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Parallelohedra and topological transitions in cellular structures

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In 1891, Fedorov showed that tilings of three-dimensional space by congruent convex polyhedra, in which all the tiles are in the same orientation, belong to just five topological classes. In 1953, Cyril Stanley Smith generalized Fedorov's result by dispensing with the convexity requirement. In this and the later work of Ferro and Fortes, solutions were obtained by applying topological transitions, of the kind that occur during grain growth, to the well-known space-filling by Kelvin 14-hedra. We demonstrate an anomalous solution to the generalized Fedorov problem that is not derivable by this method, and which provides a counter example to some conjectures suggested by O'Keeffe. Finally, a further generalization is proposed, that has relevance in the study of periodic networks. We conclude with a few examples to indicate some interesting directions for possible future developments of the idea that Fedorov and Smith had initiated.

Keywords: 3D tiling; cellular structure; Fedorov; networks; parallelohedron; polyhedron; topology

1. Introduction

The edges and the faces of a space-filling polyhedron that will tile three-dimensional Euclidean space so that all the polyhedra are congruent and in the same orientation necessarily occur in congruent and parallel pairs. There will be exactly one such 'tile' per lattice point of the underlying Bravais lattice. We shall refer to a polyhedron with this property as a *parallelohedron*. Fedorov [1] showed that *convex* polyhedra satisfying the requirement belong to just five topological classes. The Voronoi regions of three-dimensional lattices are Fedorov polyhedra. Delone [2] made use of this fact to classify the lattices and proposed a classification scheme containing 24 types of lattice, rather than the 14 of the usual classification due to Bravais.

If the convexity condition is dispensed with, the situation becomes much more complex. The first approach to the 'generalized Fedorov problem' was presented by Cyril Stanley Smith [3], in the context of shapes of grains and grain boundaries in polycrystalline alloys and the question of the largest possible number of facets that a grain can have. The problem has been investigated again more recently, by Ferro and Fortes [4], apparently without awareness of Smith's earlier contribution. The special context imposes restrictions on the kind of solutions sought. Naturally occurring cellular structures, which are observed in a wide range of contexts – polycrystalline materials, foams, and biological

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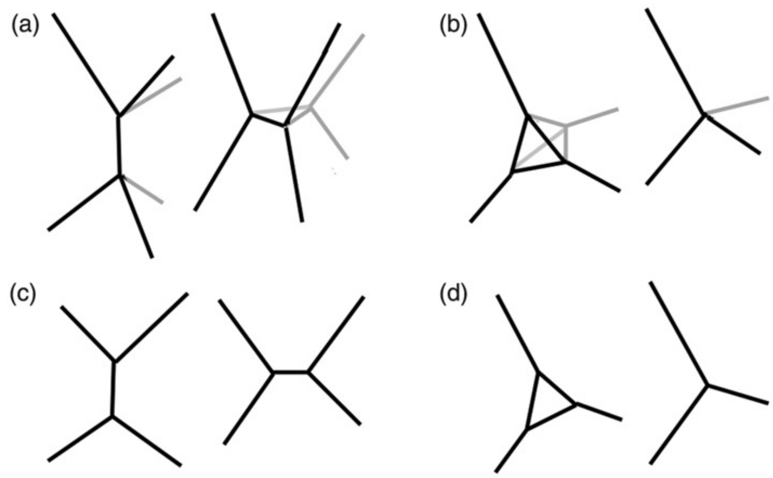

Figure 1. Topological transitions in standard cellular structures: (a) shrinkage and disappearance of an edge, bringing two separated cells into contact at a triangular face; (b) disappearance of a small tetrahedral cell; (c, d) analogous transitions in a trivalent 2D net.

systems – are, in general, characterized by the following topological characteristics: The cells are *trivalent* – every vertex of the cellular polyhedron belongs to three edges and three polygonal faces. Within the interior of the cellular structure, every vertex belongs to four edges, six faces and four cells; every edge has two vertices and belongs to three faces and three cells; every face belongs to two cells. We shall call a cellular structure with these properties a *standard cellular structure*.

Until we reach Section 7, we follow Smith [3], and Ferro and Fortes [4], in considering only parallelohedra that pack together to give a *standard cellular structure*. Smith considered only non-convex polyhedra of this kind because the resulting cellular structure can be regarded as a simplified ideal model of a polycrystalline material.

