon solids attract strong interest not only because carbon is one of the most widespread chemical elements in nature but also because there is a dramatic difference in properties between the various carbon allotropes. The distinctive feature of carbon is its flexibility in the chemical junction, as well as a high strength of the C-C bonds which allows to form many hard and superhard carbon phases. It can be exemplified by diamond that is the hardest crystalline material. Moreover, an amorphous carbon material “tisnumit” with a much higher hardness was produced from fullerite by a group of Russian scientists in 1998.^{1,2} Also, Mao *et al.* reported fabrication of superhard carbon phases by cold compression of graphite.³ Meanwhile, the superhard phase was obtained using the compression of a solvated fullerenes.⁴ These facts show that besides the well-studied diamond, many other carbon phases with fascinating properties can be synthesized; and therefore it is important to continue the search for the new carbon-based allotropes.

Special interest is paid to the search for new carbon materials with a higher hardness and bulk modulus comparing to diamond, but with a smaller band gap. The latter is essential, since diamond electronics is a promising field due to the high carrier mobility of the material, while its band gap is large, along with deep impurity levels that hinder its application. Theoretical predictions play a significant role here, as they allow estimation of not only atomic structure of the new possible carbon phases but also their physical properties evaluation.

At the moment, there is a large number of metastable carbon allotropes predicted by the quantum-chemical methods of calculation. Compressed graphite appeared as an initial material for transition to different superhard phases. A large number of possible carbon modifications can be obtained by combination of four-, five-, six-, seven-, and eight-membered carbon rings. For example, several superhard carbon phases

of such structure called M-carbon,^{5–8} W-carbon,⁹ S-carbon, H-carbon,¹⁰ F-carbon,¹¹ Z-carbon,^{12,13} O-carbon,¹⁴ and other similar structures^{12,15–19} have been theoretically predicted. hP3, tI12, and tP12 carbon structures differ significantly from the previous carbon allotropes:²⁰ these phases are by 1%–3% denser than diamond at ambient conditions and display hardness and bulk modulus comparable to diamond. Currently, Z-carbon^{12,13} is the most stable and hard material predicted by theoretical methods, but it has not exceeded the diamond’s bulk modulus and hardness. The inclusion to the Z-carbon additional diamond blocks generate another superhard carbon allotropes family investigated in Ref. 21.

In this paper, we focused on the new promising carbon allotropes prediction. We proposed several superhard carbon phases and investigated in detail their mechanical, elastic, and electronics properties. The comparison of the X-ray diffraction pattern (XRD) of the new allotropes with the experimental data shows a good correspondence prompting suggestions that there is certain similarity between the predicted and synthesized materials.

In the first part of this study, we determine the atomic structure, space group, and cell parameters of the new carbon materials and propose a classification for them. The second part is devoted to the investigation of mechanical properties of the proposed materials: we estimated the bulk modulus and Vickers hardness and compared them with the diamond and Z-carbon^{12,13} corresponding values. Further, we estimated the phase transition pressure from graphite to the new proposed structures. After that, we focused on investigation of the electronic properties of the proposed materials. We calculated the band gap, holes and electrons effective masses, and carrier mobility in such structures. Finally, the X-ray diffraction pattern was calculated and compared to the experimental data of carbon superhard structures.³

II. COMPUTATIONAL DETAILS

Prediction of the new carbon phases was performed using a density functional theory (DFT)^{22,23} in the generalized

^{a)}Author to whom correspondence should be addressed. Electronic mail: psorokin@iph.krasn.ru

gradient approximation with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional,²⁴ as implemented in the VASP package.^{25–27} The plane-wave energy cutoff was equaled to 500 eV, while the Brillouin zone was sampled using an $8 \times 8 \times 8$ Monkhorst–Pack²⁸ grid. Atomic structure optimization was carried out, while the maximum interatomic force became less than 0.01 eV/\AA . The effective masses of both electrons and holes were determined using a k-points spacing smaller than 0.01 \AA^{-1} .

To evaluate the accuracy of the chosen approach, the corresponding characteristics of a bulk diamond were calculated. It was found that the DFT-PBE method predicts the structural parameters of a diamond system with an error less than 0.06% (compared to the experimental data taken from:²⁹ $a_{\text{calc}} = 3.566 \text{ \AA}$ and $a_{\text{exp}} = 3.568 \text{ \AA}$). The bulk modulus and Vickers hardness of the diamond were determined as $B = 432.3 \text{ GPa}$ and $H_v = 93.5 \text{ GPa}$, which is in good agreement with the reference values ($B = 442 \text{ GPa}$,³⁰ $H_v = 96 \pm 5 \text{ GPa}$ (Ref. 31)). The phase transition pressure between graphite and diamond was evaluated as 2.0 GPa , which also corresponded well with the experiment (1.5 GPa (Ref. 32)). The electronic band gap of diamond was evaluated as $E_g = 4.5 \text{ eV}$, which is lower than the experimental value (5.45 eV (Ref. 33)) due to a systematic underestimation of band gap by DFT-PBE.

