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The Symmetry of Polyhedral Cages Made from Crystals

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Abstract. Geometrical and crystallo-chemical criteria for mapping real crystal structures onto various surfaces such as cylinders, cones, saddles and polyhedra are presented. In particular the requirements for retaining some of the original crystal symmetry elements when constructing cones and polyhedra from crystals are given, using real structures made of boron nitride, graphite, and aluminosilicates as illustration. This is used as the basis for building several polyhedral shell models for the aluminosilicate mineral allophane. Other possible shell structures are shown to exist provided some of the mapping requirements are relaxed.

1. Introduction

Symmetry concepts enter virtually all fields of science in one way or another. In crystallography, it is symmetry in the sense of repetition of a basic unit in (usually) three dimensions that plays a central role. Whether this basic unit is constituted of a few atoms, as in inorganic crystals, or of thousands of atoms, as in a crystallized protein, the principle is the same: a macroscopic crystal can be constructed from a starting unit with as few as one atom, and an appropriate set of symmetry operations, including translational operations.

However, crystals are not the only symmetrical structures that exist in the mineral world. To name a few famous examples, quasicrystals (SHECHTMAN *et al.*, 1984), fullerenes (KROTO *et al.*, 1985) and icosahedral packings (HUBERT *et al.*, 1998) do not possess the translational symmetry which defines crystals. Yet they are highly symmetrical, in that their structure can be obtained from a limited number of rules (non-crystallographic icosahedral symmetry operations for the cases of fullerenes and icosahedral packing, and Penrose matching rules or overlapping rules of a quasi-uni-cell for quasicrystals (STEINHARDT *et al.*, 1998)).

Of particular interest are structures of the fullerene type, or more generally polyhedral cages, because they are finite and of very small size (on the nanometric scale). In this sense their morphology is not unlike that of many biological objects.

Fullerene-type structures were originally observed in the carbon system. Later, polyhedral cages of other compositions were also found (TENNE *et al.*, 1992; STÉPHAN *et* *al.*, 1998; PARILLA *et al.*, 1999). Despite their more complex crystal structure, even aluminosilicates are known to form small hollow particles, called allophane (HENMI and WADA, 1976). Recently, models involving the mapping of various aluminosilicate crystal structures onto polyhedral cages such as icosahedra, octohedra, and tetrahedra, were constructed for allophane, by analogy with other known fullerene-type objects (BOURGEOIS and BURSILL in preparation; the octahedral model is also introduced in BURSILL and BOURGEOIS (1999)). Moreover, the feasibility of mapping a complex structure like that of an aluminosilicate onto polyhedra begs the more general question of the modalities of crystal structure mapping onto various surfaces. The resulting objects are expected to form a whole new class of ordered structures, some of which have already been found experimentally.

The purpose of this paper is to show how some crystal structures can be mapped onto various types of surfaces like cylinders, cones, saddles, and especially closed polyhedral surfaces, provided that the initial crystal and the surface possess some amount of symmetry compatibility. As will be illustrated with allophane, lack of crystallinity does not prevent these structures from exhibiting a high degree of symmetry, and beauty, also.

2. Objects onto which Crystals can be Mapped

Here we have chosen to investigate the structure of shells made of crystalline material, and with curvatures in the nanometric size region. Our main interest lies in the mapping of crystals onto *polyhedral* shells. However, the symmetry requirements for applying successfully the mapping procedure can be illustrated in a clearer manner (it is hoped) by first focusing on conical, tubular and saddle-shaped surfaces. These surfaces are open, and if carefully chosen, demand relatively little change in the original crystal structure. After considering the mapping onto polyhedra in order to generate closed cage structures (Sec. 4.4), the negatively curved equivalent, which can result in periodic, three-dimensional frameworks, will be briefly discussed (Sec. 4.5).

3. Suitable Crystal Structures

It is clear that the mapping of a crystal structure onto a surface will be very much facilitated if the crystal in question is highly anisotropic, and more specifically, if it consists of weakly interacting layers. Indeed it can be expected that in general, order perpendicular to the surface will not be retained. There are numerous layered compounds in Nature, and therefore this is not a very severe restriction.