2. Trivalent parallelohedra

Of Fedorov's five convex parallelohedra, only one packs to form a standard cellular structure. This is the 14-faced truncated cuboctahedron (sometimes called the Kelvin polyhedron). It has six square faces and eight hexagonal faces, i.e. it is a polyhedron of type $4^6 6^8$. It is the Voronoi region for the bcc lattice.

Smith [3] obtained solutions of the generalized Fedorov problem by applying to the edges and faces of the packing of Kelvin polyhedra, a topological transformation that is characteristic of the transitions that take place in a polycrystalline material during grain growth (Figure 1a). The transition can be applied to any edge of a standard cellular structure, converting it to a different standard cellular structure. Applied to all the edges of a set of translationally equivalent edges in the space-filling of Kelvin polyhedra produces a solution of the generalized Fedorov problem – a 16-faced (non-convex) parallelohedron of type $3^4 5^8 8^4$ (Figure 2). (In the figures, we employ to illustrate the parallelohedra we have, for simplicity, representing edges by straight lines and faces by minimal surfaces across their bounding polygons. This choice of visualization has no particular significance in the *topological* context we are concerned with.) Smith also obtained two 18-faced parallelohedra (a $3^4 4^6 6^2 7^4 10^2$ and a $2^2 3^4 4^4 6^4 10^4$) by applying the transformation to two

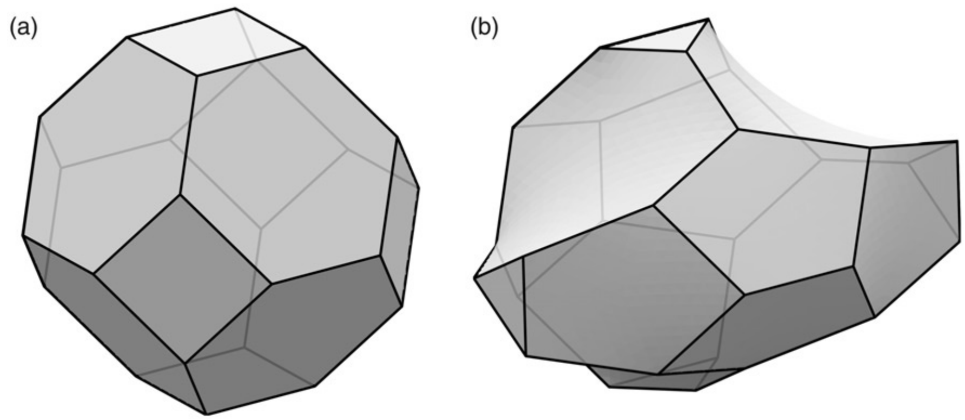

Figure 2. (a) The 14-faced Kelvin polyhedron and (b) the 16-faced non-convex parallelohedron derived from it.

sets of translationally equivalent edges, and a 20-faced parallelohedron ($3^8 5^6 9^6$) by applying it to three sets. Smith mentioned that the process can be applied again to the edges of these new parallelohedra and noted that one could go on indefinitely, producing parallelohedra with arbitrarily large numbers of faces.

Fortes and Ferro [4] carried the process beyond the first stage, producing a large number of non-convex Fedorov parallelohedra with up to 26 faces. The polyhedra, and the transformations giving rise to them, were illustrated by Schlegel diagrams. This work followed a detailed investigation by the same authors of the topological transitions that lead to grain growth, accompanied by an elucidation of the dynamics that produced the transformations [5].

3. Cellular structures and sphere packings

O'Keeffe [6] has shown that the networks of edges of the Ferro and Fortes cellular structures can be realized with straight edges of equal length, equal to the minimum distance between vertices. In other words, the configurations can be interpreted to give interesting new packings of equal spheres.

4. Digons

A trivalent polyhedron may have 'digonal' faces, a digon being a polygon with just two (curved) edges and two vertices. One of the 18-faced parallelohedra obtained by Smith has two digonal faces (Figure 3). This possibility was excluded *ab initio* in the work of Ferro and Fortes, by requiring the edges of the cells to be straight. In natural systems, there is no such requirement, so digonal faces are plausible. Observe that the 2D topological transition of Figure 1c applied to an edge of a triangular face produces a digon.

