Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 22 May 2010
Accepted 23 July 2010

Simple tilings by polyhedra with five- and six-sided faces

Olaf Delgado-Friedrichs[a] and Michael O'Keeffe[b]*

[a]Supercomputer Facility, The Australian National University, Canberra, ACT 2600, Australia, and [b]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA. Correspondence e-mail: mokeeffe@asu.edu

Thirteen tilings of space by simple polyhedra with five- and six-sided faces ('fullerenes') are reported in which there are up to 11 kinds of vertex (vertex 11-transitive). All tilings contain dodecahedra and one or more of nine other kinds of tile. The duals are tilings by tetrahedra and include the four simplest of the known Frank–Kasper intermetallic structure phases. A fifth structure involving just the Frank–Kasper coordination polyhedra has a higher average coordination number than any known or postulated Frank–Kasper phase.

1. Introduction

We start with some informal definitions. A *simple polyhedron* is one in which exactly three faces meet at each vertex and two at each edge. A *simple tiling* of Euclidean space is one in which exactly four tiles that are simple polyhedra meet at each vertex, three meet at each edge and two meet at each face.

The dual of a tiling is a second tiling obtained as follows. A new vertex is placed inside each original tile and connected to the new vertices in adjacent tiles sharing a common face by an edge through that face. To complete the construction, new tiles are constructed so that the dual of the dual is the original. In particular the dual of a simple tiling is a tiling by tetrahedra.[1] Intermetallic structures based on such tilings are often referred to as *topologically close packed* (TCP). The famous Frank–Kasper phases (described below) are conspicuous examples. A tiling and its dual are simply, almost trivially, related and we consider them as essentially one structure.

Simple polyhedra with five- and six-sided faces are often called *fullerenes* (Fowler & Manolopoulos, 1995). Two subsets of these are of special interest. The isolated-pentagon fullerenes are those in which no two pentagons have a common edge. They are famously found as the structures of carbon molecules such as C_{60} and heavier congeners. The isolated hexagon fullerenes, of which there are only four, are the basis of the (dual) structures of the Frank–Kasper phases. Fullerenes are possible with the number of faces $f = 12 + h$ (here h is the number of hexagons) for all $h > 1$ and have more than one possible topology for $h > 3$. The number of vertices is given by $v = 2f - 4$. We often give a face symbol for a fullerene as $[5^{12}.6^h]$.

[1] We note that the tiles of the dual to a tiling by tetrahedra may not have a 3-connected graph (see, for example, Fig. 12 of Delgado-Friedrichs *et al.*, 2005) and thus are not considered polyhedra *sensu stricto* by purists. This complication does not arise in the work reported here.

For a long time the only known simple tilings by fullerenes were structures dual to Frank–Kasper TCP structures, but Deza & Shtogrin (1999) discovered an additional tiling that included a $[5^{12}.6^8]$ tile. We (Delgado-Friedrichs & O'Keeffe, 2006) subsequently showed that if other examples exist they must be tilings with more than seven kinds of vertex. In the work reported here we have extended the catalog of tilings by fullerenes to tilings with up to 11 kinds of vertex. The results are almost complete; but for three tilings, one with ten kinds of vertex and two with 11 kinds of vertex, we could neither prove definitely that they were non-Euclidean nor find a satisfactory Euclidean embedding. Nevertheless, we find 13 tilings involving altogether ten different fullerenes. The methods have been described fully before and the reader is referred to our 2006 paper cited above for the specific strategy for enumerating fullerene tilings.

2. Frank–Kasper phases and clathrates

Frank–Kasper phases are TCP intermetallic compounds with atoms in 12-, 14-, 15- and 16-coordination (Frank & Kasper, 1958, 1959). The coordination polyhedra have all triangular faces and five- and six-valent vertices such that no two six-coordinated vertices have a common edge. The duals of these polyhedra are the isolated hexagon fullerenes. The most common structure types are known as the $MgCu_2$ structure type (possibly the most common binary structure in chemistry) and Cr_3Si structure type. The dual structures are known as the type-II and type-I gas hydrate structures, which have zeolite framework codes **MTN** and **MEP**, respectively. The corresponding RCSR symbols for their nets (O'Keeffe *et al.*, 2008) are **mtn** and **mep**. A third TCP structure type, named for Zr_3Al_4, has as dual the type-III clathrate structure with RCSR net symbol **zra-d**.

