Design and computer modeling of the supracrystals

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Abstract. The possibility of solid state crystalline structures, which we called supracrystals, is shown. Unlike ordinary crystals, there are no separate atoms or ions in the nodes of crystalline lattice. They are replaced by symmetric atomic associates. Symmetry classes of 2D- and 3D-supracrystals are determined. The bond length, energy per one atom, bond energy, and gap energy of 2D- and 3D-supracrystals consist of C, Si, B, N, S are calculated by the program ABINIT-5.8.4 in Hartree–Fock approximation. Unusual properties of supracrystals are of interest for their production and practical use.

Energy stability and electrical properties of the nanotubes produced from 2D-supracrystals suggested by the authors before are researched by computers modeling technic. Supracrystalline nanotubes from the atoms of carbon, silicon, boron and nitrogen, sulphur are considered. It is shown that the electrical properties of supracrystals nanotubes may be controlled in large range (from metallic to dielectric) changing their chemical composition, structure, diameter and chirality.

1. Introduction

The idea on the possibility of supracrystals existing has been advanced by us in paper [1]. In nodes of ordinary crystals the atoms or ions are located, in supracrystals they are replaced by symmetrically organized atomic associates. For all this one can always to pick out a supracell and to construct the whole crystalline lattice by its translation along epy ribs. There are two-dimensional (2D) and three-dimensional (3D) supracrystals. 2D-supracrystals represent the generalization of two-dimensional square or sixangular, in particular graphenic, nets. 3D-supracrystals may be taken into consideration as the generalization of cubic crystals. The impotent peculiarity of supracrystals is their periodicity both in large cells (supracells) and in small cells (cells of enclosing) as the nodes elements. It permits to combine the different, at times, mutually exceptive properties in one and the same crystal, for example, high conductivity and small heat conduction. Moreover, unlike the ordinary crystals, supracrystals are more porous and less dense materials. In supracells of “host’s” crystalline lattices “quest” atoms or ions may be located, what approaches such supracrystals to clathrates [2]. However the atoms (ions) in supracrystals
are banded by valent chemical bonds, but not hydrogen, electrostatic or coordination bonds as in the clathrates. Therefore, supracrystals are more thermally stable than clathrates. In this paper, we for first time attempted theoretically to calculate the main physical properties of supracrystals: cell parameters, band energy, gap energy et al. All calculations have been provided in Hartree-Fock approximation by the program ABINIT-5.8.4. [3]. For the k-points generation in Brillouin band Monchorst-Packs algorithm [4] has been used. The Broiden iteration procedure has been used as a mathematical approach. The cut energy has been automatically taken for k=6.

2. 2D-supracrystals

Two-dimensional mosaics formed only regular geometric figures (so called Kepler’s nets) are well-known [5]. There are 11 varieties of such nets (see figure1) but only 5 of them may be realized in supracrystals structure. This conclusion follows from the necessity to secure the building of a whole two-dimensional crystalline lattice by the supracell’s translation along two basic directions on a plane. Besides that, all bonds between the atoms must be equivalent.

![Kepler’s nets](image)

Figure 1. Kepler’s nets [5]. Integers at the bottom at the figure (Schlafli symbols) denotes the number and the type of regular polygons meeting in each net’s node. The powers index shows a number of identical polygons meeting in the one point and contacting with each other by their ribs.
Figure 2. shows the permissible types of supracrystalline cells forming 2D-supracrystals. Because all the bonds are equivalent, they must be formed by either identical atoms or atoms of two different kinds. In second case, homogeneous bonds as energetically less profitable, hence heterogeneous ones [6] must be absent. It means that supracrystals which consist of the different atoms don’t include triangular cells of enclosing. Here we also suggested a new, more convenient for the supracrystals description, notations. Letters X or Y in parentheses determine the symbol of chemical element. Indexes behind the parentheses are located in following order: the first index (4 or 6) determines the type of supracell, the next indexes describe the cell’s of enclosing type. At first the number of sides of node’s cell are shown, then the same are shown for surrounding cells (if there are).