5. An anomalous trivalent parallelohedron

The parallelohedra discussed above are all derived systematically from a procedure applied to the edges of the packing of Kelvin polyhedra. O'Keeffe [6] concluded his observations with some interesting unanswered questions: 'Are they, as Ferro and Fortes suggest, the only parallelohedra with the given number of faces that pack to produce 4-connected nets? Do all such structures have some 3-sided faces? Can "all" space-filling polyhedra be derived by analogous procedures?'

We illustrate here (Figure 4a), a parallelohedron that is not obtainable by the methods of Smith and of Ferro and Fortes, though it is trivalent and the cellular structure it produces is 'standard'. It therefore provides a counterexample to O'Keeffe's conjectures. It was illustrated by Delgado-Friedrichs et al. [7] as one of a few representative examples of polyhedral space-fillings obtained from an elaborate algorithmic method of classifying nets, based on Delaney symbols. The work was not specifically concerned with the Fedorov problem. The polyhedron has 6 skew octagonal faces and 12 rhombic faces. It is related in a curious way to the space-filling by rhombic dodecahedra (Voronoi regions of fcc). Figure 4b is a cluster of four rhombic dodecahedra, which produces a parallelohedron with 36 rhombic faces. It is not trivalent, but in the space-filling there are sets of four faces

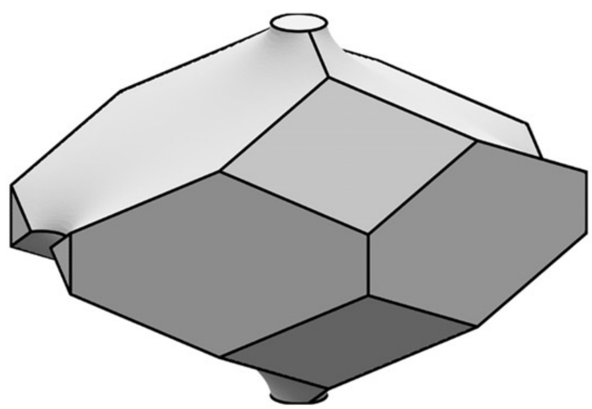

Figure 3. The 18-faced parallelohedron obtained by Smith, containing two 'digon' faces.

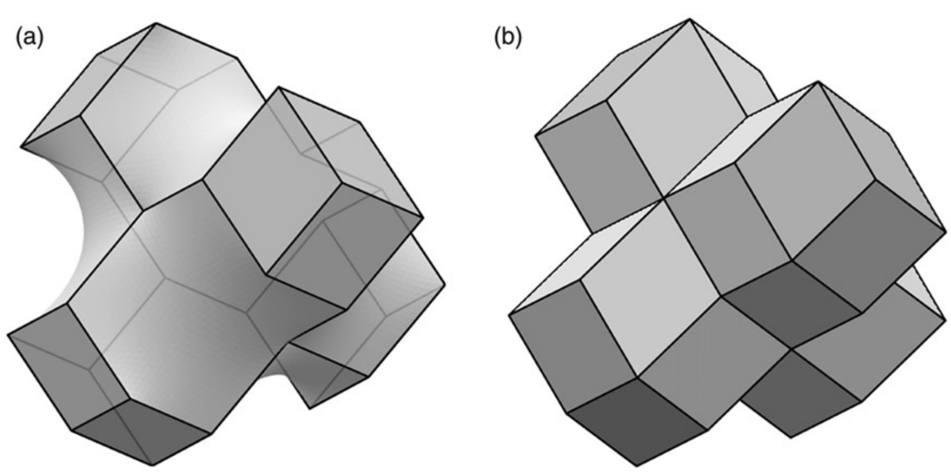

Figure 4. (a) An 18-faced trivalent parallelohedron with no triangular faces, and (b) the cluster of rhombic dodecahedra from which it can be derived.

that are shared by two cells. These sets of four faces can be replaced by skew octagonal faces, and the trivalent parallelohedron of Figure 3a is obtained.

