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Hybrid sp$^2$+sp$^3$ carbon phases created from carbon nanotubes

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Abstract. Using the density functional theory in the gradient approximation (DFT–GGA) methods was calculated the geometrically optimized structure and electronic properties for six new hybrid carbon phases. These hybrid phases consists of atoms in three - and four-coordinated (sp$^2$+sp$^3$-hybridized) states. The initial structure of the carbon phases was constructed by partial cross-linking of (8,0) carbon nanotube bundles. Sublimation energies calculated for hybrid phases above the sublimation energy of cubic diamond, however, fall into the range of values typical for carbon materials, which are stable under normal conditions. The density of electronic states at the Fermi energy for the two phases is non-zero and these phases should have metallic properties. The other hybrid phases should be semiconductors with a band gap from 0.5 to 1.1 eV.

1. Introduction
Hybrid carbon phases are crystalline compounds consisting of atoms in states with different coordination and with the hybridization of the electronic orbitals [1,2]. Hybrid carbon phases can be assigned to one of four classes – sp+sp$^2$ sp+sp$^3$ sp$^2$+sp$^3$ and sp+sp$^2$+sp$^3$ [1,2]. Graphite-diamond carbon phases consist of atoms in three- and four-coordinated (sp$^2$+sp$^3$-hybridized) atoms and have a solid three-dimensional structure. Such compounds are very interesting because of their properties that can be changed by varying the ratio of carbon atoms in the states with different hybridization. A variety of hybrid carbon materials with sp$^2$+sp$^3$-hybridized atoms have been synthesized experimentally, when exposed to fullerene condensates high pressures [3,4]. The possibility of even more variety of graphite-diamond carbon phases and nanostructures have been established theoretically [5-7]. Model build the structure of various compounds of this type are possible from the structures of the precursor (graphene layers, carbon nanotubes (CNT), or fullerene-like clusters) as a result of partial “cross-linking” or “combining” [1,2,8]. However, some of the constructed models of the hybrid phases are unstable – for example, all hybrid sp$^2$+sp$^3$ phases from graphene layers are unstable. In this study, we investigated the structure and properties of a range of hybrid phases based on carbon nanotubes bundles.

2. Methods
The initial structures of the hybrid phases were built as a result of a partial "cross-linking" or "combining" bundles of single-layer zig-zag (8,0) carbon nanotubes (Figure 1a). From built phases were selected only phases, in which the atoms with sp$^2$ and sp$^3$ hybridizations were in crystallographically equivalent positions. Nanotubes in bundles were in four-coordinated states (each nanotube have four neighbors). When "cross-linking" or "combining" between the carbon atoms of neighboring nanotubes are formed bonds (Figure 1b). The atoms forming additional covalent bonds with atoms of the neighboring nanotubes, passed from three-coordinated states in four-coordinated states (from sp$^2$ hybridized to sp$^3$-hybridized states). As a result of this process the initial structure of
the hybrid sp\(^2\)+sp\(^3\) phases were formed (Figure 1b). These structures were geometrically optimized by methods of the density functional theory in the gradient approximation [9] (Figure 1c). The calculations used a set of k-points: 12×12×12. To limit the dimensionality of a set of basis functions, the value of E\(_{\text{cutoff}}\) was set at 950 eV. Structural parameters characterizing the hybrid phases were L\(_i\) interatomic bonds and angles between them \(\phi\(_{ij}\)\) (Figure 2).

**Figure 1.** Bundle of carbon nanotubes (a), partially cross-linked carbon nanotubes (b), and phase structure after geometrical optimization (c).

**Figure 2.** Geometrically optimized structure of the unit cells and the crystal lattice of sp\(^2\)+sp\(^3\) carbon phases, obtained by cross-linking and combining nanotubes (8,0) bundles: (a) \(T\(8\,8\,0\)A\(_{4a}\)\), (b) \(T\(8\,8\,0\)B\(_{4a}\)\); (c) \(T\(8\,8\,0\)A\(_{4b}\)\); (d) \(T\(8\,8\,0\)B\(_{4b}\)\); (e) \(T\(8\,8\,0\)A\(_{4c}\)\); (f) \(T\(8\,8\,0\)A\(_{4d}\)\).

