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Coherent coexistence of nanodiamonds and carbon onions in icosahedral core-shell particles

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The general approach for describing and designing complex hierarchical icosahedral structures is discussed. Structural models of icosahedral carbon nanoparticles in which the local arrangement of atoms is virtually identical to that in diamond are derived. It is shown that icosahedral diamond-like particles can be transformed into onion-like shell structures (and *vice versa*) by the consecutive smoothing (puckering) of atomic networks without disturbance of their topological integrity. The possibility of coherent coexistence of icosahedral diamond-like core with onion shells is shown.

1. Introduction

Regular structures need not be obligatory crystalline (Mackay, 1975). The most striking example of such structures is the multilayer icosahedral packing (Mackay, 1962). It has a definite structure, which is not that of a crystal nor that of a molecule; it is not one of the space groups (or even point groups) listed in *International Tables for Crystallography* (2005); it is not a twin (although it could be described in terms of twinning). In the last decade, many new unusual structures have been reported. When encountering ordering of types unusual for classical crystallography, many authors express their surprise in such terms as 'magic', 'unprecedented', 'unique', 'puzzling', 'exotic', 'phantasmagorical' *etc*. Let us mention only a few examples: exotic close packings in small-sized clusters of colloidal microspheres (Manoharan *et al.*, 2003), new families of magic clusters (Rossi *et al.*, 2004), unexpected and geometrically unprecedented close-packed clusters (Tran *et al.*, 2004), exotic noncrystalline helices and spiral-structured wires (Gülseren *et al.*, 1998), exotic structures of tetrahedral semiconductors (Crain *et al.*, 1995), phantasmagorical fulleroids (Dress & Brinkmann, 1996; Delgado Friedrichs & Deza, 2000) *etc*.

We contend that the structures of nanoparticles are not obligatory the small relaxed cut-offs of crystalline structures. Their structures may have no relevance at all to space groups listed in *International Tables for Crystallography* (2005). We suppose that unusual structures of real nanoparticles have idealized prototypes in non-Euclidean spaces like an ideal infinite crystal serves as an idealization of a real crystal, with only one exception: their idealized 'parent' structures may not necessarily exist in the three-dimensional Euclidean space. There is nothing bad that the idealized structure as a whole cannot be embedded into Euclidean space. Its fragments inherit partially the non-Euclidean symmetry which becomes hidden. Highly symmetrical idealizations should be chosen either in symmetrical spaces of positive or negative curvature, or in projective spaces, or more generally, in a certain fibre space.

Structural inhomogeneity and coherent coexistence of fragments are characteristic of structures of nanosized particles. Spatially inhomogeneous structures, for which the local short-range order slightly differs from the short-range order of one of the stable or metastable structural modifications or one of the non-crystallographic packings, whereas different fragments are coherently joined into a whole, should exist in the nanoworld. Here we show that icosahedral carbon nanoparticles in which the local arrangement of atoms is virtually identical to that in diamond can be formed in the nanometre range. They can be transformed reversibly into onion-like shell structures without disturbance of their topological integrity. An icosahedral diamond-like core can coexist coherently with onion shells. The general principle that governs the formation of such structures takes as a basis the non-Euclidean geometry.

Although nanodiamonds have long been the subject of the close attention of researchers, the question as to their structure remains open. Diamond nanoparticles are not small-sized diamond crystals. For example, the detonation carbon particles consist most probably of a diamond-like core coated with shells having an onion-like structure with graphite inclusions (Aleksenskii *et al.*, 1999). Recently, the structural properties of nanodiamond particles synthesized by detonation and the products of their transformation into carbon onions *via* vacuum annealing have been studied by various experimental techniques (Mykhaylyk *et al.*, 2005). It has been shown that the detonation nanodiamond particles have a composite core-shell structure comprising an ordered diamond core of ~3 nm in size covered by a partially disordered outer shell of ~0.8 nm. The transformation of the nanodiamond into carbon onion proceeds from the amorphous outer shell of the particle inwards towards the diamond core. A reconstruction of C atoms located in the outer shell leads to bonding similar to those in nanocrystalline graphite. The observed structure was comparable with the structure of the bucky diamond clusters (Raty *et al.*, 2003; Raty & Galli, 2003). The *ab initio* calculations showed that at ~3 nm the reconstructed surfaces become more reasonable, thus providing an atomistic structural model based on the topology of a diamond core surrounded by a fullerene-like carbon network.