6. Relations between 2D and 3D

The 3D case and the 2D case are inter-related in several ways:

(1) The primitive transitions in a 3D cellular structure are accompanied by corresponding analogous transitions in the polyhedral cells.
(2) A section of a 3D cellular structure is a 2D tiling pattern. In the general case, where the surface of the section does not contain a vertex, cells are seen as polygonal tiles, faces as edges, and edges as vertices of the 2D tiling pattern. This consideration is of importance in stereology, in which information about a 3D structure is to be deduced from a sequence of 2D sections. One can imagine a continuous motion of a plane through a 3D cellular structure. The 2D pattern undergoes the transitions of Figure 1c and d as the plane crosses vertices.
(3) A vertex of a 3D cellular structure can be assigned a *vertex figure* – the intersection of the structure with the surface of a sphere around the vertex, that contains no other vertex. Clearly, the vertex figures of all vertices of a standard cellular structure are tetrahedral.

7. Non-standard cellular structures

So far, only parallelohedra that pack to produce a standard cellular structure have been considered. This circumstance arose because of the properties of naturally occurring structures such as polycrystalline materials, foams and biological systems. However, *non-standard* cellular structures have relevance in other contexts. 3D networks are of considerable importance in structural chemistry. A very extensive and intricate range of four-connected nets describe the structures of zeolite, silicates and aluminosilicates, and various clathrates such as the clathrate hydrates. A net can be associated with a cellular structure by introducing surface patches across ‘rings’ (minimal circuits), to provide faces. This is in fact basic to the techniques employed by Delgado-Friedrichs and co-workers in their classification of nets. The cellular structures associated with four-connected nets are not, in general, standard. Even very simple four-connected nets illustrate this. Figure 5 is a parallelohedron with eight hexagonal faces that packs to give the four-connected NbO net. It is not even trivalent; it has six four-connected vertices and twelve two-connected vertices. The vertex figure is not tetrahedral; it is a $2^4 4^2$.

Even the cellular structure associated with the well-known diamond net (D-net) is non-standard. It is a packing of polyhedra with four skew-hexagonal faces, four trivalent vertices and six divalent vertices. It is not a parallelohedron, it occurs in two different orientations. Each vertex of the D-net belongs to 10 cells and 12 faces – the vertex figure for the cellular structure is not tetrahedral; it is a $2^6 3^4$. A parallelohedron 6^7 is obtained by combining two of the basic D-polyhedra (Figure 6). The symmetry of the cellular structure ($R\bar{3}M$) is now less than that of its net of edges ($Fd\bar{3}m$).

Figure 7 is another simple example of how a parallelohedron can be obtained by combining several space-filling polyhedra. The polyhedron packing associated with the wurzite net has two different polyhedral ‘tiles’, a trihedron 6^3 (three hexagonal faces)

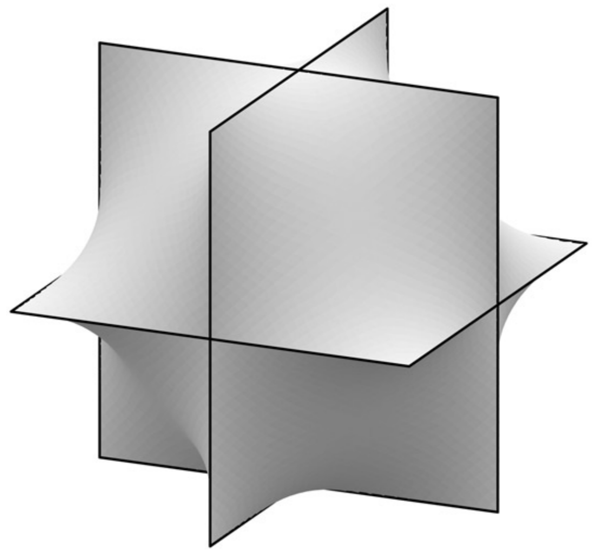

Figure 5. A non-trivalent parallelohedron 6^8 associated with the NbO net.