![Supracells of 2D-supracrystals and their notations.](image)

The possibility of carbon planar and nanotubular structures consist of five- and sevenangles, or five-, six-, and sevenangles, was theoretically demonstrated in Ref. [7]. These structures have been called
“Haekelites”. Later this name were spread to other two-dimensional structures containing non-hexagonal elements, including non-carbon ones [8,9]. Note, that 2D-supracrystals with supracell of (XY)$_{44}$ type are one of the forms of haekelitic planar structures studied in Ref. [8,9]. This structure consists of alternative atoms of boron and nitrogen forming squares and regular eightangles. At the same time, 2D-supracrystals and haekelitic structures are not equivalent each other, thought either can be rolled up to nanotubes. Firstly, not all haekelitic structures are 2D-supracrystals. Secondly, the particular properties of supracrystals best of all are observed on the level of 3D-supracrystals. In Figure 1 you can see that all 2D-supracrystals belong to tetragonal and hexagonal singonies, moreover (XY)$_{44}$ – to class $4,(X)_{44}$ – to class 4mm, (XY)$_{664}$ – to class 6, and the others – to class 6mm.

3. 3D-supracrystals

3D-supracrystals are the cubic lattices, in which nodes symmetric atomic associates forming regular or semi regular polyhedral (Platonic and Archimedean bodies accordingly [10]) are located. Supracell of 3D-supracrystals always are cubic, and permissible types of their node’s elements are given in figure 3.

![Figure 3](image_url)

**Figure 3.** Supracell of 3D-supracrystals (above left), and permissible types of node’s elements. Cubes of the binding atoms oriented to the observer for non-octahedric node’s elements are not shown.

Here we used the same notations as for 2D-supracrystals. Letters X and Y denote the symbols of chemical elements. The first index “C” behind parenthes meters determines the type of supracell (cubic). The next indexes denote regular or semi-regular polyhedron forming node’s element: O – octahedron, TO –
truncated octahedron, CO – cuboctahedron, RCO – rhombicubooctahedron. As for 2D-supracrystals, the
node’s elements consist of two different atoms are also possible here, if there are no triangles. Note, that
2D-supracrystals may be obtained by the crystallization of 4-, 5-, or 6- valent atoms, but it is necessary to
use 3- or 4- valent atoms for 2D-supracrystals construction. All 3D-supracrystals belong to the cubic
singony, moreover, (XY)$_{CTO}$ – to class 432, and others – to class m3m.

4. Physical properties of 2D-supracrystals

In table 1 the results of supracell’s parameters optimization, total energy per one atom calculations, and
bond energy for 2D-supracrystals are represented. The possibility of boron, nitrogen, carbon, and sulfur
showing among the others valency equal 3 and 4 for 2D-supracrystals construction are studies.

| Structure | $l$, Å  | $E$, eV/atom | $E_{\text{bs}}$, eV |
|-----------|--------|--------------|------------------|
| (C)$_{44}$ | 1,43   | - 12,9       | - 4,9            |
| (Si)$_{44}$ | 1,82   | - 6,3        | - 1,7            |
| (S)$_{44}$ | 1,51   | - 15,6       | - 3,4            |
| (BN)$_{44}$ | 1,38   | - 10,2       | - 2,3            |
| (C)$_{63(6)}$ | 1,86   | - 14,2       | - 2,9            |
| (Si)$_{63(6)}$ | 2,07   | - 7,3        | - 2,2            |
| (S)$_{63(6)}$ | 1,11   | - 17,2       | - 5,0            |
| (C)$_{63(12)}$ | 1,62   | - 12,3       | - 4,3            |
| (Si)$_{63(12)}$ | 2,18   | - 9,3        | - 3,7            |
| (S)$_{63(12)}$ | 1,08   | - 17,8       | - 5,6            |
| (C)$_{664}$ | 1,56   | - 11,3       | - 1,2            |
| (Si)$_{664}$ | 2,27   | - 8,7        | - 3,5            |
| (S)$_{664}$ | 1,14   | - 14,4       | - 5,2            |
| (BN)$_{664}$ | 1,44   | - 9,1        | - 2,3            |
| (C)$_{634}$ | 2,17   | - 13,3       | - 2,6            |
| (Si)$_{634}$ | 2,03   | - 9,8        | - 4,2            |
| (S)$_{634}$ | 1,01   | - 16,6       | - 4,1            |