### 3. Results and Discussion

From different variants of cross-linking and combining of single-walled nanotubes (8,0) bundles were constructed six hybrid sp\(^2\)+sp\(^3\) phases with various structures. Four phases (\(T\(8\,8\,0\)A\(_{4a}\), \(T\(8\,8\,0\)A\(_{4b}\), \(T\(8\,8\,0\)A\(_{4c}\), \(T\(8\,8\,0\)A\(_{4d}\)) were obtained as a result of "cross-linking" nanotube bundles, and two phases (\(T\(8\,8\,0\)B\(_{4a}\), \(T\(8\,8\,0\)B\(_{4b}\)) as a result of "combining". Image of crystal structure phases and their unit cells after geometrical optimization are shown in Figure 3. All six phases constructed after the geometrical optimization were sp\(^2\)+sp\(^3\)-hybridized and their structure were not transformed into the
structure of the compounds consisting of only sp$^3$ or only sp$^2$ atoms, just as observed previously for hybrid phases based on the graphene layers [7].

The estimated values of the lengths of interatomic bonds and angles between them are given in Table 1. Lengths of bonds vary in the range from 1.387 to 1.622 Å (see Table 1). Different lengths of the covalent bonds due to the fact that they are formed of different number of electron pairs. The maximum length of the bonds formed by one pair of electrons. These are bonds with lengths L$_1$, L$_2$, L$_3$ between – four-coordinated (sp$^3$-hybridized) atoms. The minimum length of bonds L$_5$, L$_6$ is observed between three-coordinated (sp$^2$-hybridized) atoms. The length of the bond L$_4$ between three-coordinated and four-coordinated atoms has an intermediate length. The short lengths of the bonds, seems to indicate that the order of bond is in the range from 1.2 to 1.5. The lengths of the bonds in the hybrid phases differ from the values characteristic of graphite and diamond. The degree of these deviations is characterized by the strength parameters Str$_1$ and Str$_2$, which are calculated as the sum of modules of the difference of bond lengths in the hybrid phase, and in the ideal structures of the diamond (1) graphite (2) (Table 2). The highest values for the strength is for the phase of T$^{(8,0)}$b$_{A4b}$ (Str$_1$ = 0.335, Str$_2$ = 0.234).

| Table 1. Values of the lengths of interatomic bonds and angles between them for sp$^2$+sp$^3$ carbon phases, obtained by cross-linking and combining bundles of single-layer CNT (8,0). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| T$^{(8,0)}$a$_{A4a}$ | T$^{(8,0)}$b$_{A4a}$ | T$^{(8,0)}$a$_{A4b}$ | T$^{(8,0)}$b$_{A4b}$ | T$^{(8,0)}$a$_{A4c}$ | T$^{(8,0)}$a$_{A4d}$ |
| L$_2$ (Å) | 1.563 | 1.535 | 1.557 | 1.621 | 1.599 | 1.481 |
| L$_3$ (Å) | 1.598 | 1.603 | 1.539 | 1.562 | 1.569 | 1.621 |
| L$_4$ (Å) | 1.581 | 1.574 | 1.606 | 1.622 | 1.618 | 1.563 |
| L$_5$ (Å) | 1.552 | 1.536 | 1.532 | 1.482 | 1.504 | 1.621 |
| L$_6$ (Å) | 1.387 | 1.404 | 1.402 | 1.424 | 1.446 | 1.563 |
| φ$_{12}$ (°) | 115.91 | 107.52 | 112.70 | 110.36 | 112.73 | 116.38 |
| φ$_{13}$ (°) | 111.83 | 114.89 | 89.51 | 83.01 | 90.03 | 115.96 |
| φ$_{14}$ (°) | 104.69 | 100.73 | 115.83 | 116.39 | 116.24 | 116.35 |
| φ$_{23}$ (°) | 109.91 | 110.49 | 129.11 | 110.38 | 90.09 | 110.33 |
| φ$_{24}$ (°) | 99.76 | 107.54 | 102.83 | 115.97 | 117.82 | 83.09 |
| φ$_{34}$ (°) | 114.20 | 114.94 | 107.38 | 112.29 | 124.77 | 110.31 |
| φ$_{45}$ (°) | 121.64 | 114.91 | 115.97 | 123.06 | 119.57 | 110.33 |
| φ$_{46}$ (°) | 114.20 | 122.26 | 119.62 | 115.97 | 117.77 | 116.36 |
| φ$_{56}$ (°) | 120.54 | 121.37 | 121.32 | 120.97 | 122.63 | 115.96 |