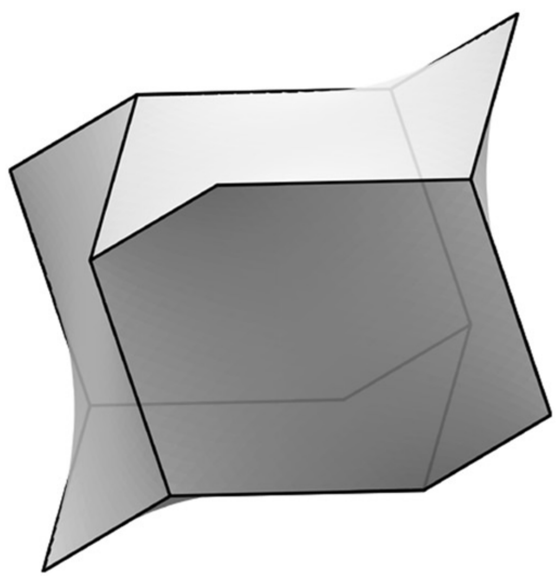

Figure 6. A 6^7 parallelohedron from a pair of saddle polyhedra of the diamond net.

and a pentahedron 6^5, both of which occur in two different orientations. Both have point group symmetry 3/mm (Figure 7a). A parallelohedron 6^{10} (Figure 7b) is obtained by combining four polyhedra. Again, we get a non-trivalent parallelohedron, but the net of edges of the space-filling is four-connected.

We shall not attempt a systematic investigation of the Fedorov problem in the more extended generality that arises when 'non-standard' cases are taken into consideration. We shall simply illustrate one more instance that has some special interest. A 14-faced space-filling polyhedron $4^2 5^8 6^4$ was introduced by Williams [8,9]. He called it the β-tetrakaidecahedron (the α-tetrakaidecahedron being the 14-faced Kelvin polyhedron).

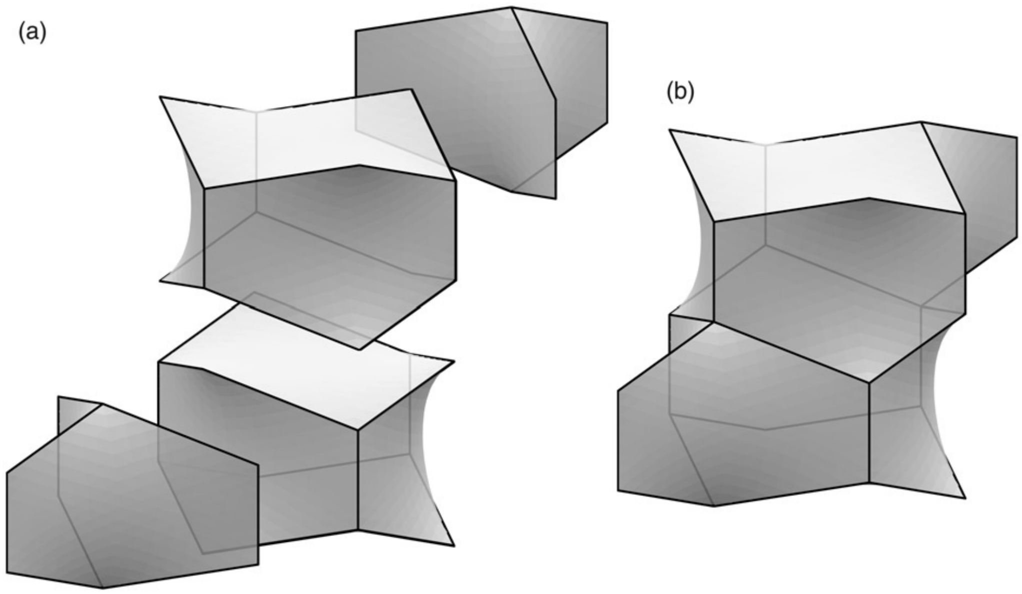

Figure 7. (a) The two saddle polyhedra associated with the wurzite net, in their two orientations. (b) The parallelohedron obtained by combining them.

