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Space fullerenes: a computer search for new Frank–Kasper structures

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A Frank–Kasper structure is a 3-periodic tiling of the Euclidean space $\mathbb{E}^3$ by tetrahedra such that the vertex figure of any vertex belongs to four specified patterns with, respectively, 20, 24, 26 and 28 faces. Frank–Kasper structures occur in the crystallography of metallic alloys and clathrates. A new computer enumeration method has been devised for obtaining Frank–Kasper structures of up to 20 cells in a reduced fundamental domain. Here, the 84 obtained structures have been compared with the known 27 physical structures and the known special constructions by Frank–Kasper–Sullivan, Shoemaker–Shoemaker, Sadoc–Mosseri and Deza–Shtogrin.

1. Introduction

A tiling is a partition of Euclidean space $\mathbb{E}^3$ into tiles, *i.e.* interiors of cages (generalized polyhedra with, possibly, 2-valent vertices, topologically equivalent to a sphere). Faces of tiles have vertices and edges but are not necessarily contained in an affine plane. A tiling is face-to-face if each face belongs to exactly two tiles; it is normal if the intersection of any two cages is a face, edge, point or Ø. A tiling is simple if four tiles meet at each vertex; tilings can be simple only if the polyhedra are 3-valent. A tiling T is 3-periodic (or crystallographic) if $\mathrm{Aut}(T)$ contains translations in three non-coplanar directions.

A fullerene (Fowler & Manolopoulos, 1995) F_n is a polyhedron with n, all of degree 3, vertices and only 5-gonal and 6-gonal faces. So, $p_5 = 12$ and $p_6 = (n/2) - 10$ for the number of faces. F_n exist for all even $n \geq 20$, except 22. The number of n-vertex fullerenes is 1, 1, 1, 2 for n = 20, 24, 26, 28, and it grows as n^9 (Thurston, 1998).

The Frank–Kasper polyhedra are all (four) fullerenes with isolated hexagons: unique ones F_{20}, F_{24}, F_{26} and one of two F_{28}, with symmetry $\mathrm{Aut}(F_n)$ = I_h, D_{6d}, D_{3h}, T_d, respectively (see Fig. 1). Crystallographers usually consider their duals as the coordination polyhedra with 6-valent vertices being possible disclinations of the local icosahedral order. These duals are called Frank–Kasper deltahedra and denoted by Z_{12}, Z_{14}, Z_{15} and Z_{16} or X, R, Q and P, respectively. Also, F_{24} is a dual bicapped hexagonal antiprism, while F_{28} is a dual tetracapped truncated tetrahedron. Duals of F_{26} and F_{28} are also called μ-phase polyhedron and Friauf polyhedron.

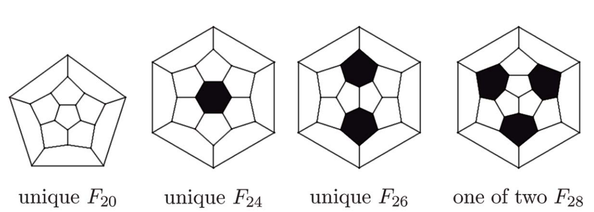


Figure 1
The four fullerenes with isolated hexagons.

A space fullerene is a simple tiling of $\mathbb{E}^3$ by any fullerenes (possibly non-congruent and with curved faces). A Frank–Kasper space fullerene or, for short, FK space fullerene, is a 3-periodic space fullerene, where any tile is isomorphic to one of four Frank–Kasper polyhedra. In crystal chemistry their duals are usually considered, introduced by Frank & Kasper (1958, 1959) and since called Frank–Kasper structures or Frank–Kasper phases, t.c.p. (tetrahedrally or topologically close-packed) structures with coordination numbers 12, 14, 15, 16. Then vertices correspond to atoms and edges correspond to atomic bonds. The terms t.c.p. and Frank–Kasper phase are usually used in crystallography and materials science, respectively. Frank–Kasper phases and McKay icosahedra are major types of locally icosahedral complex intermetallic compounds (Lord *et al.*, 2006). In physical t.c.p. phases, coordination numbers 12, 14, 15, 16 are dominating patterns, but phases similar to FK exist, for example, in giant cell structures. These Samson phases (Samson, 1968) can have, in addition to four dual FK polyhedra and truncated tetrahedra, other coordination polyhedra usually with coordination numbers in [11, 16]. The notion of nesting of fullerenes in Frank–Kasper phases is considered by Alvarez (2006).

It was proposed by Frank (1952) that liquids are characterized by icosahedral coordination, preventing easy crystallization into close-packed structures. Sheng *et al.* (2006), using sophisticated X-ray techniques, obtained detailed data on many binary non-crystalline metallic materials. They found that Frank–Kasper polyhedra statistically predominate among coordination polyhedra and Voronoi regions.

In Deza & Shtogrin (1999), a 3-periodic space fullerene, which is not FK, was given. This DS space fullerene is a tiling of $\mathbb{E}^3$ by F_{20}, F_{24} and its elongation $F_{36}(D_{6h})$ in proportion 7:2:1. In Deza & Shtogrin (2009), an infinite number of 1-periodic space fullerenes (with tiles F_{20}, F_{24}, F_{30}, F_{36}) were constructed from any infinite non-periodic plane fullerene, *i.e.* a 3-valent plane partition with 5- and 6-gonal faces only. In the Reticular Chemistry Structure Resource (RCSR) database (O'Keeffe *et al.*, 2008), seven other 3-periodic space fullerenes, which are not FK, are given; they are named **odf**, **odg**, **odh**, **odi**, **odj**, **odl** and **odm**.

A DS space fullerene is similar to the 4-valent 3-periodic tiling (also with symmetry $P6/mmm$) by F_{20}, F'_{20} (instead of F_{24}) and the same F_{36} in the fraction 3:2:1 (here F'_{20} is the 'twisted F_{20}', *i.e.* the 3-valent 20-vertex polyhedron, where 6-ring, alternating 4- and 6-gons, have three 5-gons inside and three outside). It corresponds to metallic alloy $CaCu_5$, clathrate of type H, zeolite topology DOH and clathrasil dodecasil D1H.

FK space fullerenes occur in the following:

(i) 27 ordered t.c.p. phases of metallic alloys, where cells are atoms; *cf.* Table 1.

(ii) Clathrates (compounds with one component, atomic or molecular, enclosed in a framework of another), including clathrate hydrates, where cells are solutes cavities, vertices are H_2O, edges are hydrogen bonds; clathrasils (silicate materials with clathrate structure); and zeolites (hydrated microporous aluminosilicate minerals), where vertices are tetrahedra SiO_4 or $SiAlO_4$, cells are H_2O, and edges are oxygen bridges.

(iii) Soap froths (foams, liquid crystals).

(iv) An affine version of A_{15} gives (see Weaire & Phelan, 1994)[1] a better [than Kelvin's affine variation of body-centered cubic (b.c.c.) = A_3^*] solution to the weak Kelvin problem: partition $\mathbb{E}^3$ into equal volume (not necessarily congruent) cells D of minimal surface area, *i.e.* with maximal $\mathrm{IQ}(D) = 36\pi V^2/A^3$ (the lowest energy foam of equal bubbles). Some other non-space-fullerene structures were found by Gabrielli (2009).