III. RESULTS AND DISCUSSIONS

In the present study, a number of new carbon structures were proposed. In our research, we mainly focused on the structures with high density and high stiffness, and therefore the main characteristic feature of the proposed carbon allotropes is density, elastic constants, and hardness close to those of a diamond. All investigated structures have sp^3 or a mixture of sp^3 and sp^2 hybridized bonds.

The atomic geometry of the proposed carbon structures is shown in Fig. 1. The considered structures were classified according to Pearson notation and were denoted as hP16, hP6, and oP104; their symmetry and structural information are summarized in Table I, whereas the unique coordinates are given in the supplementary material.³⁴ The hP16 structure can be considered as chemically connected AA stacked graphite layers with the alternation of hexagons with all six and four atoms connected with the neighbored layers (Fig. 1(a)). The hP6 structure could be represented as spirals of pentagonal rings along the c-axis (Fig. 1(b)) bound together in a hexagonal network. Also, such structure could be represented as fallen apart fullerenes C_{20} spirally connected with each in a hexagonal grid. oP104 is a layered structure consisted of two types of layers. One layer includes the periodically repeated carbon clusters along the b-axis (Fig. 1(c)) which consist of eight six-member carbon rings. The second layer could be represented as an orthorhombic network with two repeated eight-member rings bonded together and surrounded by alternating four-, five-, and six-member carbon rings in the (b, c) plane.

Firstly, the elastic properties of the proposed structures were investigated. Each structure was hydrostatically compressed and dilated, at every step the geometry optimization

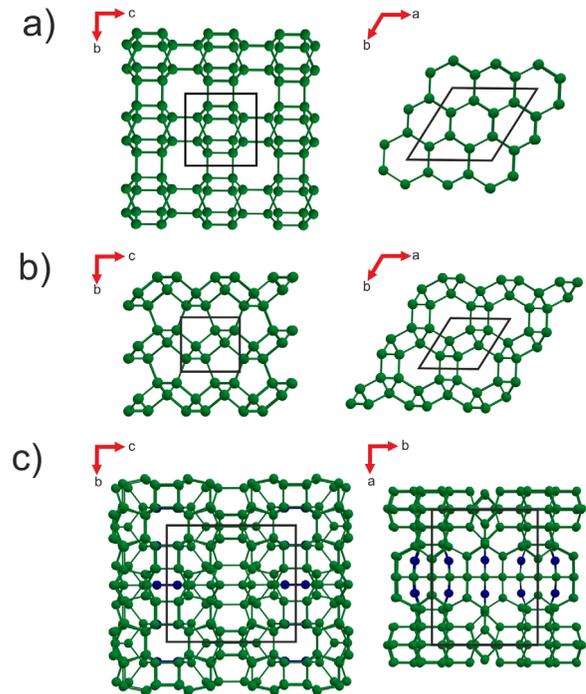


FIG. 1. Atomic structures of the proposed new carbon allotropes: (a) hP16; (b) hP6; (c) oP104. Black rectangle shows the unit cells of the structures.

was carried out. The obtained data of energy dependence on the volume change were used to determine the bulk modulus (B) using a Murnaghan's equation of state:^{35,36}

$$E(V) = E_0 + \frac{9B_0V_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{2/3} \right] \right\}, \quad (1)$$

where E_0 , B_0 , B'_0 , and V_0 are ground state energy, bulk modulus at zero pressure, derivative of the bulk modulus at zero pressure, and equilibrium volume, respectively.

The calculated bulk moduli of the proposed phases are presented in Table II and compared to the hardest known materials with determined atomic structure (diamond and Z-carbon^{12,13}). Among the considered structures, hP6 has the greatest value of the B (372.8 GPa), whereas oP104 and hP16 display lower values.

TABLE I. Crystal data for carbon phases considered in this study.

Pearson symbol	Space group	ρ (g/cm ³)	Unit cell (Å)
hP16	$P6/mmm$	3.144	$a = 5.15$ $c = 4.42$
hP6	$P6122$	3.208	$a = 3.57$ $c = 3.38$
oP104	$Pnmm$	3.225	$a = 9.79$ $b = 7.71$ $c = 8.52$
Diamond cF8	$Fd\bar{3}m$	3.470	$a = 3.56$

TABLE II. Elastic properties of the proposed materials in correspondence with diamond and Z-carbon, as well as phase transition pressure values from graphite to the proposed structures. Here, B , C_{11} , H_v , and P_t are the bulk modulus, elastic modulus, Vickers hardness, and phase transition pressure, respectively. The experimental values for diamond are given within brackets.