For comparison we’ll give the values of energy per one atom for graphenic nets calculated by the same
method made from: carbon’s atoms – -15,3eV/atom, silicon’s atoms – -8,7eV/atom, boron’s and
nitrogen’s atoms – -11,2eV/atom. Hence, all types of considered 2D-supracrystals are stable, but
energetically less profitable with comparison of corresponding graphenic layers. The comparison between
different 2D-supracrystalls shows that more stable are the crystals consist of sulfur’s atoms and less stable
are silicon structures. As a rule, more stable are (X)$_{63(12)}$ and (X)$_{63(6)}$ 2D-supracrystals containing
triangular cells of enclosing. It may be explained by their greater stability to deformations. The rules of
crystallographic directions choice (in terms of Miller’s indexes) in supracell are shown in figure 4. The results of gap energy calculations for the same 2D-supracrystals as in table 1 are represented in table 2.

![Figure 4](image)

**Figure 4.** The rules of crystallographic directions choice in 2D-supracrystals with square and sixangular supracells. The direction [10] and [01] are equivalent and can be denoted as <10>. By analogy the directions [211], [121], and [112] can be denoted by a common symbol <211>, and [011], [101], [110] as <011>. Symbols X and Y denote the axes of crystallophysical coordinates.

**Table 2.** Calculated values of gap energy ($E_g$) for basic directions in 2D-supracrystals.

| Structure | $E_g^{<10>}$, eV | $E_g^{<11>}$, eV | $E_g^{<211>}$, eV | $E_g^{<011>}$, eV |
|-----------|-----------------|-----------------|-----------------|-----------------|
| (C)$_{44}$ | 0.66            | 0.09            |                 |                 |
| (Si)$_{44}$ | 0.8             | 1.3             |                 |                 |
| (S)$_{44}$  | 2.1             | 2.7             |                 |                 |
| (BN)$_{44}$ | 0.7             | 1.2             |                 |                 |
| (C)$_{63(6)}$ | 1.37           | 1.45            |                 |                 |
| (Si)$_{63(6)}$ | 1.5             | 1.9             |                 |                 |
| (S)$_{63(6)}$ | 2.2             | 3.3             |                 |                 |
| (C)$_{63(12)}$ | 0.69          | 0.91            |                 |                 |
| (Si)$_{63(12)}$ | 1.0             | 1.3             |                 |                 |
| (S)$_{63(12)}$ | 2.4             | 3.6             |                 |                 |
| (C)$_{66(4)}$ | 1.72           | 2.21            |                 |                 |
| (Si)$_{66(4)}$ | 2.2             | 2.4             |                 |                 |
| (S)$_{66(4)}$ | 6.1             | 8.2             |                 |                 |
| (BN)$_{66(4)}$ | 2.0             | 2.5             |                 |                 |
| (C)$_{63}$  | 1.12            | 1.41            |                 |                 |
| (Si)$_{63}$  | 1.3             | 1.6             |                 |                 |
| (S)$_{63}$   | 2.9             | 3.7             |                 |                 |

In table 2 you can see that with respect to electric current all considered structures, except dielectrical ones (X)$_{66(4)}$ and (XY)$_{66(4)}$, show semiconductors properties. Only sulfur already forms dielectric 2D-supracrystals.
5. Physical properties of 3D-supracrystals

In table 2 the results of supracell’s parameters, energy per one atom, and bond energy for 3D-supracrystals calculations are represented. The calculations have been carried out for the carbon’s atoms possessing the valency equal 4, sulfur’s atoms forming, among others, 4-, 5-, and 6-valent bonds, and 5-valent phosphorous.

| Structure | $l$, Å | $E$, eV/atom | $E_b$, eV |
|-----------|-------|--------------|----------|
| (S)CO     | 2,1   | - 7,2        | - 6,6    |
| (P)CO     | 2,7   | - 5,8        | - 5,2    |
| (C)CTO    | 1,3   | - 5,8        | - 4,2    |
| (S)CTO    | 1,7   | - 6,3        | - 5,4    |
| (S)CCO    | 0,9   | - 5,8        | - 4,9    |
| (Si)CRCO  | 1,5   | - 6,1        | - 5,2    |
| (P)CRCO   | 2,7   | - 4,6        | - 4,2    |

Compare the results given in table 1 and table 3 we can see that energy per one atom in 3D-supracrystals are essentially higher then in 2D-supracrystals, i.e. the potential pits where there atoms are located are less deep, and 3D-supracrystals are less stable then 2D-supracrystals.