The four Frank–Kasper coordination polyhedra are often symbolized as *X*, *R*, *Q* and *P* and we use those symbols also for

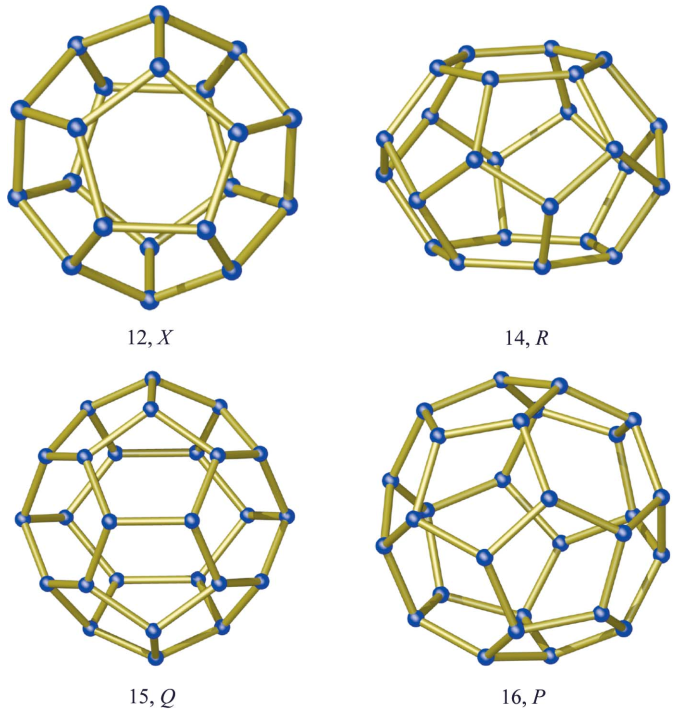

Figure 1
The isolated hexagon fullerene polyhedra, duals of the Frank–Kasper polyhedra.

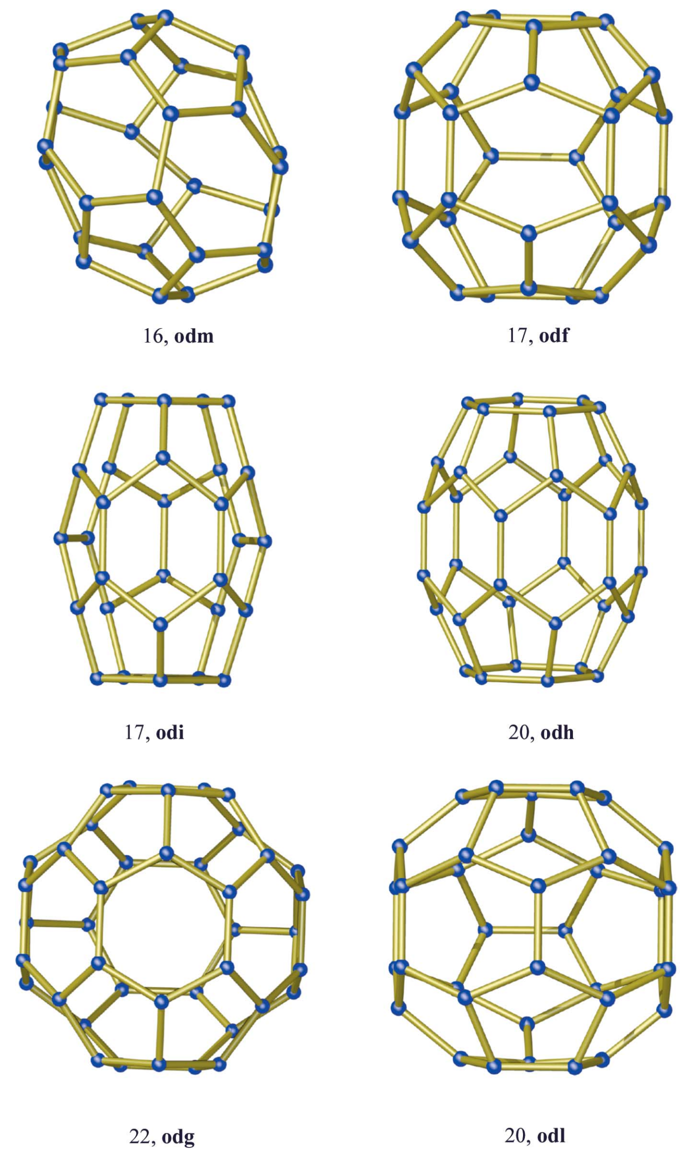

Figure 2
Simple polyhedra with five- and six-sided faces in tilings reported here. The numbers are the number of faces and the three-letter symbol is the RCSR symbol of the net in which they occur.

the dual polyhedra with 12, 14, 15 and 16 faces, respectively; they are shown in Fig. 1. We can then describe the polyhedral make-up of the three basic clathrate structures as I = XR_3, II = X_2P, III = $X_3R_2Q_2$.