Crystal structures based on the graphitic-type trigonal lattice such as in carbon and boron nitride (BN) constitute the simplest examples of layered structures. Each layer is monoatomically thin, and consists of planar trigonal bonds. Experimentally these carbon or BN layers have been found in the form of nanotubes (IIJIMA, 1991), cones (HAN *et al.*, 2000; BOURGEOIS *et al.*, 2000b), and polyhedral shells—the so-called fullerenes (KROTO *et al.*, 1985).

Other, more complicated layered structures, like sulphides, fluorides and chlorides are also good candidates. Examples of nanotubes and polyhedral cages have already been discovered in each of these systems (TENNE *et al.*, 1992; ROSENFELD HACOHEN *et al.*, 1998;

PARILLA *et al.*, 1999, respectively).

Structures as complex as silicates are known to exhibit similar behaviours to the aforementioned compounds. The most drastic case of high curvature is shown by the natural mineral imogolite, which consists of a single aluminosilicate layer rolled into a tube 2 nm in diameter (CRADWICK *et al.*, 1972). Another interesting, if still mysterious example, is given by allophane, a hollow cage a mere 4–5 nm in diameter (HENMI and WADA, 1976). Larger silicate objects with cylindrical and conical geometries such as in the minerals asbestos and halloysite have also been known to exist for some time (YADA, 1967).

The above clearly shows that certain crystalline materials can readily display curved and polyhedral shapes. It is therefore of interest to understand the underlying symmetry compatibilities between the original crystal and the polyhedral, tubular... etc product.

4. Symmetry Requirements for Successful Mapping

4.1. Tubes

Tubes are remarkable in that they can be produced from a flat lattice without the breaking of a single bond. In other words any layer can be mapped onto a cylinder, provided the strain associated with the tube's curvature is not excessive. This is called conformal invariance, and is illustrated in Fig. 1 for a boron nitride sheet (a) and an aluminosilicate layer as in imogolite (b).

4.2. Cones

The property of conformal invariance characteristic of tubes does not apply to cones. A flat sheet can be made into a cone if a sector is removed from it, and the two cut edges are joined. The angle of the sector, D_θ, is restricted to special values which are directly related to the symmetry of the lattice (see Fig. 2). For a hexagonal lattice such as in graphitic

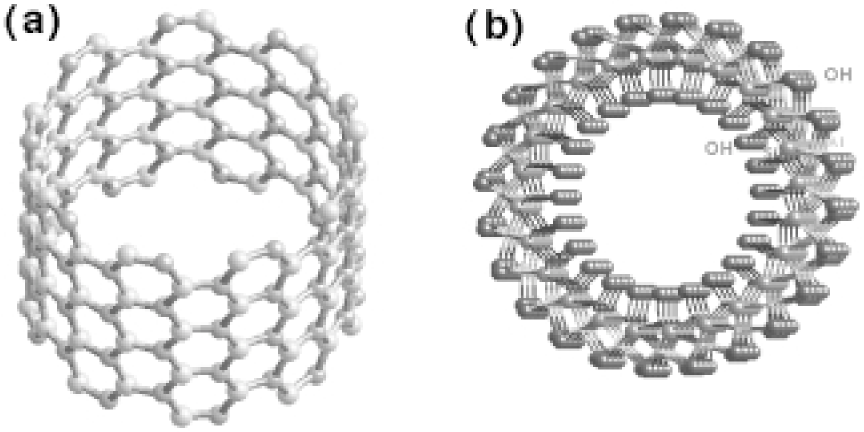

Fig. 1. (a) A boron nitride nanotube. Apart from some bond bending arising from the high curvature of the tube, the original BN lattice has been preserved. (b) The complex aluminosilicate lattice based on the mineral gibbsite can also be mapped onto a highly curved cylinder, as found in imogolite tubes.