For examples, see Sloan & Koh (2007), Jeffrey (1984) for clathrate hydrates, Meier & Olson (1992) for zeolites, and O'Keeffe & Hyde (1996) for crystal structures.

Especially important are FK space fullerenes A_{15} and C_{15}. They correspond to clathrate hydrates of type I, II; zeolite topologies MEP, MTN; clathrasils melanophlogite, dodecasil 3C; and metallic alloys Cr_3Si, $MgCu_2$, respectively. Their unit cells have, respectively, 46, 136 vertices and 8 (2 F_{20} and 6 F_{24}), 24 (16 F_{20} and 8 F_{28}) cells. The FK space fullerenes σ, Z, C_{14} are dual to clathrate hydrates of type III, IV and V, respectively.

A_{15} and C_{15} are also extremal in the following sense. For all 27 previously known physical FK space fullerenes, their average coordination number $\overline{f}$ (mean number of faces per cell in the fundamental domain) is within [13.(3), 13.5] and mean face size of a cell $\overline{q}$ is within [5.1, 5.(1)]. Both lower bounds are realized by C_{15}, while upper ones are realized by A_{15}. In fact, Nelson & Spaepen (1989) conjectured $5.1 \leq \overline{q} \leq 5.(1)$, *i.e.* $13.(3) \leq \overline{f} \leq 13.5$ for any FK space fullerene.

However, DS space fullerene has $\overline{q} = 56/11 \simeq 5.091$ and $\overline{f}$ = 13.2, the smallest to date. On the other hand, $\overline{f}$ = 13.(5) > $\overline{f}(A_{15})$ for three new FK space fullerenes [with fraction, *i.e.* respective proportion of 20-, 24-, 26-, 28-vertex polyhedra, (3, 4, 2, 0)] found in this paper.

All previously known FK space fullerenes have fractions which are linear combinations of those of A_{15}, C_{15} and Z. This was observed by Yarmolyuk & Kripyakevich (1974) for the 20 FK space fullerenes known in 1974. As a general conjecture, this Yarmolyuk–Kripyakevich rule was motivated by Shoemaker & Shoemaker (1986), when 24 FK space fullerenes were known. We obtained five counterexamples to this conjecture.

Examples of non-Euclidean analogs of space fullerenes are tilings of 3-sphere by F_{20} (120-cell) and of hyperbolic 3-space by F_{24} (Löbell space), *cf.* for example, Vesnin (1989). Also, the convex hull of vertices of the hexagonal plane tiling {63}, realized on a horosphere (regular honeycomb {633}), have only 6-gonal 2-faces; its fundamental domain is not compact but has finite volume.

In the RCSR database, the space fullerenes DS, C_{14}, C_{15}, A_{15}, Z, —, μ, σ, T are named **mds**, **mgz-x-d**, **mtn**, **mep**, **zra-d**, **muh**, **mur**, **sig** and **tei**.

2. Explicit constructions

The major skeleton $\mathrm{Maj}(\mathcal{T})$ of a space fullerene $\mathcal{T}$ is a graph with the vertices being the cells of $\mathcal{T}$ and an edge between vertices if the corresponding cells share a 6-gonal face. For example, the A_{15} phase has an infinity of infinite paths going in three different directions, while the Z structure has an infinity of layers {63} stacked with an infinity of infinite paths passing through the hexagons.

In Sadoc & Mosseri (1985, 1999) an inflation procedure is described. Here we extend it slightly so that it takes one FK space fullerene and returns another FK space fullerene. For $m \geq 3$ call snub Prism$_m$ (or Löbell m-polyhedron) the 3-valent plane graph with two m-gonal faces separated by two m-rings of 5-gons. Of course, snub Prism$_5$ is F_{20} and snub Prism$_6$ is F_{24}, while snub Prism$_3$ is the Dürer octahedron and snub Prism$_4$ is the dual bi-capped 4-antiprism. Given a simple tiling $\mathcal{T}$ by cells P, we define the inflation $IFM(\mathcal{T})$ to be the simple tiling such that:

(i) Every cell P contains a shrunken copy P' of P in its interior.

(ii) On every vertex of P there is an F_{28}.

(iii) On every face of P' with m edges there is a snub Prism$_m$ which is contained in P.

Keeping in mind that the newly created F_{28} are contained in four different cells P, the operation IFM restricted to FK space fullerenes gives

[1] This was realized as the futurist swimming complex 'Water Cube' (or 'Building of Bubbles') at the Beijing Olympic Games, 2008.

$$\begin{cases} F_{20} \to F_{20} + 12F_{20} + \frac{20}{4}F_{28}, \\ F_{24} \to F_{24} + \{12F_{20} + 2F_{24}\} + \frac{24}{4}F_{28}, \\ F_{26} \to F_{26} + \{12F_{20} + 3F_{24}\} + \frac{26}{4}F_{28}, \\ F_{28} \to F_{28} + \{12F_{20} + 4F_{24}\} + \frac{28}{4}F_{28}. \end{cases}$$

Thus if $\mathcal{T}$ is an FK space fullerene of fraction $(x_{20}, x_{24}, x_{26}, x_{28})$, then $IFM(\mathcal{T})$ is also an FK space fullerene of fraction $(x'_{20}, x'_{24}, x'_{26}, x'_{28})$ with

$$\begin{cases} x'_{20} = 13x_{20} + 12x_{24} + 12x_{26} + 12x_{28}, \\ x'_{24} = 3x_{24} + 3x_{26} + 4x_{28}, \\ x'_{26} = x_{26}, \\ x'_{28} = 5x_{20} + 6x_{24} + \frac{13}{2}x_{26} + 8x_{28}. \end{cases}$$

The FK space fullerene $IFM(A_{15})$ was given by Sadoc & Mosseri (1985), where it was noticed that it has the same average coordination number as the T phase; it is named **tep** in the RCSR database. Every edge of the major skeleton of $\mathcal{T}$ corresponds to a path of three edges in the major skeleton of $IFM(\mathcal{T})$ with two additional vertices coming from F_{24}. The other component of the major skeleton of $IFM(\mathcal{T})$ is the skeleton of $\mathcal{T}$ from the F_{28} placed at the vertices of $\mathcal{T}$. *A priori*, $IFM(\mathcal{T})$ does not follow the Yarmolyuk–Kripyakevich rule. In Fig. 2 we give $IFM(A_{15})$ and the underlying cells.