Yarmolyuk & Kripyakevich (1974*a*,*b*) appear to have been the first to point out that all known Frank–Kasper phases had structures in which the relative numbers of polyhedra were linear combinations of the polyhedral compositions of these three basic types; *i.e.* their structures could be expressed as *a*I + *b*II + *c*III with *a*, *b* and *c* positive integers. Discussions with examples are given by Shoemaker & Shoemaker (1986), Sullivan (1999) and O'Keeffe (1999). Up to now no real or proposed structures were known that did not fit into this pattern; here we adduce the first example.

3. The new tilings

The tilings reported here for the first time have RCSR symbols starting **od**.... Fig. 2 illustrates the six fullerene polyhedra other that *X*, *R*, *Q* and *P* of Fig. 1 that we have found in the fullerene tilings and indicates the tiling in which it is found. Each of the new tiles occurs in just one new tiling but the 20-face tile in **odh** was also found earlier in **mds**. A notable new tile is the $[5^{12}.6^4]$ isomer of *P* with edge-sharing hexagons which occurs in **odm**. Others have 17, 20 or 22 faces.

Some details of the tilings are given in Table 1. There *p q r s* is the transitivity, which indicates that there are *p* kinds of vertex, *q* kinds of edge, *r* kinds of face and *s* kinds of tile in the simple tiling, and *d* is the flag transitivity.[2] The tilings themselves are illustrated in Fig. 3. Full crystallographic data are given in the RCSR database at http://rcsr.anu.edu.au/ (O'Keeffe *et al.*, 2008).

odk is the new Frank–Kasper structure that does not have a tile composition in the I–II–III triangle as illustrated in Fig. 4. It has an average number of faces, $\langle f \rangle = 13.55$, that is larger than any other known fullerene tiling. **mds**, the tiling of Deza & Shtogrin (1999), has the smallest $\langle f \rangle = 13.20$.

The duals of the new structures are plausible structures for intermetallic compounds, but we have not found any of them as existing known structures. Known TCP structures with a wider range of coordination numbers than the Frank–Kasper phases appear to have tilings in which four tetrahedra meet at an edge, so that the dual simple tilings have some four-sided faces; see O'Keeffe (1999) for some examples.

[2] A flag is a group consisting of a vertex, an edge, a face and a tile all mutually incident.

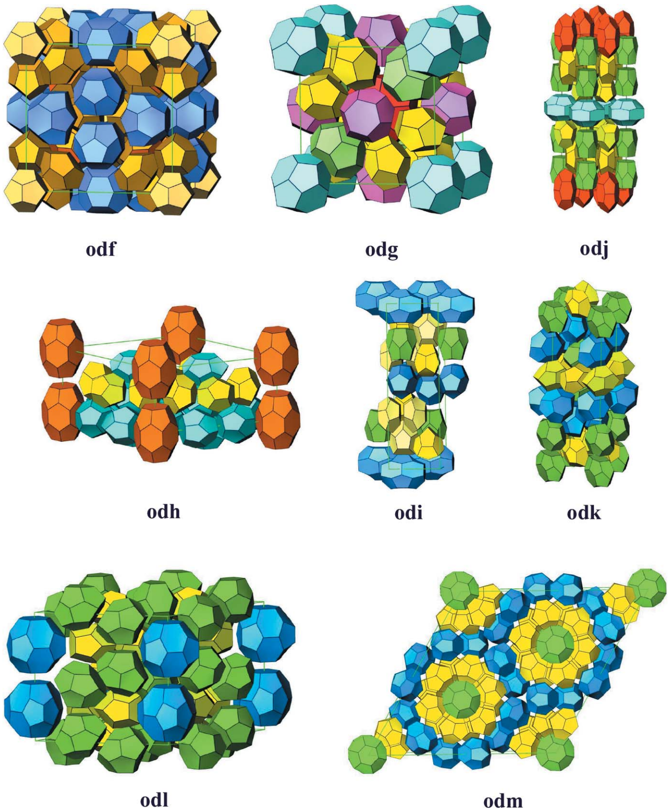

Figure 3
The new tilings by polyhedra with five- and six-sided faces reported in this paper. Tiles with the same number of faces have the same color.

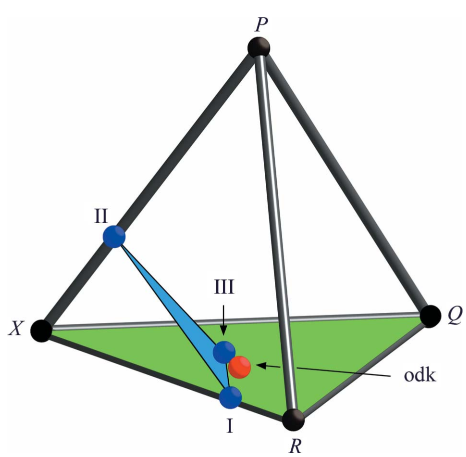

Figure 4
The Frank–Kasper tetrahedron *XPQR*. All previously known tilings by the *X*, *P*, *Q*, *R* polyhedra fall in the blue triangle I–II–III. **odk** is the new structure outside that triangle. *X*, *Q*, *R*, I, III and **odk** are all in the green plane.