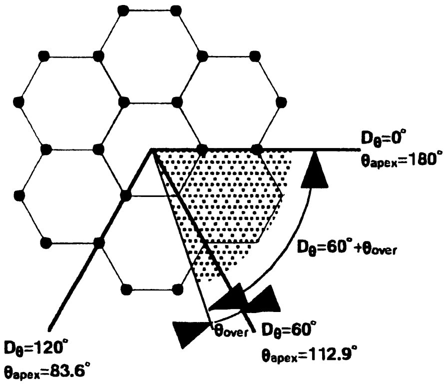

Fig. 2. Formation of a cone from a flat sheet: a sector of angle D_θ is removed and the two edges of the cut are joined together. D_θ must take on special values which reflect the symmetry of the lattice of the flat sheet.

carbon, D_θ must be a multiple of 60°. For BN, the set of allowed values decreases to multiples of 120° (see Fig. 3). If these conditions on D_θ are met, the lattice will have been preserved everywhere except at the apex of the cone, consisting of a topological defect: a two-membered ring in Fig. 3(a). The requirement on D_θ mentioned earlier is then equivalent to a restriction on apical ring-defects, and also on cone apex angles. For BN the defects must be even-membered (i.e. a square for example, or a two-membered ring as in Fig. 3(a)), or a line defect will occur (Fig. 3(b)). BN cones synthesized in the laboratory were indeed observed to obey these conditions (Bourgeois *et al.,* 2000a, b).

Conical sheets are important because they arise from a single topological defect, and therefore they illustrate in a simple way the importance of symmetry compatibility between the original crystal structure and the surface it is mapped onto.

4.3. Saddles

Saddle-shaped surfaces are the negatively-curved equivalent of cones. They can be obtained from a flat sheet by a very similar procedure to that outlined in Sec. 4.2. Instead of removing a sector from the flat lattice, a sector is added. This causes the sheet to buckle in opposite directions and hence to become saddle-shaped. As for cones, the lattice is modified only at the "apex" or saddle point, with the presence of a ring defect. For a hexagonal lattice this defect is a ring with more bonds than a hexagon. Again, restrictions on the size of the ring apply, and they are in fact identical to the previous (cone) case. Figure 4 shows such an object for carbon. The sole defect is a seven-membered ring.

4.4. Polyhedra

In a topological sense, polyhedra are much more complicated than either cones or saddles. If one again considers the trigonal lattice of graphitic structures, it can be deduced from Euler's theorem that twelve pentagonal rings, or six squares (or four triangles... etc) must be present if the sheet is to close onto itself. A closed shell with twelve pentagons located equidistantly will exhibit icosahedral morphology, whereas six squares will be

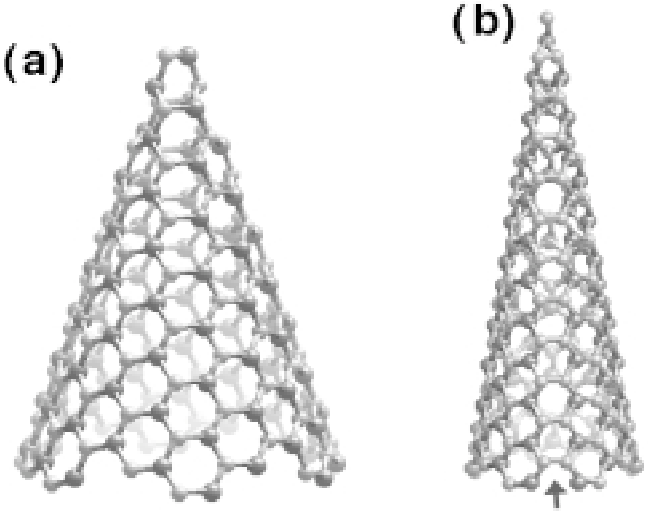

Fig. 3. Two boron nitride seamless cones. In (a) the particle resulted from the introduction of an even (two)-membered ring, and the local symmetry of the BN lattice has been preserved everywhere except at the apex of the cone. On the other hand, the particle shown in (b) has an odd (one)-membered ring, which is responsible for a defect line of B-B or N-N bonds (see arrow).