In Deza & Shtogrin (2009) a construction of only 1-periodic space fullerenes is described, which generalize Deza & Shtogrin (1999). In order to extend it slightly, for any $m \geq 3$ let us denote by BSPrism$_m$ the 3-valent plane graph obtained by inserting the ring of m 6-gons in the middle of the rings of 5-gons of snub Prism$_m$; its symmetry is D_{mh}. Take an infinite 3-valent plane graph G with faces of size $m \in \mathcal{M}$. The DS construction $DS(G)$ is a tessellation of the Euclidean space by polyhedra snub Prism$_m$, BSPrism$_m$ and F_{20}: on each of the two opposite m-gon of the polyhedron BSPrism$_m$ we put a snub Prism$_m$ on each of two m-gonal faces. This structure is stacked in infinite lines. The residual space is then filled with F_{20}. For the tessellation {63} by hexagons of the Euclidean plane, the space fullerene $DS(\{63\})$ was found by Deza & Shtogrin (1999) and is the first example found of a 3-periodic space fullerene which is not an FK space fullerene. Later, the properties of this space fullerene were discussed in detail by Delgado-Friedrichs & O'Keeffe (2006) and all 3-periodic space fullerenes with at most seven orbits of flags were classified. There are five types: A_{15}, C_{15}, Z, C_{14} and DS with 3, 3, 5, 7 and 7 orbits, respectively. In order for $DS(G)$ to be a space fullerene it is necessary and sufficient that G has faces of size 5 or 6 only. The only periodic case is {63} but there are some non-periodic structures if one takes a plane fullerene. Then there are at most six 5-gonal faces as discussed by Deza & Shtogrin (2009) and the number of possibilities is countable.

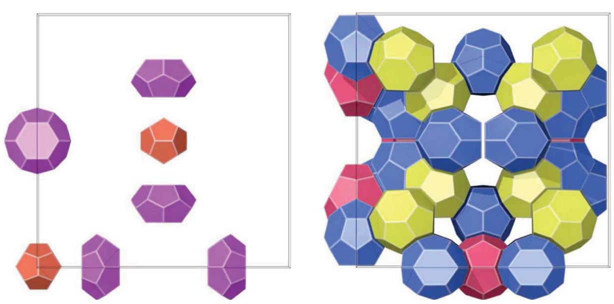


Figure 2
The inflation on the A_{15} structure: the shrunken cells of A_{15} and the generated F_{28}.

In §2.2 of Frank & Kasper (1959) a construction of FK space fullerenes is described, which is further described by Sullivan (2000). In Sullivan's description the input of the construction is a tiling of the plane by regular triangles and squares and the output is a 1-periodic space fullerene with $x_{28} = 0$, which is shown to satisfy the Yarmolyuk–Kripyakevich rule. The resulting space fullerene is 3-periodic if and only if the initial plane tiling is 2-periodic. Another name for the construction is hexagonal t.c.p. phases (Kuo *et al.*, 1986); see also Fig. 3.

In Shoemaker & Shoemaker (1972) a method for generating FK space fullerenes, called pentagonal t.c.p., is given that generalizes the generalized Laves phases of §2.1 of Frank & Kasper (1959), the square-lozenge construction of Kuo *et al.* (1986), and the previous constructions of Pearson & Shoemaker (1969), Shoemaker & Shoemaker (1968) and Kripyakevich (1970). The input of the construction is a plane tiling by, not necessarily regular, quadrangles and triangles with vertex configurations (3^6), $(3^2, 4, 3, 4)$, $(3^3, 4^2)$, (4^4), (3^5), $(3^4, 4)$ and $(3^5, 4)$ allowed. Some of the edges are doubled, and the non-doubled edges are colored red and blue so that:

(i) Every square contains exactly two doubled edges on opposite sides.

(ii) Every triangle contains exactly one double edge.

(iii) For every face the non-doubled edges are of the same color.

(iv) If two faces share a black edge then their color (red or blue) is the same if and only if their sizes are different.

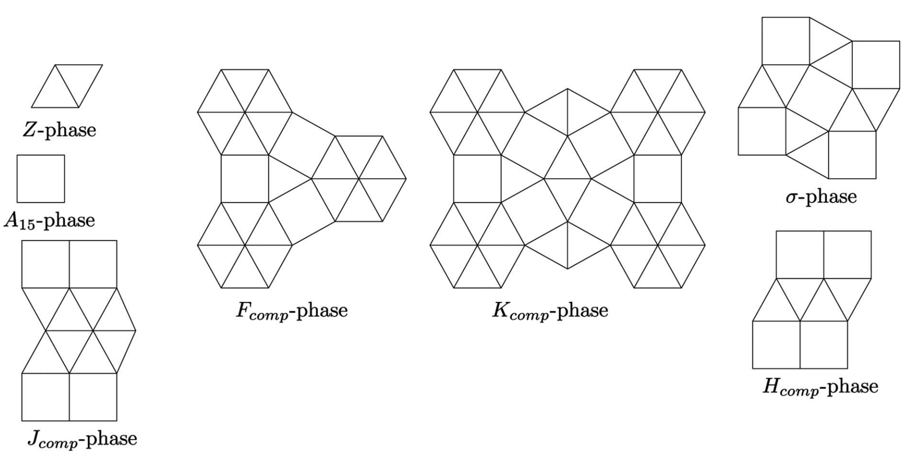


Figure 3
The plane tilings corresponding to the physical space fullerenes with $x_{28} = 0$.

The paper by Shoemaker & Shoemaker (1972) contains a detailed description of the obtained structures. Once the doubled edges are chosen, the colored red/blue edge is uniquely defined up to the color choice of one edge, and the obtained FK space fullerene has $x_{24} = x_{26}$. In Fig. 4 for each such FK space fullerene we give a translation tile for the corresponding plane tiling with the required doubled edges indicated; edge colors are not given since they are easy to obtain.

3. Computer computation method

The full enumeration of Frank–Kasper structures is a very difficult problem. The above constructions show that some non-3-periodic structures exist and that within the 3-periodic framework there are a large variety of possible structures. Thus it seems that a general mathematical description of all space fullerenes is impossible and we consider instead the subproblem of enumerating FK space fullerenes whose fundamental domain is not too large. Here we consider only the combinatorial problem; we do not distinguish between structures if they can be perturbed without changing the adjacencies between cells. Thus we provide a list of possible combinatorial candidates that can be used to match some physical structures or used as a starting point for some optimization procedures such as, for example, the Kelvin problem or Hamiltonian energy minimization.

A cell complex $\mathcal{C}$ is a family of cells with inclusion relation such that the intersection of any two cells is either empty or a single cell. A cell complex is pure of dimension 3 if the cells that are maximal for inclusion have dimension 3. It is closed, or has no boundary, if any two-dimensional cell is contained in