Table 1
Known simple tilings by polyhedra with five- and six-sided faces and fewer than 12 kinds of vertex.

p q r s is the transitivity defined in the text and *d* is the flag transitivity. $\langle f \rangle$ is the average number of faces per tile.

Symbol	Symmetry	*p q r s d*	Tiles	$\langle f \rangle$
mep	$Pm\bar{3}n$	3 4 3 2 23	$[5^{12}] + 3[5^{12}.6^2]$	13.500
mtn	$Fd\bar{3}m$	3 4 2 3 17	$2[5^{12}] + [5^{12}.6^4]$	13.333
zra-d	$P6/mmm$	5 8 7 3 40	$3[5^{12}] + 2[5^{12}.6^2] + 2[5^{12}.6^3]$	13.428
mgz-x-d	$P6_3/mmc$	7 11 8 3 68	$2[5^{12}] + [5^{12}.6^4]$	13.333
mds	$P6/mmm$	7 11 9 4 56	$7[5^{12}] + 2[5^{12}.6^2] + [5^{12}.6^8]$	13.200
odf	$Im\bar{3}$	9 15 10 4 130	$17[5^{12}] + 6[5^{12}.6^5]$	13.304
odg	$P\bar{4}3m$	10 16 12 5 119	$12[5^{12}] + 5[5^{12}.6^2] + [5^{12}.6^4] + [5^{12}.6^{10}]$	13.263
odh	$P6/mmm$	10 17 14 5 114	$9[5^{12}] + 10[5^{12}.6^2] + [5^{12}.6^8]$	13.400
odi	$P4_2/nmc$	11 19 14 4 153	$6[5^{12}] + [5^{12}.6^2] + 2[5^{12}.6^5]$	13.333
odj	$P6/mmm$	11 17 14 6 96	$10[5^{12}] + 4[5^{12}.6^2] + 2[5^{12}.6^3] + [5^{12}.6^8]$	13.294
odk	$P4_2/mnm$	11 19 13 4 156	$3[5^{12}] + 4[5^{12}.6^2] + 2[5^{12}.6^3]$	13.555
odl	$P6_3/mcm$	11 20 14 4 170	$8[5^{12}] + 6[5^{12}.6^2] + [5^{12}.6^8]$	13.333
odm	$R\bar{3}c$	11 21 15 3 228	$6[5^{12}] + [5^{12}.6^2] + 3[5^{12}.6^4]$	13.400

Crystallographic data for all the structures dual to those reported here in *Systre*-readable format (*Systre* is available at http://www.gavrog.org/) are available as supplementary material.[3]

Work at ASU is supported by a grant (DMR 0804828) from the US National Science Foundation.

References

Delgado-Friedrichs, O., Foster, M. D., O'Keeffe, M., Proserpio, D. M., Treacy, M. M. J. & Yaghi, O. M. (2005). *J. Solid State Chem.* **178**, 2533–2554.
Delgado-Friedrichs, O. & O'Keeffe, M. (2006). *Acta Cryst.* A**62**, 228–229.
Deza, M. & Shtogrin, M. (1999). *Southeast Asian Math. Soc. Bull.* **23**, 1–11.
Fowler, P. W. & Manolopoulos, D. E. (1995). *An Atlas of Fullerenes.* Oxford University Press.
Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184–190.
Frank, F. C. & Kasper, J. S. (1959). *Acta Cryst.* **12**, 483–499.
O'Keeffe, M. (1999). In *Foams and Emulsions*, edited by J. F. Sadoc & N. Rivier. Dordrecht: Kluwer Academic Publishers.
O'Keeffe, M., Peskov, M. A., Ramsden, S. J. & Yaghi, O. M. (2008). *Acc. Chem. Res.* **41**, 1782–1789.
Shoemaker, D. P. & Shoemaker, C. B. (1986). *Acta Cryst.* B**42**, 3–11.
Sullivan, J. M. (1999). In *Foams and Emulsions*, edited by J. F. Sadoc & N. Rivier. Dordrecht: Kluwer Academic Publishers.
Yarmolyuk, Ya. P. & Kripyakevich, P. I. (1974*a*). *Kristallografiya*, **19**, 539–545.
Yarmolyuk, Ya. P. & Kripyakevich, P. I. (1974*b*). *Sov. Phys. Crystallogr.* **19**, 334–337.

[3] Crystallographic data discussed in this paper are available from the IUCr electronic archives (Reference: AU5108). Services for accessing these data are described at the back of the journal.