Fivefold symmetry in diamond has been observed experimentally by a number of researchers (Bühler & Prior, 2000; Son & Chung, 2004). The icosahedral morphology was interpreted as a result of multiple twinning of cubic crystals. It was noted that, among several forms of these multiple twins, there exist almost perfect icosahedra. The fivefold symmetry clearly manifests itself in the electron diffraction patterns. Some larger particles had semi-coherent boundaries but the small particles of several nanometres in size seemed to have fully coherent interfaces.

Recently, structural models of icosahedral diamond nanoparticles compatible with onion-like structures were developed (Shevchenko & Madison, 2006*a*,*b*; Shevchenko *et al.*, 2006). Different diamond-like structural fragments in such particles are coherently joined into a whole so that the local arrangement of atoms is universally tetrahedral (not only inside the fragments but also at their interfaces) and virtually no different from that in the diamond. The central part of particles is similar to that of compact carbon clusters with tetrahedral bonding and icosahedral symmetry (Zeger & Kaxiras, 1993). In order to explain the special features of icosahedral nanoparticles, we propose the general approach based on applying the cut-and-project procedure to certain parent structures originally devised in elliptical space.

2. Constructing icosahedral packings: general procedure and applications

Let us demonstrate how an icosahedral diamond-like nanoparticle can be constructed if it is treated as a nanostructure with coherent boundaries and is composed of insignificantly distorted fragments of diamond and lonsdaleite. The geometric principles used for assembling such structures are based on the local approach (Shevchenko *et al.*, 2004, 2005). Within this approach, nanoparticles with coherent boundaries in the general case are assembled from a limited set of building blocks determined by the fundamental manifolds and the principles of assembling are governed by the topological properties of a fibre bundle. The great diversity of 'unusual' structures can be obtained by mapping or projecting fragments of highly symmetrical structures from different non-Euclidean spaces into the three-dimensional Euclidean space or mapping these fragments onto curved manifolds embedded into the Euclidean space. In particular, the substructures of polytopes, *i.e.* regular tilings of the three-dimensional space with positive curvature, are of special interest. They may be considered as regular tilings of the three-dimensional Riemannian space or (being embedded into four-dimensional Euclidean space) as four-dimensional analogues of Plateau polyhedra or as abstract group manifolds with corresponding Coxeter groups (Coxeter, 1973).

An icosahedron can be assembled by joining 20 slightly distorted regular tetrahedra face to face. This simplest consideration leads to the classical concept of multiple twinning widely used when describing the diamond-like structures (Bühler & Prior, 2000; Shenderova *et al.*, 2003; Son & Chung, 2004). The Euclidean space may not be filled by ideal tetrahedra or icosahedra but there exists the closest packing of ideal tetrahedra in the curved space – namely the {3,3,5} polytope. Cutting various fragments from it and projecting them with slight distortions into the Euclidean space, one can obtain a lot of finite packings with almost icosahedral arrangement of atoms everywhere (*e.g.* Sadoc & Mosseri, 1982; Kléman, 1989; Lord & Ranganathan, 2001; Lord *et al.*, 2006). In the general case, each tetrahedron may suffer unique distortions during this procedure, so that the true icosahedral symmetry of the packing as a whole may be hidden or lost. The formation of an icosahedral packing is not at all an accidental cyclic twinning of nearly suitable building blocks. Only simplest icosahedral structures may be considered as cyclic multiple twins. We are sure as well that it is not enough for shells to have suitable sizes like Russian dolls to build up the regular multishell structures. In the general case, there exist rigorous assembling rules, which are strictly predefined by the true group-theoretical equivalence of corresponding blocks in the parent structure, which may be not realizable in the Euclidean space but does exist in a certain curved (or projective) space.