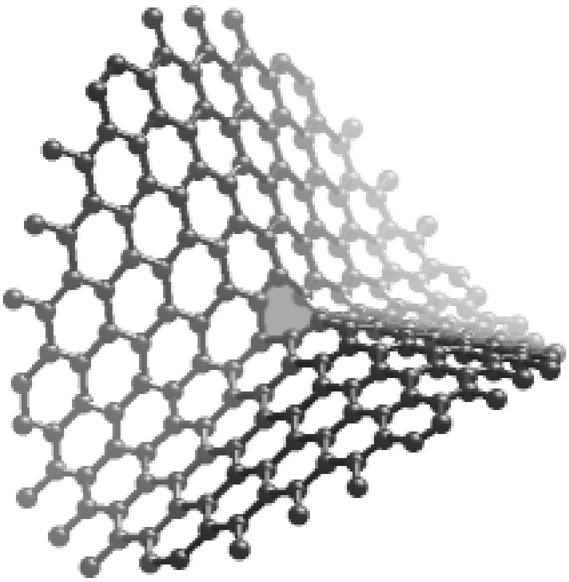

Fig. 4. A saddle-shaped surface for carbon. Hexagonal symmetry has been retained everywhere except at the saddle point, where a topological defect, a heptagon, is located.

associated with the shape of an octahedron, and four triangles with that of a tetrahedron. Just as in the case of cones and saddles, symmetry conditions have the effect that BN should prefer the octagonal morphology (see Fig. 5(a)), whereas carbon can display any of the possible polyhedral shapes. However, the lesser strain associated with the icosahedron will make it the most favoured form. And it is indeed what is observed with Buckminsterfullerene, or C_{60} (Fig. 5(b)).

Only a few simple examples have been given so far, but a similar study can be carried out for any type of layered compound. In fact, Pawley (1962) investigated systematically all possible mappings of layers onto the main polyhedron types. The symmetry of the flat lattices was considered to be adequately described by one of the seventeen crystallographic plane groups. 44 possibilities were found, for a restricted number of polyhedra types. Of these 44, the above-mentioned octahedral cage was the most commonly encountered object.

On the basis of such study, the aluminosilicate mineral gibbsite (see Fig. 6(a)), which is the backbone of imogolite tubes, and also perhaps of allophane hollow shells, can be expected to map onto octahedra only. This is due to the presence of oxygen octahedra. Such a model is depicted in Fig. 6(b), near its four-fold rotation axis. The diameter of the cage is about 4 nm, which is close to the size of allophane particles. It was discovered that a pseudo-icosahedral mapping was also possible, by using the point group m3m (instead of $m\bar{3}\bar{5}$ for the icosahedral point group). The resulting cage structure is shown in Fig. 6(c). Despite the loss of the five-fold symmetry axes, symmetry incompatibility is evident from the strained connections at the edges of the triangular facets (see arrows). However, the octahedral structure still appears to be the most reasonable model on the basis of the highest resolution transmission electron microscopy image available for allophane (see figure 1 in Wada *et al.* (1988)) (Bourgeois and Bursill in preparation). Nevertheless, the exploitation of the different symmetry elements of a polyhedron, as illustrated by the pseudo-icosahedron model, may lead to additional mapping possibilities, which seem worth exploring both theoretically and experimentally.