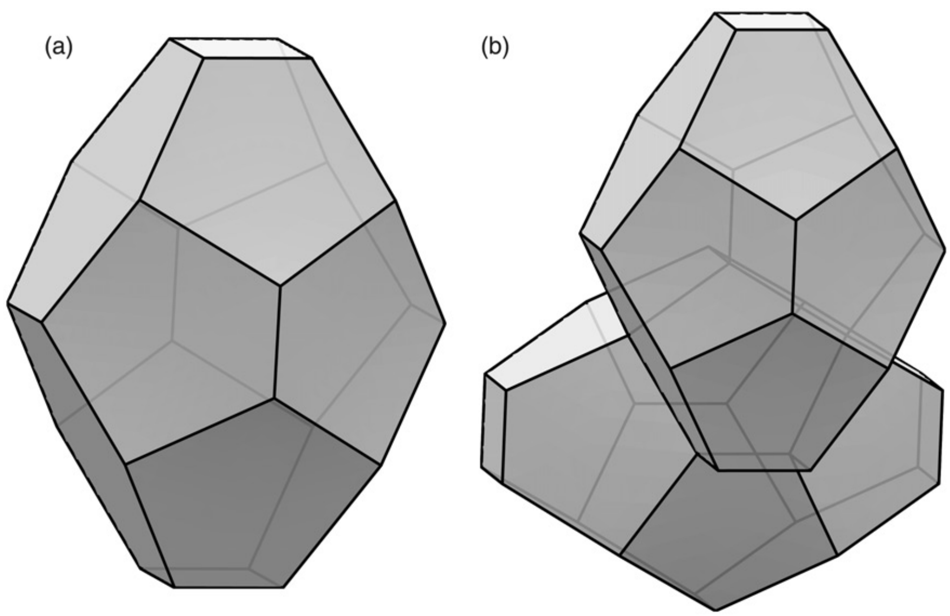

Figure 8. (a) The space-filling polyhedron W_2 and (b) a parallelohedron obtained from a pair of them.

O'Keeffe [10] reintroduced it and named it $W_2 14$, or simply W_2. It is shown in Figure 8a. Observe that it can be derived from an elongated Kelvin polyhedron $4^6 6^8$ by applying the transformation of Figure 1c to two opposite edges. It is easy to see how W_2 packs to produce a space-filling. The space-filling is a layered structure in which each layer is related in an obvious way to a well-known 2D pentagonal tiling pattern – the dual of

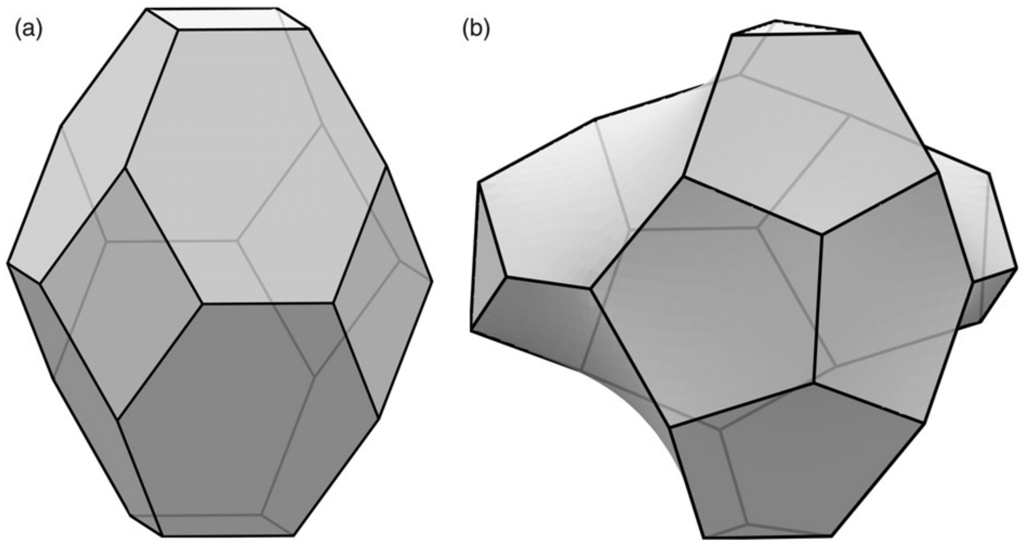

Figure 9. (a) An elongated Kelvin polyhedron and (b) the 16-faced parallelohedron in its maximal-symmetry form, obtained from it.

Kepler's tiling 3.3.4.3.4 of squares and equilateral triangles. O'Keeffe [6] has applied the basic transformation that Smith, and Ferro and Fortes, applied to the Kelvin solid, obtaining a 16-faces space-filling polyhedron $W_2$16. However, W_2 is not a parallelohedron. It occurs in two different orientations in alternate layers. Combining a pair of them, we get a true parallelohedron $4^4 5^{14} 6^8$ (Figure 8b). Again, we get a non-trivalent parallelohedron (five of its vertices are tetravalent), which nevertheless produces a four-connected net.