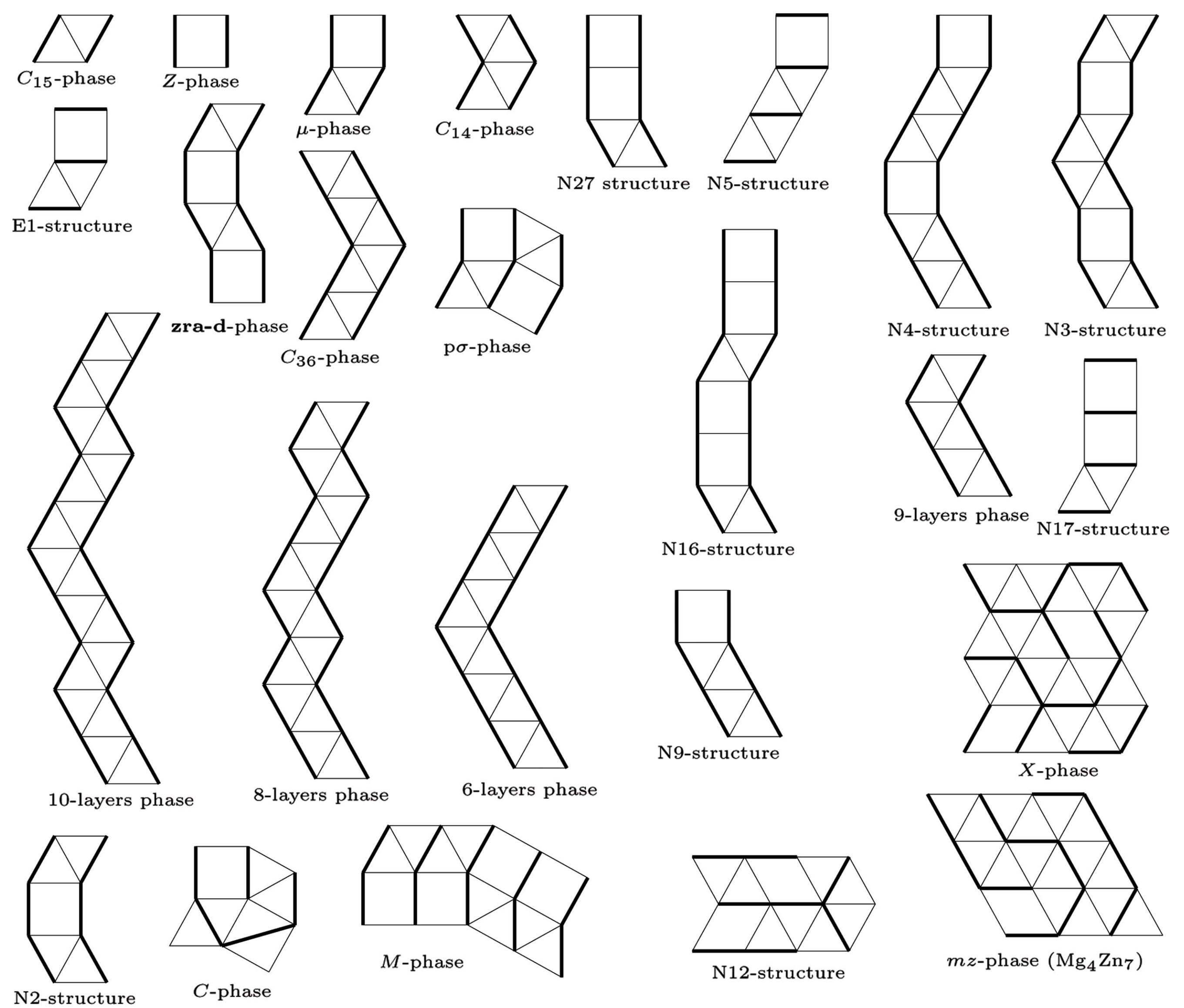


Figure 4
The list of graphs representing FK space fullerenes described as pentagonal t.c.p. For physical phases the name is indicated. For new space fullerenes with known fraction we give the name *Ex*-structure with *x* the entry in Fig. 6 and Table 2. For new space fullerenes with new fraction we give the name *Nx*-structure with *x* the entry in Fig. 7 and Table 3.

Table 1
List of known physical space fullerenes.

For each such FK space fullerene we give the name of the phase, a representative alloy, the space group, the number of cells in a fundamental domain, the average coordination number, the fraction sequence, the partition of cells into orbits and a description of the major skeleton.

No.	Phase	Representative alloy	Group	Fundamental domain	$\bar{f}$	Fraction	Cell orbits	Major skeleton
1	C_{14}	$MgZn_2$	$P6_3/mmc$	12	13.333	(2, 0, 0, 1)	$(8_{2,6}, 0, 0, 4_4)$	(0, 0, 4)
2	C_{15}	$MgCu_2$	$Fd\bar{3}m$	6 × 4	13.333	(2, 0, 0, 1)	$(16_{16}, 0, 0, 8_8)$	(0, 0, 2)
3	C_{36}	$MgNi_2$	$P6_3/mmc$	24	13.333	(2, 0, 0, 1)	$(16_{4,6^2}, 0, 0, 8_{4^2})$	(0, 0, 8)
4	6-layers	MgCuNi	$P6_3/mmc$	36	13.333	(2, 0, 0, 1)	$(24_{12,2,4,6}, 0, 0, 12_{4^3})$	(0, 0, 12)
5	8-layers	$MgZn_2 + 0.03MgAg_2$	$P6_3/mmc$	48	13.333	(2, 0, 0, 1)	$(32_{12,4^2,6^2}, 0, 0, 16_{4^4})$	(0, 0, 16)
6	9-layers	$MgZn_2 + 0.07MgAg_2$	$R\bar{3}m$	18 × 3	13.333	(2, 0, 0, 1)	$(36_{18,3,6,9}, 0, 0, 18_{6^3})$	(0, 0, 6)
7	10-layers	$MgZn_2 + 0.1MgAg_2$	$P6_3/mmc$	60	13.333	(2, 0, 0, 1)	$(40_{12^2,2,4^2,6}, 0, 0, 20_{4^5})$	(0, 0, 20)
8	mz	Mg_4Zn_7	$C2/m$	55 × 2	13.345	(35, 2, 2, 16)	$(70_{2,4^9,8^4}, 4_4, 4_4, 32_{4^8})$	(2, 2, 16)
9	X	$Mn_{45}Co_{40}Si_{15}$	$Pnnm$	74	13.351	(23, 2, 2, 10)	$(46_{2,4^5,8^3}, 4_4, 4_4, 20_{4^5})$	(4, 4, 20)
10	T	$Mg_{32}(Zn, Al)_{49}$	$Im\bar{3}$	81 × 2	13.358	(49, 6, 6, 20)	$(98_{2,24^2,48}, 12_{12}, 12_{12}, 40_{16,24})$	(6, 6, 20)
11	C	$V_2(Co, Si)_3$	$C2/m$	25 × 2	13.360	(15, 2, 2, 6)	$(30_{2,4^3,8^2}, 4_4, 4_4, 12_{4^3})$	(2, 2, 6)
12	**zra-d**	K_7Cs_6	$P6_3/mmc$	26	13.384	(7, 2, 2, 2)	$(14_{12,2}, 4_4, 4_{2^2}, 4_4)$	(4, 0, 4), $2\mathbb{Z}(0, 2, 0)$
13	$p\sigma$	Th_6Cd_7	$Pbam$	26	13.384	(7, 2, 2, 2)	$(14_{2,4,8}, 4_4, 4_4, 4_4)$	2(2, 2, 2)
14	μ	Mo_6Co_7	$R\bar{3}m$	13 × 3	13.384	(7, 2, 2, 2)	$(21_{18,3}, 6_6, 6_6, 6_6)$	(2, 0, 2), $\mathbb{Z}(0, 2, 0)$
15	M	$Nb_{48}Ni_{39}Al_{13}$	$Pnma$	52	13.384	(7, 2, 2, 2)	$(28_{4^3,8^2}, 8_{4^2}, 8_{4^2}, 8_{4^2})$	2(4, 4, 4)
16	R	$Mo_{31}Co_{51}Cr_{18}$	$R\bar{3}$	53 × 3	13.396	(27, 12, 6, 8)	$(81_{18^4,3,6}, 36_{18^2}, 18_{18}, 24_{18,6})$	(12, 6, 8)
17	K	$Mn_{77}Fe_4Si_{19}$	$C2$	55 × 2	13.418	(25, 19, 4, 7)	$(50_{2,4^{12}}, 38_{2,4^9}, 8_{4^2}, 14_{2,4^3})$	(5, 2, 1), (6, 0, 2), (8, 2, 4)
18	Z	Zr_4Al_3	$P6/mmm$	7	13.428	(3, 2, 2, 0)	$(3_3, 2_2, 2_2, 0)$	$\mathbb{Z}(0, 2, 0)$, $\mathbb{Z}^2(2, 0, 0)$
19	P	$Mo_{42}Cr_{18}Ni_{40}$	$Pnma$	56	13.428	(6, 5, 2, 1)	$(24_{4^4,8}, 20_{4^3,8}, 8_{4^2}, 4_4)$	2(6, 4, 2), $4\mathbb{Z}^2(2, 0, 0)$
20	δ	MoNi	$P2_12_12_1$	56	13.428	(6, 5, 2, 1)	$(24_{4^6}, 20_{4^5}, 8_{4^2}, 4_4)$	4(5, 2, 1)
21	ν	$Mn_{81.5}Si_{18.5}$	$Immm$	93 × 2	13.440	(37, 40, 10, 6)	$(74_{16,2,4^2,8^6}, 80_{16,4^2,8^7}, 20_{4^3,8}, 12_{4,8})$	(10, 8, 2), (12, 2, 4), $9\mathbb{Z}^2(2, 0, 0)$
22	J_{comp}	Complex	$Pmmm$	22	13.454	(4, 5, 2, 0)	$(8_{1^2,2,4}, 10_{2^3,4}, 4_{2^2}, 0)$	$\mathbb{Z}(2, 4, 0)$, $4\mathbb{Z}^2(2, 0, 0)$
23	F_{comp}	Complex	$P6/mmm$	52	13.461	(9, 13, 4, 0)	$(18_{6^3}, 26_{12,2,6^2}, 8_{2,6}, 0)$	$\mathbb{Z}(6, 2, 0)$, $\mathbb{Z}(6, 6, 0)$, $7\mathbb{Z}^2(2, 0, 0)$
24	K_{comp}	Complex	$Pmmm$	82	13.463	(14, 21, 6, 0)	$(28_{1^2,2^3,4^5}, 42_{2^3,4^7,8}, 12_{2^4,4}, 0)$	$\mathbb{Z}(10, 4, 0)$, $\mathbb{Z}(10, 8, 0)$, $11\mathbb{Z}^2(2, 0, 0)$
25	H_{comp}	Complex	$Cmmm$	15 × 2	13.466	(5, 8, 2, 0)	$(10_{2,4^2}, 16_{4^2,8}, 4_4, 0)$	$\mathbb{Z}(2, 2, 0)$, $3\mathbb{Z}^2(2, 0, 0)$
26	σ	$Cr_{46}Fe_{54}$	$P4_2/mnm$	30	13.466	(5, 8, 2, 0)	$(10_{2,8}, 16_{8^2}, 4_4, 0)$	$2\mathbb{Z}(4, 2, 0)$, $4\mathbb{Z}^2(2, 0, 0)$
27	A_{15}	Cr_3Si	$Pm\bar{3}n$	8	13.500	(1, 3, 0, 0)	$(2_2, 6_6, 0, 0)$	$3\mathbb{Z}^2(2, 0, 0)$