However, the bond energy is commensurable with the bond energy for 3D-supracrystals made up from corresponding atoms. In figure 5 you can see the crystallographic directions for which in table 4 the calculated values of gap energy for the same 3D-supracrystals as in table 3 are represented.

![Figure 5](image.png)

**Figure 5.** The basic crystallographic directions in 3D-supracrystals. Axial directions [100], [010], [001] are equivalent and further are denoted as <100>. Diagonal directions of the type [110], [011], [101] also are equivalent and are denoted as <010>. The directions of a cube’s space diagonals of the type [111] are denoted by symbol <111>. 
According to the results given in table 4 for the considered 3D-supracrystals only carbon and, by a some stretch, phosphorous can demonstrate semiconductors properties in the structures \((\text{C})_{\text{CTO}}, (\text{P})_{\text{CRCO}},\) and even in the case of axial directions of electric current propagation. In all other cases the considered above 3D-supracrystals are dielectrics.

### 6. Supracrystals nanotubes

The nanoribbons are defined as two-dimensional nanostructures in the form of flat strips of 10–100 nm width and of 100 μm and more length.

![Figure 6. Types of nanoribbons (X)_{44}](image1)

![Figure 7. Types of nanoribbons (X)_{64}](image2)
The asymmetrical nanoribbons may be rolled up to the nanotubes. If one roll up the nanoribbon around the axis not coinciding with the ribbon’s axis, the nanotubes will appear with chirality angel differ from $0^\circ$ and $45^\circ$ (in the case of square supracells). Except of represented on these figures nanoribbons one can cut nanoribbons with more complicated boundaries.

**Figure 7.** Geometric parameters of supracrystalline nanotubes
| structure | Type of atoms | $|E_{HT}-E_{2D}|$ eV/at | Number of supercell on diametr | $E_{\text{gap}}$ eV |
|-----------|--------------|-----------------|------------------------------|-----------------|
| 1         |              | 2               | 3                            | 4               | 5               |
| (X)$_{44}$ | Si           | 0.068           | (6)                          | 0               | 0               |
| (n,0)     |              | 0.059           | (8)                          | 0.11            |                 |
|           |              | 0.051           | (9)                          | 0.29            |                 |
|           |              | 0.031           | (11)                         | 0.59            |                 |
|           |              | 0.076           | (6)                          |                 | 0               |
|           |              | 0.065           | (8)                          |                 | 0               |
| C         |              | 0.062           | (9)                          | 0.27            |                 |
|           |              | 0.041           | (11)                         | 0.36            |                 |
|           |              | 0.063           | (6)                          | 0.11            |                 |
|           |              | 0.051           | (8)                          | 0.31            |                 |
| B-N       |              | 0.045           | (9)                          | 0.42            |                 |
|           |              | 0.028           | (11)                         | 0.63            |                 |
|           |              | 0.045           | (6)                          | 1.51            |                 |
|           |              | 0.037           | (8)                          | 1.79            |                 |
| S         |              | 0.032           | (9)                          | 2.02            |                 |
|           |              | 0.011           | (11)                         | 2.16            |                 |
| (X)$_{44}$ | Si           | 0.101           | (6)                          | 0               |                 |
| (n,n)     |              | 0.091           | (8)                          | 0.49            |                 |
|           |              | 0.089           | (9)                          | 0.62            |                 |
|           |              | 0.073           | (11)                         | 0.85            |                 |
|           |              | 0.112           | (6)                          |                 | 0               |
|           |              | 0.098           | (8)                          | 0               |                 |
| C         |              | 0.086           | (9)                          | 0               |                 |
|           |              | 0.077           | (11)                         | 0.06            |                 |
|           |              | 0.097           | (6)                          | 0.50            |                 |
| B-N       |              | 0.087           | (8)                          | 0.70            |                 |
|           |              | 0.076           | (9)                          | 0.82            |                 |
|           |              | 0.069           | (11)                         | 0.97            |                 |
Table 5. Continues