The relation between this parallelohedron and the one obtained by 16-faced parallelohedron (Figure 2b) discovered by Smith, is quite interesting. In Figure 9, we have applied Smith's procedure to an *elongated* Kelvin polyhedron (the scaling factor is 1.3449). The resulting parallelohedron in this case has greater symmetry – it has a $\bar{4}$-symmetry, which is obvious in Figure 9. Note that the cellular structures obtained from Figures 8b and 9b can both be built from layers that follow the same 2D pentagon pattern.

8. Augmentation of nets

A simple method of deriving a different net from a given simple net is well known. This is *truncation*, and is straightforwardly analogous to vertex truncation of polyhedra. Applied to the net of edges of a standard cellular structure, it replaces the four-connected vertices by extra tetrahedral cells, as in Figure 1b. For a four-connected vertex where the four edges are coplanar or nearly coplanar, a variant of the procedure is to replace the vertex by a quadrilateral, thus, producing four three-connected vertices around the original vertex, as in the augmented NbO net (Figure 10). Augmentation of triply periodic nets by truncation is a valuable process for discovering new networks; in particular for designing new clathrate-type materials of with the useful property of large 'cages' (see, for example, O'Keeffe et al. [11]).

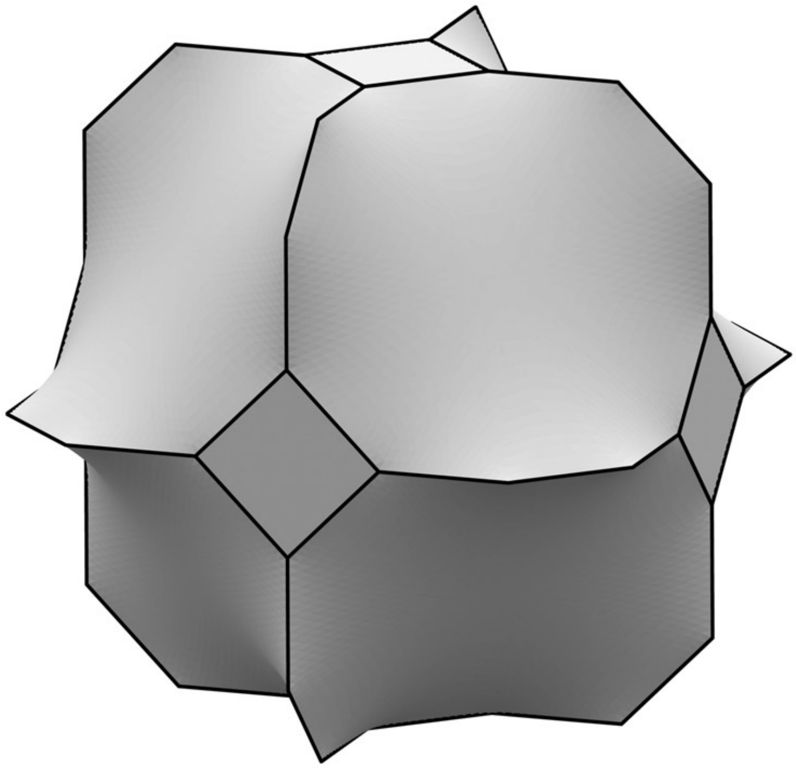

Figure 10. Parallelohedron for the truncated NbO net.

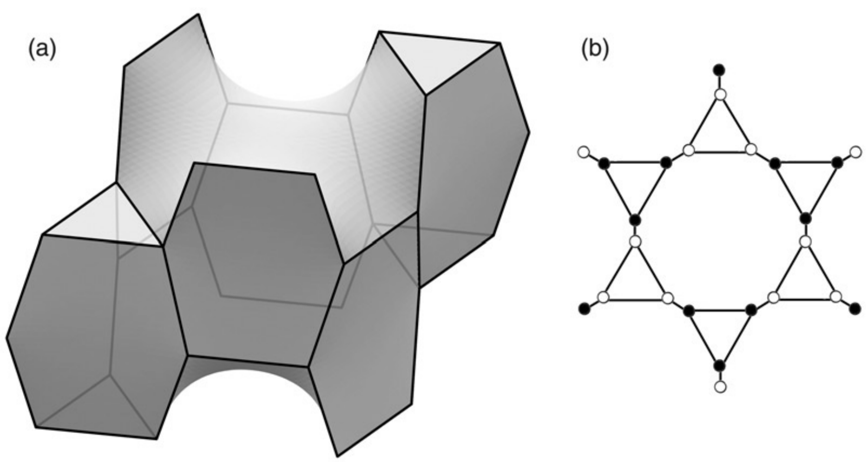

Figure 11. Net derived from wurzite net. (a) A parallelohedron $3^4 6^8 12^2$ that generates it and (b) view along the 3-fold axis with vertices at 0 and $c/2$ indicated by black circles and open circles.