two three-dimensional cells. For short, a C_3-complex is a closed pure three-dimensional cell complex.

Given a Frank–Kasper structure $\mathcal{F}$, we associate the C_3-complex defined by the inclusion between vertices, edges, triangles and tetrahedra. If a structure is periodic and the number of vertices per unit cell is specified, then the list of possible candidates is finite and can actually be enumerated on a computer for a fixed size. However, a key problem occurs: how can one recognize whether a C_3-complex arises from a Euclidean tiling? This problem is related to difficult questions of topology of three-dimensional manifolds which, in practice, are solved efficiently by the program *3dt* (Delgado-Friedrichs, 2000*a*) implemented from Delgado-Friedrichs (1990).

We find it easier to deal with the enumeration problem of FK space fullerenes instead of their dual, *i.e.* Frank–Kasper structures. The combinatorial objects we are looking for are the infinite periodic tilings of the Euclidean space $\mathbb{E}^3$ by those four polyhedra.

In order to reduce the size of a combinatorial enumeration problem, a common method is to work with the quotient manifold of $\mathbb{E}^3$ by the group G of combinatorial symmetries of the space. We can describe combinatorially any tiling of $\mathbb{E}^3$ by vertices, edges, faces and cells with their incidence relations. However, this is not always possible in the quotient. If the group is only made of translations and the fundamental domain is sufficiently large, then the incidence method also works. But suppose that one takes the tiling of $\mathbb{E}^3$ by unit cubes; then we have in the quotient only one vertex, edge, face and cell, and this is clearly insufficient. An efficient system for working in this context, named the Delaney symbol, has been devised (see Dress, 1987; Delgado-Friedrichs *et al.*, 1995).

A flag f in a C_3-complex is a sequence (F_0, F_1, F_2, F_3) of faces with $F_i \subset F_{i+1}$. If $0 \le i \le 3$, then the flag $\sigma_i(f)$ is the one differing from f only in the dimension i. Suppose $\mathcal{C}$ is a C_3-complex, with a group G acting on it. The Delaney symbol of $\mathcal{C}$ with respect to G is a combinatorial object containing:

(i) The orbits O_k of complete flags under G.

(ii) The action of σ_i on those orbits for $0 \le i \le d$.

(iii) For each orbit O_k and integers $0 \le i < j \le d$ the number $m_{i,j}(k)$, which is the smallest $m > 0$ such that $(\sigma_i\sigma_j)^m(f) = f$ for all $f \in O_k$.

The quotient $\mathcal{C}G$ is an orbifold. If $G = \mathrm{Aut}(\mathcal{C})$, we speak simply of the Delaney symbol of $\mathcal{C}$. A consequence of Dress (1987) is that a periodic tiling is uniquely described by its Delaney symbol. The key point of this theorem is that $\mathbb{E}^3$ is simply connected.