The angles between the bonds in the hybrid phases have values that differ from the typical values for ideal structures of diamond and graphite. So, four-coordinated atoms, the angles between bonds vary in the range from 83.01° to 129.11°, which differs significantly from the angle of 109.47°, which is characteristic for diamond. The angles between bonds for three-coordinated atoms change from 110.33° to 123.06°, which is also different from the angle of 120°, typical for graphite. Such deviations of the angles of atomic bonds indicate the presence of significant stresses in the structure of the hybrid phase. Quantitative characteristics of these stresses are deformation parameters Def$_1$ and Def$_2$, which is calculated as the sum of modules of differences of the angles in a hybrid phase in the ideal structures of the diamond (1) graphite (2) (Table 2). In the most stressed condition of sp$^3$ atoms in the phase T$^{(8,0)}$a$_{A4c}$ (Def$_1$ = 72.50°) and sp$^2$ atoms in phase T$^{(8,0)}$a$_{A4d}$ (Def$_2$ = 17.35°). However, the values of deformation parameters for the other phases are of the same order as for the most stressed. The density of the hybrid phases is less than the density of cubic diamond. Two phases have a density of ~ 2.7 g/cm$^3$, and the density of the other phases is less than the density of graphite (Table 2).

The unit cell of the hybrid phases containing from 16 to 32 atoms. The number of atoms in sp$^2$-hybridized state to the number of atoms in the sp$^3$-hybridized state for the five phases ratio of 1:1. In
the phase of $T_{(8,0)A_{4a}}$ number of sp$^2$-hybridized atoms is twice the number of sp$^3$-hybridized atoms. The ring parameters of atoms in four-coordinated conditions in the different hybrid phases differ significantly (Table 2). In addition to hexagonal rings, there are also four-, eight- and twelve-coordinated rings, which, apparently, are the reason for the presence of stresses in the structure phases.

Table 2. Structural parameters, unit cell parameters and values for the complete and total energy ($E_{tot}$), differential energy ($\Delta E_{tot}$), sublimation energy ($E_{sub}$), density ($\rho$) and band gap ($\Delta E_{g}$) of carbon sp$^2$+sp$^3$ phases obtained by cross-linking and combining the bundles of single layer (8,0) CNT (for comparison, G – graphite, D – diamond).

| Phase | $T_{(8,0)A_{4a}}$ | $T_{(8,0)A_{4b}}$ | $T_{(8,0)A_{4c}}$ | $T_{(8,0)A_{4d}}$ | $T_{(8,0)A_{4d}}$ | $T_{(8,0)A_{4d}}$ | $T_{(8,0)A_{4d}}$ | $T_{(8,0)A_{4d}}$ | $T_{(8,0)A_{4d}}$ |
|-------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| a (Å) | 7.451            | 9.958            | 7.686            | 6.399            | 8.950            | 6.399            | 2.487            | 3.596            |                  |
| b (Å) | 7.451            | 4.271            | 4.293            | 4.253            | 4.380            | 4.253            | 2.487            | 3.596            |                  |
| c (Å) | 4.229            | 7.361            | 7.816            | 6.399            | 12.114           | 6.399            | 7.333            | 3.596            |                  |
| α (°) | 90               | 73.14            | 106.04           | 90.05            | 70.60            | 90               | 90               |                  |                  |
| β (°) | 90               | 47.32            | 93.39            | 96.36            | 46.19            | 83.72            | 90               | 90               |                  |
| γ (°) | 90               | 90               | 73.30            | 70.59            | 104.36           | 70.59            | 120              | 90               |                  |
| N (at) | 32               | 24               | 32               | 16               | 32               | 16               | 4                | 2                |                  |
| Rng1  | 6^481            | 6^121            | 4^683            | 4^65             | 4^6^5            | 4^6^5            | -                | 6^6              |                  |
| Str1  | 0.276            | 0.287            | 0.276            | 0.335            | 0.273            | 0.159            | 0                | -                |                  |
| Str2  | 0.114            | 0.106            | 0.092            | 0.234            | 0.193            | 0.235            | -                | 0                |                  |
| Def1  | 28.47            | 24.53            | 57.92            | 48.50            | 72.50            | 48.36            | -                | 0                |                  |
| Def2  | 7.970            | 8.720            | 5.730            | 8.060            | 5.290            | 17.35            | 0                | -                |                  |
| sp$^2$sp$^3$ | 1:1              | 2:1              | 1:1              | 1:1              | 1:1              | 1:1              | ∞                | 0                |                  |
| $E_{tot}$ (eV) | -5021.2          | -3768.1          | -5018.2          | -2511.9          | -5021.7          | -2511.9          | -629.35          | -314.55          |                  |
| $E_{tot}$ (eV/at) | -156.91          | -157.01          | -156.82          | -156.99          | -156.93          | -156.99          | -157.34          | -157.28          |                  |
| $\Delta E_{tot}$ (eV) | 0.43             | 0.33             | 0.52             | 0.35             | 0.196            | 0.35             | 0                | 0.06             |                  |
| $E_{sub}$ (eV/at) | 7.35             | 7.45             | 7.26             | 7.43             | 7.37             | 7.43             | 7.78             | 7.72             |                  |
| $\Delta E_{g}$ (eV) | 0.5              | 0               | 0.196            | 0.126            | 0.126            | 0.418            | 0                | 5.6              |                  |
| $\rho$ (g/cm$^3$) | 2.718            | 1.529            | 2.774            | 1.832            | 1.982            | 2.059            | 2.2              | 3.5              |                  |