As a special case, an icosahedron built up of 20 tetrahedra may be obtained as a result of the cut-and-project procedure by choosing the packing origin in one of the vertices of polytope {3,3,5} and confining oneself to cutting no more than nearest neighbours. But the abilities of the approach will not rest by designing just another ordinary multiple twin. For instance, the rod-like and zigzag structures spatially compatible with interpenetrating multilayer icosahedral packings may be designed by projecting the polytope fragments onto the Clifford surfaces. As known, the Clifford surfaces are special kinds of manifolds of zero Gaussian curvature defined in the elliptical space. Corresponding surfaces in the Euclidean space are cylinders. Thus, the structures of multilayer nanotubes and 'magic' nanowires may be designed.

New packings with nearly icosahedral motif may be derived using the generalized cut-and-project procedure. First, one can increase the number of shells in the packing up to the equatorial cut-off of the polytope. Second, one can shift the origin of the structure being projected from vertex towards face or cell centre in the curved space. Third, one can perform the geodesic design of highly symmetrical structure in the curved space and only afterwards apply the cut-and-project procedure. Besides, one can increase the complexity of the non-Euclidean packing by taking multiple copies of the polytope in the same way as face-centred or body-centred cubic lattices may be derived from a simple cubic lattice in the Euclidean space.

Another way is to fill the fundamental regions of the non-Euclidean structure by slightly distorted multiple copies of some Euclidean packing which leads to the ‘decorated’ polytope. For example, every 120 tetrahedra in the structure of polytope {3,3,5} may be considered in curved space as a full analogue of the unit cell of a crystal. Then the tetrahedrally shaped fragments of some cubic crystal lattice may be cut out and projected into the unit tetrahedron of the polytope {3,3,5} so that the face-to-face boundaries between nearest ‘decorated’ tetrahedra would reproduce the atomic structure of the $\Sigma3$ twin boundaries in cubic crystals. In the curved space, the tetrahedral fragments should be multiplied by the generators of the Coxeter group [3,3,5]. After that, the fragments of the decorated polytope should be projected back into the Euclidean space resulting in a family of complex icosahedral diamond-like shell packings.