Several works have been carried out towards direct enumeration of the Delaney symbol in order to obtain

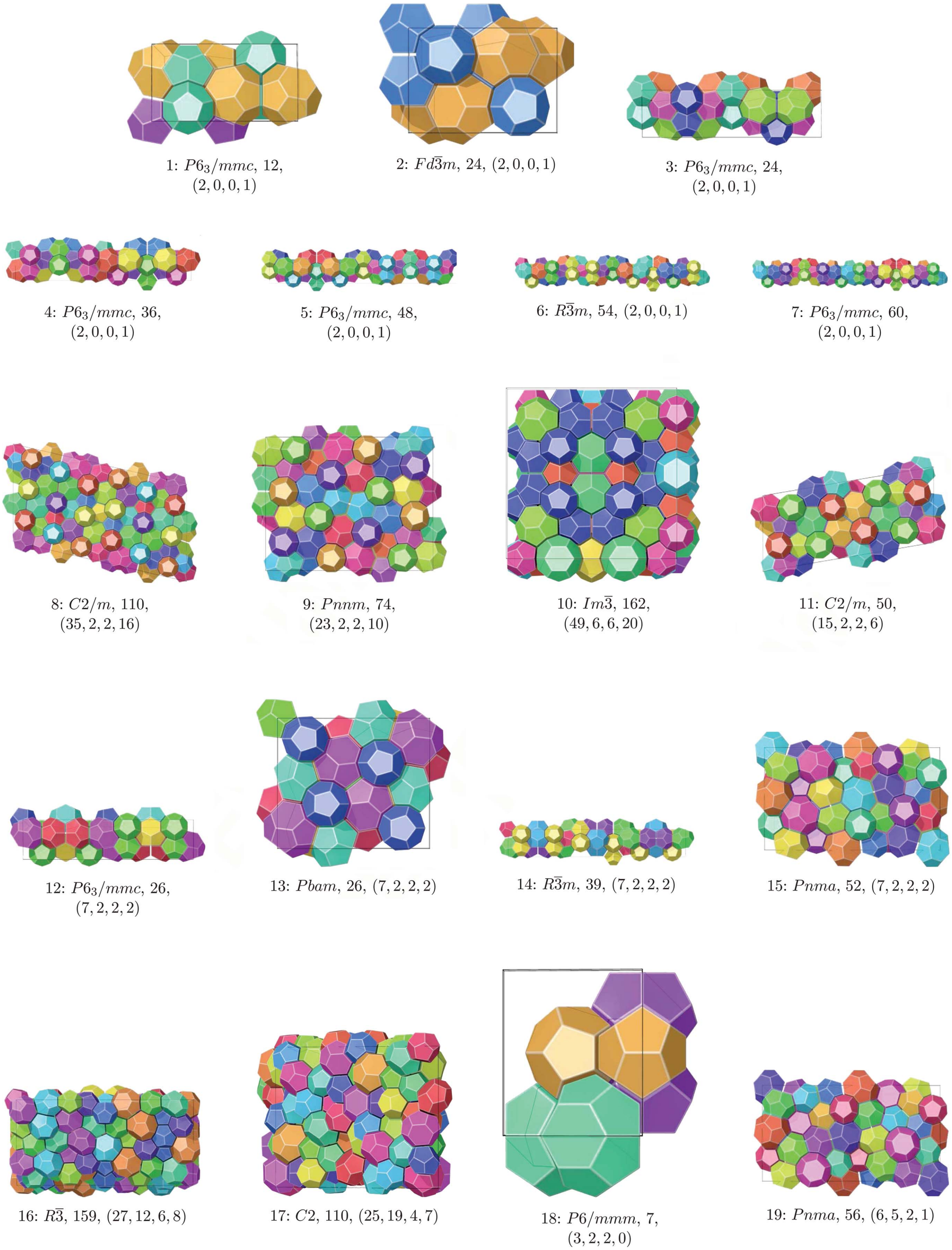


Figure 5
Known physical space fullerenes.

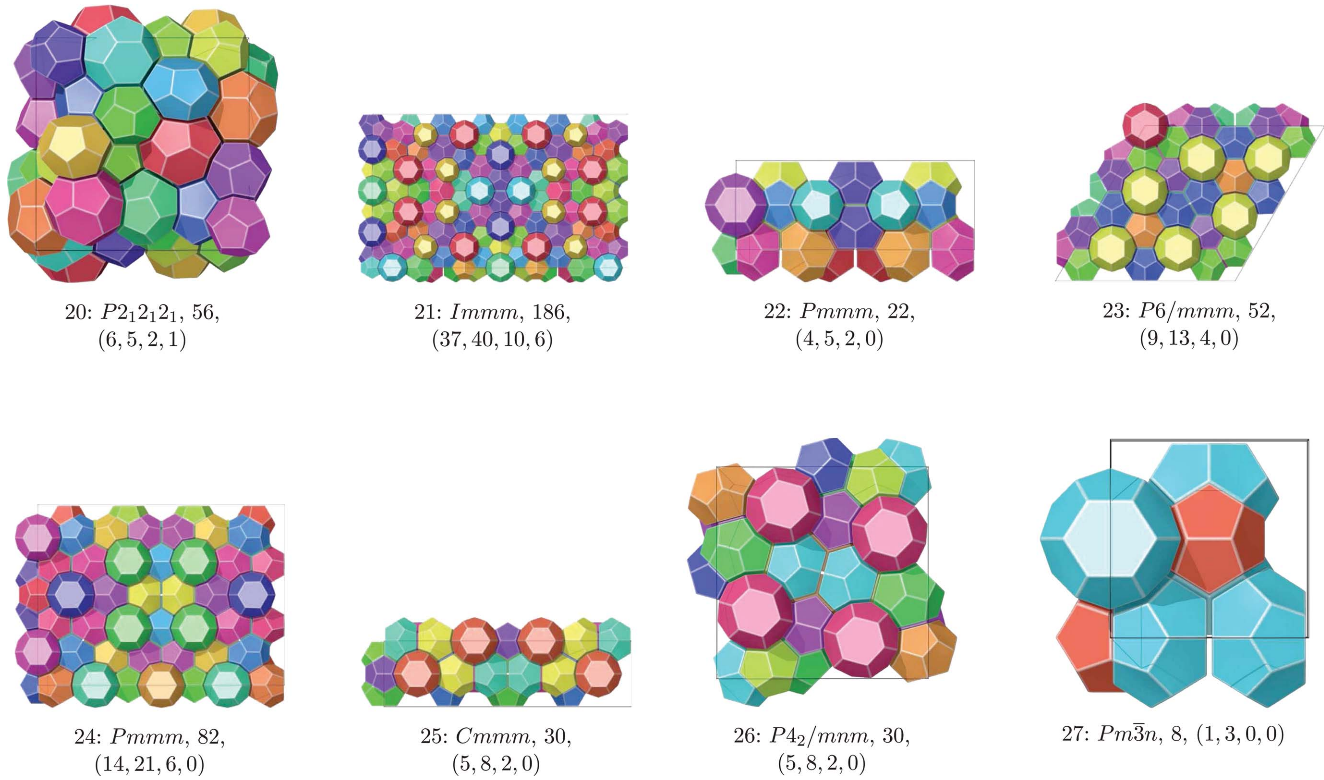


Figure 5 (continued)

periodic tilings (see Delgado-Friedrichs, 2000*b*; Delgado-Friedrichs *et al.*, 2006; Delgado-Friedrichs & O'Keeffe, 2007). Since in our case we do not have any symmetry assumptions, we cannot derive full enumeration results. A similar work is the enumeration in Delgado-Friedrichs & O'Keeffe (2006) of the space fullerenes with at most seven orbits of flags. However, in the case of FK space fullerenes it is difficult to impose the specific type of the obtained cells. So, instead of enumerating Delaney symbols, we enumerate orientable finite $\mathcal{C}_3$-complexes, whose maximal cells are Frank–Kasper polyhedra.