Total energy $E_{tot}$ (per atom) for all phases is less than for graphite and diamond (Table 2). The difference of total energy of the hybrid phases relative to the energy of graphite $\Delta E_{tot}$ is changed from 0.33 to 0.52 eV/at. Sublimation energies for hybrid phases lies in the range of 7.26 to 7.45 eV/at. Most sublimation energy is observed for the phase of $T_{(8,0)A_{4a}}$ ($E_{sub}$ = 7.45 eV/at). Apparently, this phase should be the most stable. However, the sublimation energy of all investigated hybrid phases are in the range of values typical for carbon materials, available stable under normal conditions, and all these phases can be synthesized.

The results of calculations of the density of electronic states of the hybrid phases is shown in Figure 4. For the two phases, $T_{(8,0)A_{4a}}$ and $T_{(8,0)A_{4b}}$ the density of electronic states at the Fermi level is nonzero, the bandgap is zero and the phase should have metallic properties. For the remaining four phases of the bandgap ranges from 0.126 to 0.5 eV. These structures must be narrow-gap semiconductors.

4. Conclusions

Thus, the calculations of the structure and properties of six new hybrid sp$^2$+sp$^3$ carbon phases based on bundles of carbon nanotubes (8,0). These phases can stably exist under normal conditions. It is possible to synthesize them as a result of polymerization of carbon nanotubes or molecular compounds having the carbon structure of the frame close to the structure of fragment phases. The conductive
properties of the hybrid phases can be metal or semiconductor, so these phases may find applications as materials for electronic equipment.

Figure 3. Bandstructures of sp²+sp³ carbon phases, obtained by merging and combining bundles of single-layer CNT (8,0): (a) T_{(8,0)aA4d}; (b) T_{(8,0)bA4d}; (c) T_{(8,0)aA4b}; (d) T_{(8,0)bA4b}; (e) T_{(8,0)aA4c}; (f) T_{(8,0)bA4d}.

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References
[1] Belenkov E A, Greshnyakov V A 2013 Phys. Solid State 55(8) 1754
[2] Belenkov E A, Greshnyakov V A 2013 Carb. Mat. 28(4) 273
[3] Nunez-Regueiro M, Monceau P, Russat A, Bernier P, Zahab A 1991 Nature 354 289
[4] Brazhkin V V, Lyapin A G 1995 JETP Let. 42 350
[5] Bucknum M J, Hoffmann R 1994 J. Am. Chem. Soc. 116 (25) 11456
[6] Kuc A, Seifert G 2006 Phys. Rev. B. 74 214104
[7] Belenkov E A, Ivanovskii A L, Ul’yanov S. N, Shabiev F K 2005 J. Str. Chem. 46(6) 961
[8] Belenkov E A, Tingaev M I 2015 Let. on mat. 5(1) 15
[9] Koch W A, Holthausen M C 2001 Chemist’s Guide to Density Functional Theory. 2nd edition (Weinheim: Wiley-VCH Verlag GmbH) 293 p