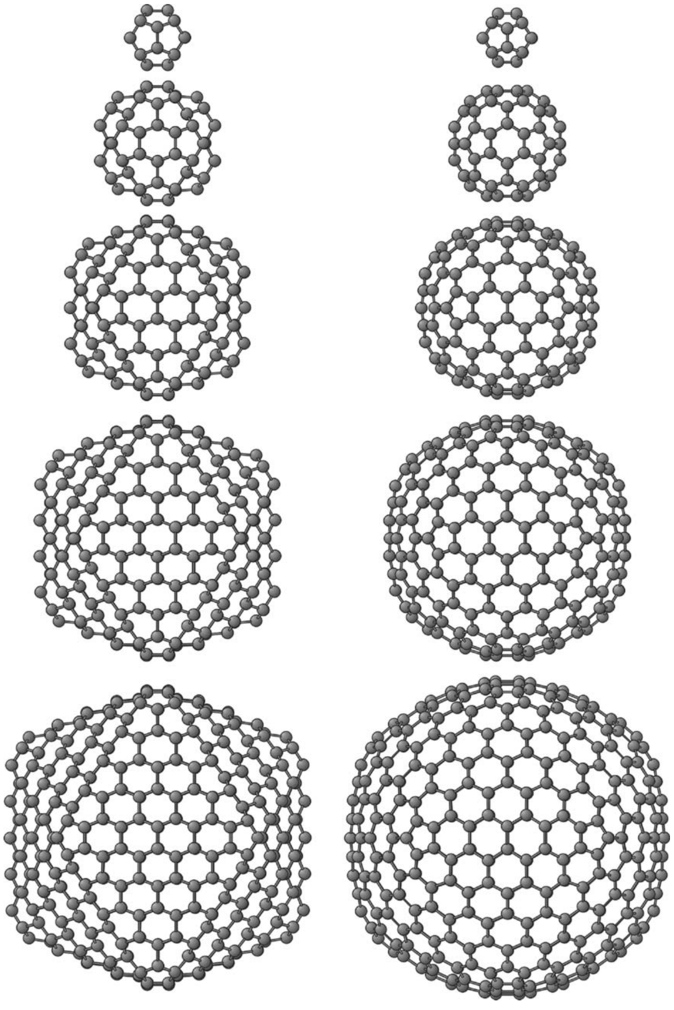

Figure 1

Formation of icosahedral nanoparticles with coherent boundaries. The consequent shells (from top to bottom) consist of 20, 80, 180, 320 and 500 atoms, respectively (view along the twofold axis of the icosahedron). Left: shells forming the diamond-like particle. Right: shells forming the onion-like particle. Both sets of shells may be reversibly transformed into each other by smoothing and puckering of atomic networks. Combining shells from both sets results in the composite icosahedral core-shell particle with diamond core coherently joined with an onion shell.

Constructed in such a way, diamond nanoparticles have a shell structure and a nearly spherical shape. In the simplest case (Shevchenko & Madison, 2006*a*), each shell contains $20k^2$ atoms (20, 80, 180, 320, 500, ...), and the particle as a whole consists of $20k(k+1)(2k+1)/6$ atoms (20, 100, 280, 600, 1100, ...), where k is the total number of shells. Special cases of this ‘magic’ series are provided by endohedral nanodrops of the $(H_2O)_{100}$ water, which were found in cavities of giant oxomolybdate clusters (Müller *et al.*, 2003), and the $(H_2O)_{280}$ Dzugutov clusters (Doye *et al.*, 2001). These numbers are also characteristic of carbon onions (Terrones *et al.*, 2003). Icosahedral diamond-like particles can undergo reversible transformation into onions by shell smoothing and backward puckering without any jumps of atoms between shells or migrations of atoms within intershell spacings. Let us illustrate this.

Fig. 1 shows the consecutive shells of an example of the icosahedral diamond-like nanoparticle. Its structure may be described either in terms of building units (Shevchenko & Madison, 2006*a*) or in terms of closed shells (Shevchenko & Madison, 2006*b*). In terms of building units, the core of this particle consists of 20 atoms forming a regular dodecahedron. Columns of ‘barrels’ are attached to each of its faces. The number of barrels in each column is defined by the frequency parameter of the geodesic design of the polytope. In general, each column should be terminated by dodecahedra from both sides. Each dodecahedron in the structure of an arbitrary icosahedral diamond-like nanoparticle corresponds to a certain vertex of the polytope {3,3,5}, whereas columns of barrels correspond to its edges. Dodecahedra and barrels form a scaffold. The remaining space should be regularly filled with fragments of diamond and lonsdaleite. The lonsdaleite fragments fill the surfaces corresponding to the faces of the polytope in the curved space. The diamond fragments fill the volume inside the tetrahedra corresponding to the cells of the polytope. In the simplest case, there is only one central dodecahedron and twelve columns of barrels in an icosahedral diamond-like nanoparticle (Shevchenko & Madison, 2006*a*). Another example has been reported elsewhere (Zeger & Kaxiras, 1993).

A generalized cut-and-project procedure makes it possible to design a lot of structures characterized by almost perfectly tetrahedral bonding of atoms and icosahedral point symmetry. The analogous structures with tetrahedral or dihedral point symmetry and almost icosahedral motif are possible, too. Similarly, related structures of multishell nanowires with hidden icosahedral motif may be designed. An example of the diamond-like helical structure has been presented recently (Shevchenko & Madison, 2006*a*). On the one hand, the arrangement of nearest neighbours in that structure is almost like that in a diamond crystal and, on the other hand, it has the overall symmetry characteristic of the Boerdijk–Coxeter helix. All these structures (multishell spherical particles and wires) are structurally compatible. It means they can interpenetrate each other and may be joined together coherently according to the rules of the parent structure existing in the curved space. Let us emphasize that such complex interpenetrating coherent nanosized structures are not twins in the classical meaning of this word.

