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Negatively curved cubic carbon crystals with octahedral symmetry

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ABSTRACT

After several ad hoc proposals of new 2-dimensional carbon structures, interest in their actual synthesis has begun to increase. One needs a clear orientation or criteria to describe those carbon structures in an appropriate way. In the present paper, we propose a systematic method for discovering new stable structures of carbon crystals with sp^2-bonding using advanced mathematical methods. There are two key ideas: geometric descriptions based on *curvatures*, *symmetries*, etc. and the *standard realization* of crystal lattices via harmonic theory to identify stable coordinates. We apply this new method to study negatively curved carbon crystals with octahedral symmetry after Mackay–Terrones [1], and identify several new structures. The stability and electronic states of the proposed structures are investigated using first principles calculations.

1. Introduction

Many types of 2-dimensional carbon structures have been proposed and even synthesized in the past several decades via ad hoc methodologies. Representative examples of such structures include Buckminster fullerene C_{60}, single-wall carbon nano tubes (SWNTs), and graphite-like sheets. From a mathematical viewpoint, these structures can be classified into three categories according to the Gauss curvature of their surfaces. The surfaces of structures in the first category have positive curvature, those in the second category have zero curvature, and those in the third have negative curvature. The first category includes fullerenes, whereas the second includes SWNTs and graphite-like sheets. A natural question follows: do negatively curved carbon structures exist?

In 1991, Mackay and Terrones [1] proposed a carbon crystal structure, now called the Mackay–Terrones Schwarzite crystal, or simply the Mackay crystal. Its atomic structure is a triply-periodic trivalent (sp^2-bonding) network, which consists of 6- and 8-membered rings. Moreover, all carbon atoms in the structure lie on the Schwarz minimal P-surface, which has a negative Gauss curvature. Lenosky et al. [2] also found

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a negatively curved carbon crystal with 6- and 7-membered rings. These are examples of the third category of 2-dimensional carbon structures described above, because their surfaces have a negative curvature.

Because surfaces with negative curvatures are mathematically more stable under local deformation, it is promising for synthesis and thus of interest to study them in a systematic way and give them appropriate geometrical descriptions.

In the present paper, we propose a mathematical method for identifying stable carbon crystal structures, which are triply periodic, trivalent, negatively curved networks with octahedral symmetry after Mackay. Herein, we call them *Mackay–Terrones-like Schwarzites*, or *Mackay-like crystals* in short. The octahedral symmetry of the structure plays an important role. Since we require the structures to be triply periodic in order to span 3-dimensional space, the lattice of periodicity is cubic ([3, Theorem 3]) and the primitive cell (the fundamental domain of the periodicity) shapes the truncated octahedron. In the future, Mackay-like crystals may be used as junctions in more complicated 3-dimensional jungle-gym-like structures. Deza and Dutour [4] classified fullerene-like structures that are positively curved finite carbon structures with icosahedral symmetry.

Our method consists of three steps. First, we classify possible topological networks for Mackay-like crystals under certain reasonable assumptions using combinatorial arguments. Second, we determine their atomic coordinates in actual space. Here, we use the notion of the *standard realization*. The mathematical definition of a crystal lattice and its standard realization were introduced by Kotani and Sunada [5] to study stable atomic configurations of crystal structures in the sense of all atoms are in mechanically balancing positions. The standard realization turns out to be very useful in the systematic search for stable configurations of a given topological structure. In fact, Sunada [6] proposed a new sp^2-bonding crystal structure (K4 crystal) as a diamond twin using the standard realization. The stability and material properties of the K4 carbon crystal were investigated by Itoh et al. [7] and others [8,9].

Naito [10] established an algorithm to determine the coordinates of atoms in the standard realization of a crystal lattice. However, it is generally rather complicated to obtain actual coordinates for the standard realizations by applying the algorithm. Here, we are able to determine the coordinates with a geometric consideration by using the octahedral symmetries effectively.

Finally, we identify stable structures and determine the corresponding electronic structures using first principles calculations.

2. Results and discussion

2.1. Classification of networks

We look at the network in a primitive cell and extend it to the whole space as a triply periodic structure. The vertices and edges of the network represent positions at which carbon atoms and the covalent bonds between them can be placed, respectively. As explained in Fig. 1, we can find networks of Mackay-like crystals by determining networks in the hexagonal domains shown in Fig. 1b. Since the hexagonal domains have dihedral group D_3 symmetry, we should determine networks in the kite-like region (Fig. 1c). By reversing the above process, it is clear that the network of any Mackay-like crystals must have octahedral symmetry.

Now we look for a carbon 3-dimensional crystal by sp^2-bonding only. By topologically deforming the kite-like region onto a disk, we assume the following natural conditions on the networks in the disk: (1) Any inner vertex is of degree 3. (2) Any vertex on the boundary is joined with the two neighboring vertices on the boundary, or with an inner vertex and not with both neighboring vertices on the boundary. (3) A network is planar and connected, and there are at least four vertices on the boundary. (4) A network does not have a consecutive sequence of odd vertices on the boundary. (5) A network is triangle-free.

Mathematically, it is easy to see that there is no network with an odd number of vertices satisfying the above conditions (for additional mathematical details, see [3, Theorem 1]). Moreover, networks satisfying the above conditions have at least 6 vertices. Fig. 2 shows all of the possible 6- and 8-vertex networks satisfying the above conditions. For Mackay-like crystals with octahedral symmetry, the Euler polyhedron theorem implies that the primitive cell should contain at least one k-membered ring with $k \geqslant 7$. If a network consists of 6- and 8-membered rings only, the number of 8-membered rings should be 12, whereas a network consisting of 6- and 7-membered rings should have 24, 7-membered rings. Using these networks, as we stated above, we can obtain networks in the primitive cell, as shown in Fig. 1a.

Now we move to the second step, identifying the spatial coordinates of the topological structures we classified above. Stable configuration of atoms in a crystal lattice should be the standard realization of the crystal lattice. The standard realization is the equilibrium configuration of all perturbations with respect to atoms and lattices, and satisfies the discrete Poisson equations of the network with periodic boundary conditions. It is a complex process to obtain the coordinates of the standard realization of a given crystal lattice. Here, we succeeded by making use of geometric observations in an essential way, as explained in the supplementary mathematical discussion [3].

2.2. Geometrical stability

We investigated the stability of the structures classified above by calculating the phonon spectrum. We used the numbering scheme shown in Fig. 2. Our new proposed structures are `6-1-1-p`, `6-1-2-p`, `6-1-3-p`, and `8-4-2-p` crystals (see Fig. 3). Phonon spectra calculations indicate that these four structures are mechanically stable (see Fig. 4).

The structure predicted by Mackay–Terrones [1] was among the structures we classified, and was designated `8-2-1-p`. Although the Mackay crystal was proposed in 1991, the present paper is the first presentation of its phonon spectrum that we are aware of. Lenosky et al. [2] found a carbon network consisting of only hexagons and heptagons on the Schwarz minimal P-surface, which we classified as `8-4-1-p`. Both the Mackay crystal and the Lenosky crystal are shown to be stable below.

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