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| (X)_{44} | 0.067 | 0.056 | 0.047 | 0.032 |
| (n.n) | (6) | (8) | (9) | (11) |
| S | 2.10 | 2.50 | 2.60 | 2.70 |
| (X)_{63(12)} | 0.043 | 0.032 | 0.027 | 0.021 |
| Si | 0.27 | 0.27 | 0.38 | 0.59 |
| (n,0) | (6) | (8) | (9) | (11) |
| (n,n) | 0.12 | 0.12 | 0.75 | 1.15 |
| C | 0.27 | 0.27 | 0.38 | 0.59 |
| (n,0) | (6) | (8) | (9) | (11) |
| (n,n) | 0.11 | 0.19 | 0.44 | 0.67 |
| S | 0.67 | 0.83 | 1.17 | 1.33 |
| (n,0) | (6) | (8) | (9) | (11) |
| (X)_{63(6)} | 0.028 | 0.026 | 0.026 | 0.015 |
| Si | 1.12 | 1.18 | 1.60 | 1.76 |
| (n,0) | (6) | (8) | (9) | (11) |
| (n,n) | 1.5 | 1.9 | 1.9 | 1.9 |
|   | 1   | 2          | 3          | 4          | 5          |
|---|-----|------------|------------|------------|------------|
|   |     | X_{63(6)} | C          | (n,0)      | (n,n)      |
|   |     | 0.035     | 0.031      | 0.030      | 0.020      | 0.50       |
|   |     | (6)       | (8)        | (9)        | (11)       | {1,37}     |
|   |     | 0.034     | 0.024      | 0.021      | 0.018      | 0.97       |
|   |     | (6)       | (8)        | (9)        | (11)       | 1.90       |
|   |     | C          | (n,0)      | (n,n)      |            |            |
|   |     | 0.062     | 0.047      | 0.034      | 0.032      | 0.08       |
|   |     | (6)       | (8)        | (9)        | (11)       | {1,72}     |
|   |     | 0.061     | 0.044      | 0.034      | 0.031      | 0.20       |
|   |     | (6)       | (8)        | (9)        | (11)       | {2.21}     |
|   |     | 0.044     | 0.037      | 0.025      | 0.021      | 0.45       |
|   |     | (6)       | (8)        | (9)        | (11)       | 2.05       |
|   |     | Si         | (n,0)      | (n,n)      |            |            |
|   |     | 0.050     | 0.032      | 0.025      | 0.025      | 1.25       |
|   |     | (6)       | (8)        | (11)       |            | 1.90       |
|   |     | 0.050     | 0.037      | 0.027      | 0.024      | 1.70       |
|   |     | (6)       | (8)        | (9)        | (11)       | {2,2}      |

In figure parentheses gives $E_{\text{gap}}$ value for planar structure.

So,

The energy per one atom for 2D supracrystals is of the same order as for graphene and haekelites one. Hence, such crystals may exist at the room temperature.

The electric properties of 2D supracrystals depend of its chemical composition and symmetry type, and may vary from metallic up to dielectric.

2D supraercrystalline sheets can be cut into the nanoribbons and rolled up to the nanotubes. The less the diameter of nanotube the greater it energy stability and the less gap energy. Changing the composition,
structure, diameter and chirality one can obtain the nanotubes with necessary value of conductivity: from dielectric to metallic.

3D-supracrystals also may exist at the room temperature, vary their electric properties from semiconducting up to dielectric and have more loose structure than usual crystals.

7. Conclusions
First of all we’ll note that some of 2D-supracrystals suggested, in particular, (BN)$_{44}$ already were described before within the framework of haekelitic structures research. It’s thermal stability has been proved, what indirectly confirm the validity of our results. As for 3D-supracrystals, our investigation in this area seems to be pioneer one. Thermal stability, semiconductoral properties and friability, what is the reason of a high electronus velocity, first of all, carbonic and boron-nitrogen supracrystals, permits to hope that they will come in place of traditionally used silicon in the micro- and nanoelectronic devices. Supracrystalline nanotubes can found the application as for semiconductor devices as for dielectric, for example, from sulfur, covers of nanowires. Friable, with large cameras 3D-supracrystals may be used as containers for composite materials and hydrogen’s accumulators in fuel elements of hydrogen energetics.

Acknowledgments
We acknowledge the Russian Foundation for Basic Research for providing financial support (Project № 10-02_97002-r_povolzhye_a) and the authors of program ABINIT for useful consultations.

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