Name	B (GPa)	C_{11} (GPa)	H_v (GPa)	P_t (GPa)
Diamond	432.3 (442 (Ref. 30))	1136.8 (1080 (Ref. 37))	93.5 (96 ± 5 (Ref. 31))	2.0 (1.5 (Ref. 32))
Z-carbon	424.3	...	90.5	6.0
hP16	361.7	939.8	86.0	24.7
hP6	372.8	884.5	87.3	8.7
oP104	361.4	1027.3	89.4	20.7

Besides stiffness, which is characterized by the bulk modulus, an important mechanical characteristic of the material is its resistance to indenter penetration which is called hardness. Experimentally, hardness is defined as a ratio of the load on the surface to the indentation area. Such property is an integral characteristic of the material including its matter's ductility, elastic stiffness, plasticity, strength, toughness, viscosity, etc., and cannot be calculated directly by *ab initio* method. A number of empirical approaches^{38,39} have been developed in recent years, and in this work we used a method suggested by Gao *et al.*,³⁹ which allows to estimate Vickers hardness (H_v) only from the relaxed geometry using the $H_v = 556 N_a/d^{2.5}$ equation in assumption of nonpolar bonds in the material. Here, d is the bond length in angstroms and N_a is the number of covalent bonds per unit area. Obtained bulk modulus and hardness of all proposed structures are presented in Table II. One can see that the new phases have high bulk modulus and hardness values compared to a diamond and the hardest known materials.

At the next step, we evaluated values of phase transition pressures from graphite to the new carbon phases. The phase transition pressure was defined as equality of the Gibbs free energies of two phases

$$G = E_{tot} + pV - TS, \quad (2)$$

which is equaled to the slope of the common tangential line between the dependences of total energy on the volume for both of considered phases.⁴⁰ Fig. 2 shows the dependences of total energies on the volume for all proposed carbon allotropes in comparison to graphite and diamond. A dashed line in Fig. 2 shows the tangential line between graphite and diamond. These points defined the initial and final values of the volumes and corresponding energies. The phase transition pressure obtained from the illustrated tangential line slope is equal to 2 GPa. All calculations were carried out under 0 K without entropy contribution to Gibbs free energy (2).

The calculated values of phase transition pressures for all new structures are shown in Table II. One can see that graphite transforms to the hP16 and oP104 structures at the phase transition pressure from 20 GPa to 25 GPa. However, the phase transition pressure of hP6 structure is much smaller than 25 GPa and equals to 8.7 GPa. Comparing these phase transition pressures for the new carbon allotropes to the

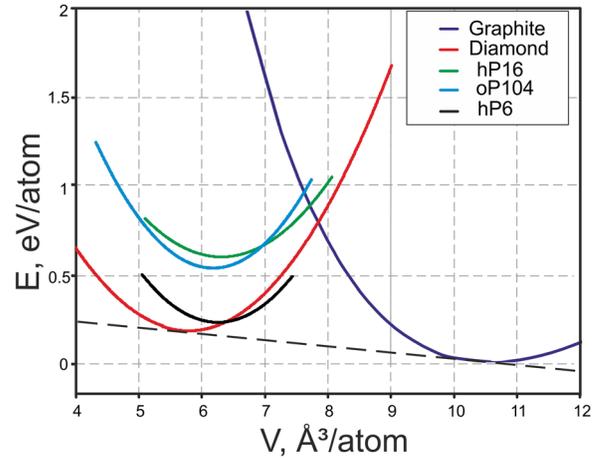


FIG. 2. The dependences of total energies on the unit volume for all proposed carbon allotropes in comparison to graphite and diamond. Energy of graphite corresponding to equilibrium volume is denoted as zero. The dashed common tangent indicates the transition between graphite and diamond.

experimental data of Mao *et al.*,³ where a new superhard carbon phase harder than diamond was fabricated under ambient temperature and pressure up to 24 GPa, it may be noted that the transition pressures for the proposed structures are similar to the experimental value. Thus, it is possible to assume that the new proposed carbon phases could exist in the experimentally fabricated superhard sample by Mao *et al.*³