In terms of closed shells, there are puckered and smoothed shells. Inserting the puckered consecutive shells (Fig. 1, left) into another one obtains the diamond-like particle. The same shells but smoothed (Fig. 1, right) form nested fullerene–onion. Both sets of shells are equal topologically and may be reversibly transformed by smoothing and puckering of atomic networks. It should be emphasized that, in the framework of the mechanism under consideration, the transformation of an icosahedral diamond-like nanoparticle into a shell nanoparticle is not accompanied by breaking of any chemical bonds and leads only to a change in their character and direction. In terms of atomic orbitals, the reversible structural transformations in carbon nanoparticles correspond to dehybridization and rehybridization of the bonds. The topological integrity of the network as a whole remains unchanged.

Another possibility is the coherent coexistence of diamond-like core with onion-like shells. Let us suppose that outer shells undergo the smoothing transformation, whereas the inner core remains diamond-like. This case corresponds to the composite icosahedral core-shell particle without any grain boundaries (in the classical sense) between diamond-like and graphite-like fragments. It is the special type of ordering specific for the nanostate, which cannot be explained in classical terms of twinning or polysyntaxy.

Thus, the structures of icosahedral diamond-like nanoparticles can simultaneously involve fragments with specific features of diamond, lonsdaleite, graphite and carbon onions joined coherently. They can serve as a good model accounting for the structure of detonation nanodiamonds, as well as for the structural transformations of nanodiamonds into onion-like carbon structures and *vice versa* (Aleksenskii *et al.*, 1999; Banhart *et al.*, 1997; Tomita *et al.*, 2000, 2002; Roddatis *et al.*, 2002; Ponomareva & Chernozatonskii, 2003; Banhart, 2004; Mykhaylyk *et al.*, 2005).

3. Concluding remarks

We have discussed the general approach for describing and designing non-crystallographic packings based on the cut-and-project procedure applied to highly symmetrical non-Euclidean structures and especially to regular polytopes. The geodesic design of fundamental regions in curved space or filling them by other fragments (repeated cut-and-project procedure) opens the way to design the most general hierarchic structures. The most vivid examples of such 'unusual' structures are those of nanoparticles although the true chemical or physical nature of the subunits being packed should be considered to be secondary.

The icosahedral packings were often described as multiple twins. We consider the icosahedral packing as a united whole, as a fragment of the corresponding non-Euclidean packing. Various parts of the real structure correspond to certain parts of the parent non-Euclidean structure and, moreover, they are assembled by rules, which in turn have prototypes among the group operations of the parent structure. From this point of view, the atomic displacements in various distant parts of the 'multiply twinned' nanoparticle should be concerted. Like the atomic displacements in neighbouring unit cells of a crystal define the structural transitions between macroscopic crystalline phases, the displacements in fundamental regions of the corresponding non-Euclidean parent structure serve the models of structural transitions in nanoparticles. The diamond-to-onion transition is considered as an example.

Let us suppose that the part of the parent structure in curved space underwent the structural transition, whereas another part did not. After projecting both parts into Euclidean space, one gets the nanosized analogue of the polysyntactic intergrowth (or twin) with *curved coherent interfaces*. The coherent coexistence of fragments in composite core-shell carbon particles represents an example of such intergrowth. In a general case, the coherent boundary should be the minimal surface of a definite genus.

The proposed approach has pure geometrical nature. It makes it possible to design quite realistic complex structures without any reference to the chemical nature of packed subunits or chosen interacting potential, as well as before any fitting or minimization procedure.

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