A graph is 3-connected if, after removing any two vertices of it, it remains connected. It is well known that 3-connected graphs admit at most one realization as plane graphs. The Frank–Kasper polyhedra are 3-connected, so we can encode a $\mathcal{C}_3$-complex whose cells are Frank–Kasper polyhedra by pairs (F_0, F_3) instead of flags (F_0, F_1, F_2, F_3) for Delaney symbols.

Two restrictions are made on the $\mathcal{C}_3$-complexes that we enumerate: we assume orientability and that no cell has a self-adjacency, but multiple adjacencies are allowed. Those two restrictions give additional speed but limit *a priori* the complexes we can obtain. We cannot exclude that some FK space fullerenes with less than 20 cells per fundamental domain have been missed, though this is unlikely.

The enumeration algorithm is a simple tree search of all possibilities. We add cells one by one and we keep track of the faces that are contained in only one cell for which further cells have to be added. The program returns a list of orientable manifolds $\tilde{M}$ and we test whether their universal covering M is the Euclidean space $\mathbb{E}^3$ using *3dt*. The manifold $\tilde{M}$ is not necessarily a three-dimensional torus; the reason for this is that in dimension 3 there exist ten groups (called Bieberbach groups) whose elements different from identity do not fix any point, and thus ten different 3-manifolds whose universal cover is the Euclidean plane. Six of those manifolds are orientable and there are thus six possible Bieberbach subgroups of the automorphism groups of the obtained manifold that can be factored out in the computation. This explains why we can obtain some FK space fullerenes with large fundamental domains: their symmetry group is big and thus the manifold $\tilde{M}$ is small.

The computer search was a large-scale computation lasting months. Experimentally, we found out that if we increase the number n of cells in the fundamental domain reduced by the Bieberbach group action by 1 then the running time is multiplied by a factor between 2 and 3. We use parallel computers for subdividing the tree search into a number of independent runs. One possibility which we have not considered is to use symmetries to reduce the running time. This could potentially divide the running time by a significant factor but it would not change the fact that as n grows the growth of the computation is at least exponential.

4. Description of obtained structures

The fraction sequence $(1, 3, 0, 0)$ is unique, *i.e.* there is a unique space fullerene A_{15} with this fraction. The FK space

Table 2
List of new space fullerenes with known fraction.

For each such FK space fullerene we give the space group, the number of cells in a fundamental domain, the average coordination number, the fraction sequence, the partition of cells into orbits and a description of the major skeleton.

No.	Group	Fundamental domain	$\bar{f}$	Fraction	Cell orbits	Major skeleton
1	*Cmmm*	13 × 2	13.384	(7, 2, 2, 2)	$(14_{2,4,8}, 4_4, 4_4, 4_4)$	$(0, 2, 2), \mathbb{Z}^2(2, 0, 0)$
2	*Cmcm*	26 × 2	13.384	(7, 2, 2, 2)	$(28_{4^3,8^2}, 8_8, 8_8, 8_8)$	$(0, 4, 4), 2\mathbb{Z}^2(2, 0, 0)$
3	*Cmca*	14 × 2	13.428	(3, 2, 2, 0)	$(12_{4,8}, 8_8, 8_8, 0)$	$2\mathbb{Z}(2, 2, 0)$
4	*Cmca*	28 × 2	13.428	(3, 2, 2, 0)	$(24_{8^3}, 16_{8^2}, 16_{8^2}, 0)$	$2\mathbb{Z}(4, 4, 0)$
5	*Cmcm*	28 × 2	13.428	(3, 2, 2, 0)	$(24_{16,4^2}, 16_{4^2,8}, 16_{4^2,8}, 0)$	$\mathbb{Z}(0, 4, 0), 2\mathbb{Z}(2, 2, 0), \mathbb{Z}^2(4, 0, 0)$
6	$I\bar{4}m2$	14 × 2	13.428	(6, 5, 2, 1)	$(12_{4,8}, 10_{2,8}, 4_4, 2_2)$	$(1, 2, 1), 2\mathbb{Z}^2(2, 0, 0)$
7	$P2_12_12$	28	13.428	(6, 5, 2, 1)	$(12_{4^3}, 10_{2,4^2}, 4_4, 2_2)$	$2\mathbb{Z}/2\mathbb{Z}(5, 2, 1)$
8	$Cmc2_1$	28 × 2	13.428	(6, 5, 2, 1)	$(24_{4^4,8}, 20_{4^3,8}, 8_{4^2}, 4_4)$	$(6, 4, 2), 2\mathbb{Z}^2(2, 0, 0)$
9	$Cmc2_1$	28 × 2	13.428	(6, 5, 2, 1)	$(24_{4^4,8}, 20_{4^3,8}, 8_{4^2}, 4_4)$	$2(3, 2, 1), 2\mathbb{Z}^2(2, 0, 0)$
10	$P2_12_12_1$	56	13.428	(6, 5, 2, 1)	$(24_{4^6}, 20_{4^5}, 8_{4^2}, 4_4)$	$2(10, 4, 2)$
11	$I4_1/amd$	22 × 2	13.454	(4, 5, 2, 0)	$(16_{8^2}, 20_{16,4}, 8_8, 0)$	$(2, 4, 0), 4\mathbb{Z}^2(2, 0, 0)$

fullerenes with fraction (2, 0, 0, 1) are called Laves space fullerenes. A continuum of them exists but, for energetic reasons, only short layer stackings are found in real systems. Their physical realizations, Laves phases (or, to specify main contributors, Friauf–Laves–Komura phases), are chemically intermetallic FK compounds with the approximate formula AB_2 where atom $A \simeq (3/2)^{1/2}$ larger; there are about 1400 of them (see Thoma, 2001).