An interesting alternative possibility for deriving new and unexpected nets from a given net is to apply the procedure of Figure 1a to sets of edges. From a four-connected net, a new net is obtained, which is also four-connected and contains extra triangular rings. Figure 11 indicates the result of applying the procedure to the set of all edges parallel to the 3-fold axis of the structure. The result is the net designated as *net 36* in the

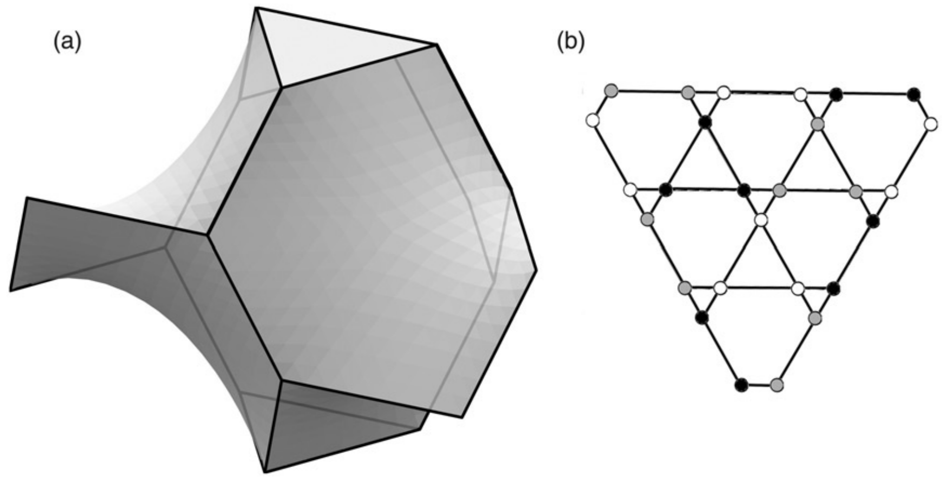

Figure 12. Net derived from the D-net. (a) A parallelohedron $3^2 7^6$ that generates it and (b) view along a 3-fold axis.
Note: Black, grey and white circles indicate vertices at 0, $c/3$ and $2c/3$, respectively.

O'Keeffe's investigation of possibilities for four-connected nets with three-rings. Its relation to the wurzite net is surprising.

In Figure 12, the same procedure has been applied to the set of edges parallel to a 3-fold axis in the diamond net. In this case, there are two ways of applying the transformation of Figure 1a to an edge: with either a right-handed or a left-handed twist, so we obtain an enantiomorphic pair of nets by operating on a set of parallel edges of the D-net. This net has also been described by O'Keeffe [12], who designated it as *net 38*.

9. Summary and conclusions

The topological characteristics of naturally occurring cellular structures (polycrystalline materials, foams and biological systems) lead to the concept of 'standard' cellular structures. These are monohedral tilings of three-dimensional space in which the tiles are related by translations; the tiles are *parallelohedra*. The concept has been continuously developed, since Fedorov's discovery of the five classes of convex parallelohedra. Non-convex parallelohedra were first considered by C.S. Smith in connection with questions of grain shapes and grain growth in polycrystalline materials, and Smith's ideas have been explored further by Ferro and Fortes. Apart from one anomalous case, all known 'standard' structures of this kind have been derived by applying topological transitions to the Kelvin 14-hedron. The existence of the anomalous parallelohedron $4^{12}8^6$ raises the open question whether there are any other such anomalous cases. We have drawn attention to a further generalization to some 'non-standard' parallelohedra that contribute significantly to the study of the periodic networks that are important in structural chemistry (sphere-packing problems, triply-periodic nets of zeolites, silicates, clathrates, etc.). The examples we have given serve to indicate the need for further exploration.

Acknowledgements

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