We studied in detail the electronic properties of the proposed phases. The densities of states (DOSs) and band structures for all predicted phases are plotted in Fig. 3. All proposed carbon structures display large (>1.3 eV, also, the systematic band gap underestimation should be taken into account) indirect band gaps (Table III). The top of the valence band for hP16 and hP6 structures is located at the Γ point and L point, respectively, whereas the bottom of the conduction band is located at the $2/3$ along the $\Gamma \rightarrow A$ line (Fig. 3(a)) and at the $2/5$ of $\Gamma \rightarrow A$ line (Fig. 3(b)), respectively. The band structure of oP104 (Fig. 3(c)) displays a 1.3 eV semiconducting band gap with location on the valence band top and a conduction band bottom at the S and X points, respectively. The band of small width at the -1 eV is originated from the intermediate sp^2/sp^3 -hybridized bonding between the carbon atoms colored by blue in Fig. 1(c).

The prospective application of the proposed crystals in electronics is defined by the band gap larger than 1 eV and high mobility of the carriers. The latter was estimated using the deformation potential theory under the effective mass approximation proposed by Bardeen and Shockley more than 60 years ago,³⁷ where carrier mobility is defined as follows:

$$\mu = \frac{(8\pi)^{\frac{1}{2}} e \hbar^4 C_{11}}{3m^* \hbar^2 (k_B T)^{\frac{3}{2}} E_1^2}, \quad (3)$$

where effective mass $m^* = \hbar(\partial^2 E/\partial k^2)^{-1}$, C_{11} is an elastic modulus (Table II), E_1 is a deformation potential which

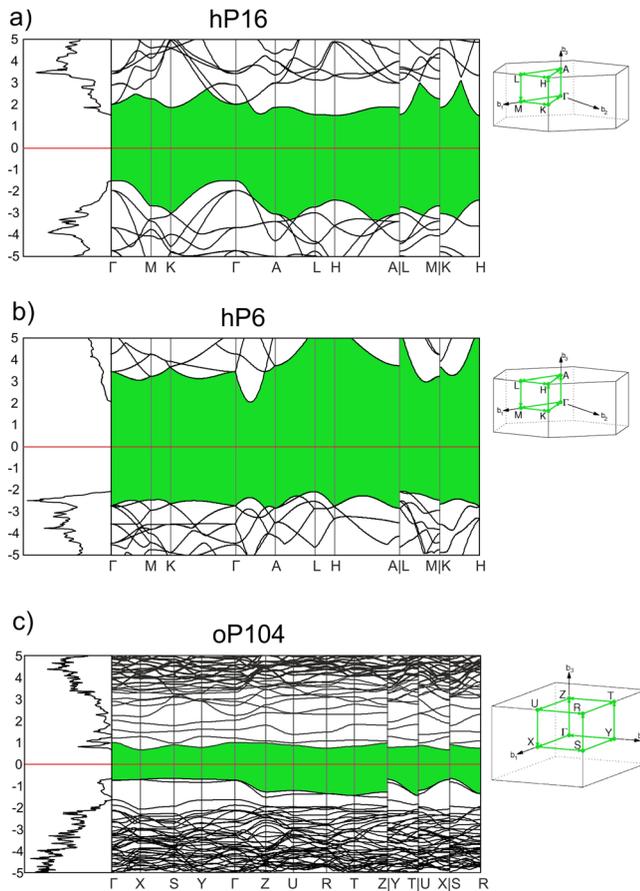


FIG. 3. Electronic properties of the proposed carbon allotropes: (a) hP16, (b) hP6, (c) oP104. Fermi level is denoted as a horizontal red line, the band gap is filled by the green color. On the right, the Brillouin zones for all structures are shown.

determined the strength of electron-phonon coupling. To obtain the deformation potential E_1 , the band structures of the hydrostatically compressed and dilated unit cells were calculated. From the variation of the bottom of the conduction band for electrons and the top of valence band for holes, we got two straight lines from the slopes of which the E_1 values were evaluated.

This approach was first applied for a diamond structure. We followed Bardeen's work³⁷ where deformation potential E_1 was evaluated in assumption that the electron effective mass is equal to a free electron mass. Using the available

experimental data of mobility ($900 \text{ cm}^2/\text{V s}$) and elastic constant (1080 GPa), the authors obtained the 8.8 eV deformation potential for electrons. Here, we evaluate the deformation potential value directly from *ab initio* calculation which gave us the values of 16.81 eV that are about two times larger, but the calculated effective mass of carriers was roughly two times smaller (0.572) than the mass of free electron which gave us the close mobility value of $968 \text{ cm}^2/\text{V s}$. Nevertheless, such value is several times lower than the experimental data⁴¹ which can be explained by the fact that in the applied theory it is assumed that the scattering of a thermal electron or hole arises mostly from the acoustic phonons, and therefore the method can be applied to estimate the carrier mobility at temperatures much lower than Debye temperature. We have found that the 100 K is low enough for a good correspondence between theory and experiment for a diamond (Table III). We used this temperature for estimation of carriers mobility for all the considered phases; the obtained transport characteristics (effective masses and mobility for both electrons and holes) are summarized in Table III. The calculated values show that the considered phases display the mobility of the carriers equal to or higher than that of a diamond.