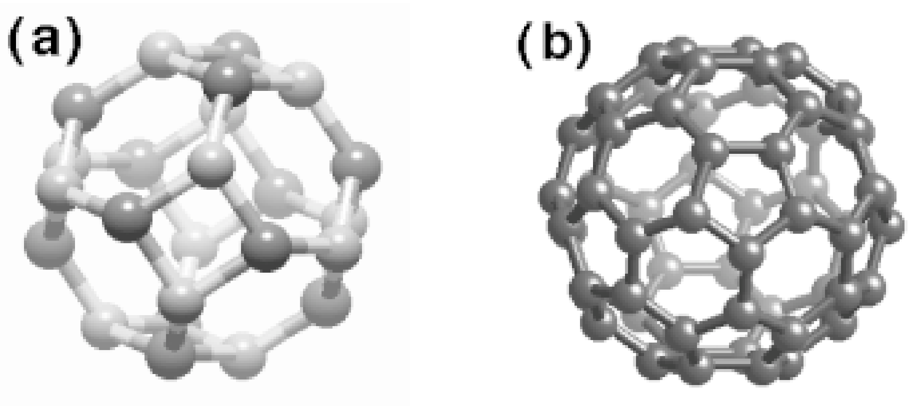

Fig. 5. (a) An octahedral shell of BN, with a square at each of its six vertices. (b) C_{60} with its characteristic twelve pentagonal rings and icosahedral symmetry.

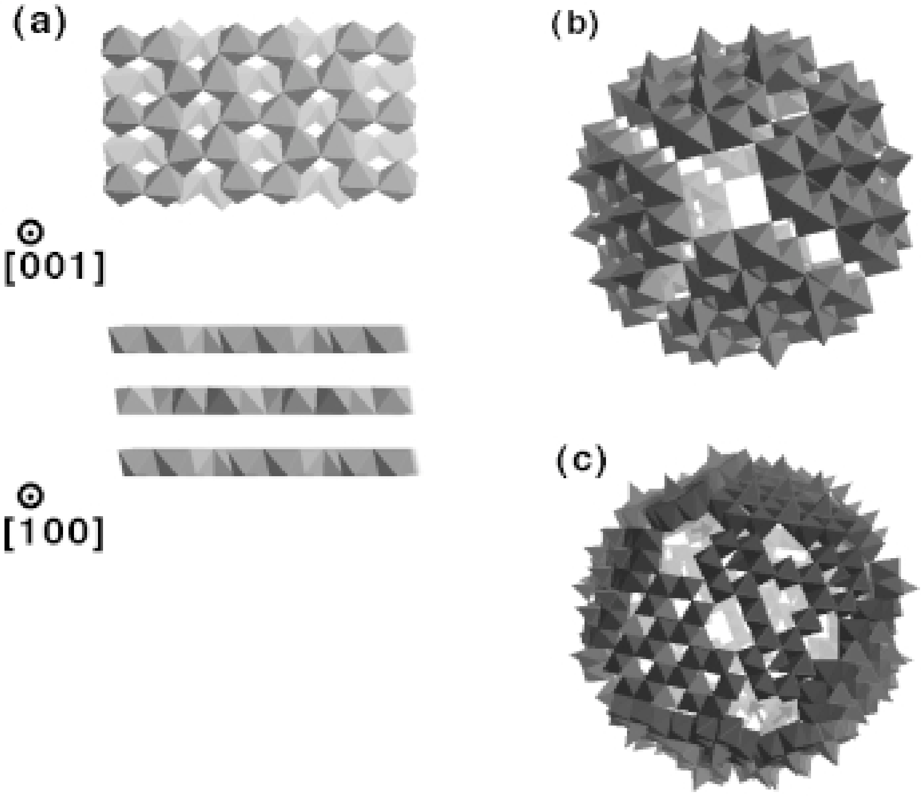

Fig. 6. (a) A gibbsite layer, the basis of the imogolite and possibly the allophane structures. (b) Octahedral model for allophane. (c) Pseudo-icosahedral model; two edges between triangular sheets are indicated by arrows.

4.5. Periodic, negatively curved surfaces

The first proposed model for negatively curved surfaces made from crystals is due to Mackay and Terrones (1991), for carbon. It consists of a monolayer of graphite with strategically placed heptagons, thus forcing the sheet to buckle into an infinite three-dimensional framework. A similar idea was used by Hyde (1993) for alumino-silicates to build periodic frameworks of negative curvature. It was even suggested that allophane might represent such a structure. However the fairly stringent symmetry requirements mentioned in the present paper were not taken into account.

5. Conclusion

The requirements for mapping crystal structures onto various types or surfaces, and in particular closed, polyhedral shells, were investigated. Despite the need for symmetry compatibility between the starting crystal structure and the surface, a number of such novel ordered structures can already be synthesized, and many more can be expected to be produced in the future.

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