Also, we attempted to answer the question how to identify the proposed structures. One of the main atomic structure determination methods is X-ray diffraction. Here, we simulated the XRD pattern of all the proposed structures and compared them to the experimentally obtained XRD by Mao *et al.*³ for a superhard carbon phase. Diffraction patterns of all the structures were simulated using an experimental wavelength equal to 0.3329 \AA (Fig. 4). In assumption that cold compression of graphite performed in the Ref. 3 leads to the formation of the mixed graphite-like sp^2 and sp^3 phases, here we considered a mixture of graphite and a new carbon phase XRD patterns. We plotted the data for the compressed structures with a 23.9 GPa experimental pressure at which the superhard phase was found. XRD patterns of the structures display similarities with the experimental spectra. Among all the considered structures, oP104 displays the closest shape of the peaks at a range of 8° – 11° to the experimental XRD. We suppose that the difference between the experimental and the simulated peaks shape is due to the possible formation of the regions with amorphous carbon in the experimentally obtained material.

TABLE III. Band gap, deformation potential E_{1c} for the bottom of the conduction band and E_{1v} for the top of valence band, relative effective masses of electrons and holes, calculated electronic and hole mobility μ of the considered materials along the main directions of symmetry at 100 K in comparison with diamond. In the latter case, the experimental values given from Refs. 42 and 43 are shown in the parentheses.

Pearson symbol	E_g (eV)	E_{1c} (eV)	E_{1v} (eV)	Relative electron effective mass	Relative hole effective mass	Electron mobility μ ($\text{cm}^2/\text{V s}$)	Hole mobility μ ($\text{cm}^2/\text{V s}$)
Diamond cF8	4.5	16.81	14.37	0.572	0.783	5567.9 (5500) ⁴²	3229.8 (6000) ⁴³
hP16	3.7	11.62	16.09	0.336 (ΓA)	0.402 0.998 (ΓA)	33874.7	11286.8 1160.4
hP6	4.1	12.36	12.55	0.308 (ΓA)	0.298 0.608 (AL)	34840.3	37016.8 6193.4
oP104	1.3	12.26	13.34	0.722 (ΓX) 0.961 (XS)	0.598 0.416 (YT)	4898 2397	6631.9 16412.6

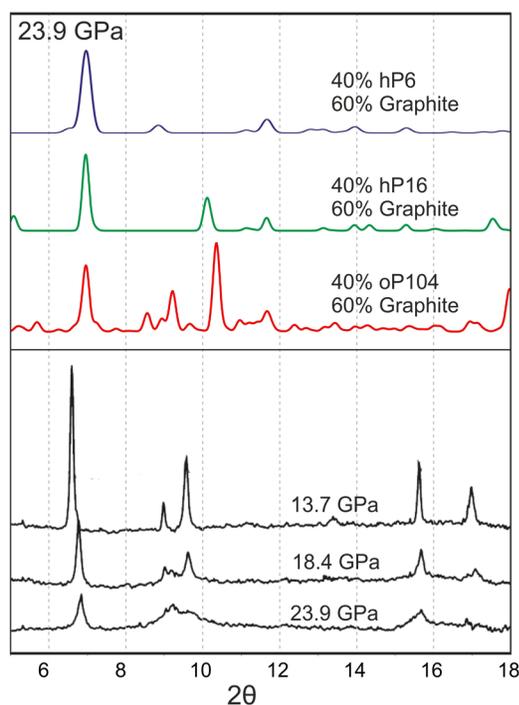


FIG. 4. Simulated X-ray diffraction patterns for the mixture of graphite (60%) and new carbon allotropes (40%) under the pressure equals to 23.9 GPa in correspondence with the experimental data of Mao *et al.*³

IV. CONCLUSION

In conclusion, the physical properties of the new proposed superhard carbon allotropes were discussed. All the studied structures are superhard semiconductors which display a band gap larger than 1.3 eV and the mobility of the carriers several times larger than in case of diamond, which makes these materials promising for electronics. The phase transition pressures between graphite and the new structures are lower than 25 GPa, prompting suggestions that experimental fabrication is possible. The obtained data for phase transition pressures and X-ray diffraction patterns can account for experimental observations.

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