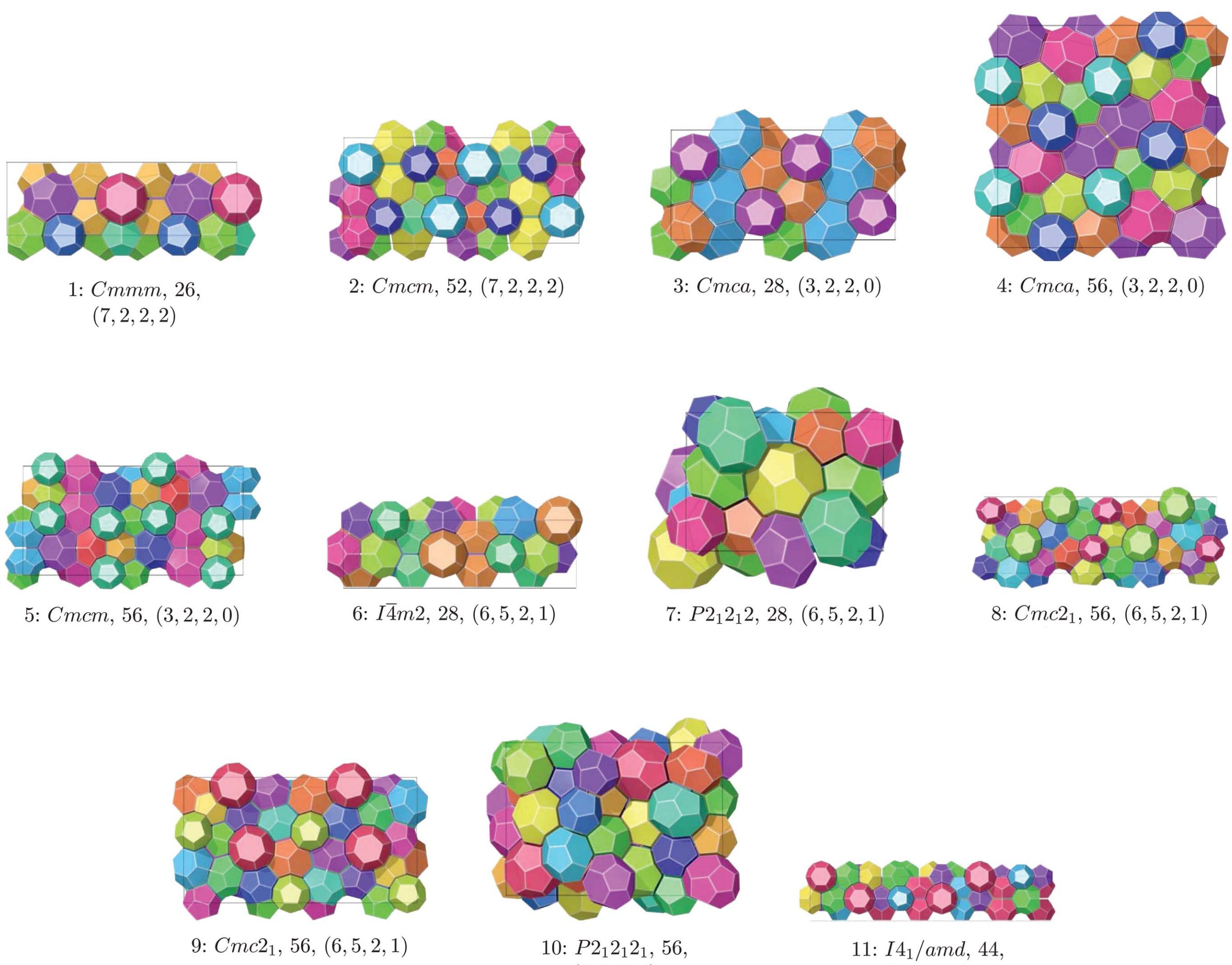

1: $Cmmm$, 26, (7, 2, 2, 2)
2: $Cmcm$, 52, (7, 2, 2, 2)
3: $Cmca$, 28, (3, 2, 2, 0)
4: $Cmca$, 56, (3, 2, 2, 0)
5: $Cmcm$, 56, (3, 2, 2, 0)
6: $I\bar{4}m2$, 28, (6, 5, 2, 1)
7: $P2_12_12$, 28, (6, 5, 2, 1)
8: $Cmc2_1$, 56, (6, 5, 2, 1)
9: $Cmc2_1$, 56, (6, 5, 2, 1)
10: $P2_12_12_1$, 56, (6, 5, 2, 1)
11: $I4_1/amd$, 44, (4, 5, 2, 0)

Figure 6
New space fullerenes with known fraction.

Table 3
List of other new space fullerenes.

For each such FK space fullerene we give the space group, the number of cells in a fundamental domain, the average coordination number, the fraction sequence, the partition of cells into orbits and a description of the major skeleton.

No.	Group	Fundamental domain	$\bar{f}$	Fraction	Cell orbits	Major skeleton
1	$Pmmn$	38	13.368	(11, 1, 4, 3)	$(22_{2,4^3,8}, 2_2, 8_{2^2,4}, 6_{2,4})$	$(2, 4, 6), \mathbb{Z}(0, 4, 0)$
2	$P\bar{6}m2$	19	13.368	(11, 2, 2, 4)	$(11_{2,3,6}, 2_2, 2_{1^2}, 4_{2^2})$	$(2, 0, 4), \mathbb{Z}(0, 2, 0)$
3	$P6_3/mmc$	38	13.368	(11, 2, 2, 4)	$(22_{12,4,6}, 4_4, 4_4, 8_{4^2})$	$(4, 0, 8), 2\mathbb{Z}(0, 2, 0)$
4	$P6_3/mmc$	38	13.368	(11, 2, 2, 4)	$(22_{12,4,6}, 4_4, 4_{2^2}, 8_{4^2})$	$(4, 0, 8), 2\mathbb{Z}(0, 2, 0)$
5	$Cmmm$	19 × 2	13.368	(11, 2, 2, 4)	$(22_{2,4,8^2}, 4_4, 4_4, 8_{4^2})$	$(0, 2, 4), \mathbb{Z}^2(2, 0, 0)$
6	$Immm$	19 × 2	13.368	(11, 2, 2, 4)	$(22_{2,4,8^2}, 4_4, 4_4, 8_8)$	$(0, 2, 4), \mathbb{Z}^2(2, 0, 0)$
7	$Pmmn$	38	13.368	(11, 2, 2, 4)	$(22_{2,4^5}, 4_4, 4_4, 8_{2^2,4})$	$(0, 4, 8), 2\mathbb{Z}^2(2, 0, 0)$
8	$Pmma$	38	13.368	(11, 2, 2, 4)	$(22_{2^5,4^3}, 4_4, 4_4, 8_{4^2})$	$(0, 4, 8), 2\mathbb{Z}^2(2, 0, 0)$
9	$R\bar{3}m$	19 × 3	13.368	(11, 2, 2, 4)	$(33_{18,6,9}, 6_6, 6_6, 12_{6^2})$	$(2, 0, 4), \mathbb{Z}(0, 2, 0)$
10	$P3_221$	57	13.368	(11, 2, 2, 4)	$(33_{3,6^5}, 6_6, 6_{3^2}, 12_{6^2})$	$(6, 6, 12)$
11	$Cmcm$	38 × 2	13.368	(11, 2, 2, 4)	$(44_{16,4,8^3}, 8_8, 8_8, 16_{4^2,8})$	$(0, 4, 8), 2\mathbb{Z}^2(2, 0, 0)$
12	$Cmc2_1$	38 × 2	13.368	(11, 2, 2, 4)	$(44_{4^5,8^3}, 8_{4^2}, 8_{4^2}, 16_{4^4})$	$(4, 4, 8)$
13	$P4_2/mmc$	32	13.375	(9, 2, 2, 3)	$(18_{2,8^2}, 4_4, 4_4, 6_{2,4})$	$(0, 4, 6), 2\mathbb{Z}^2(2, 0, 0)$
14	$P4_2/mmc$	20	13.400	(5, 2, 2, 1)	$(10_{2,8}, 4_4, 4_4, 2_2)$	$(0, 4, 2), 2\mathbb{Z}^2(2, 0, 0)$
15	$P12/m1$	20	13.400	(5, 2, 2, 1)	$(10_{1^2,2^2,4}, 4_{2^2}, 4_{2^2}, 2_2)$	$(2, 4, 2), \mathbb{Z}^2(2, 0, 0)$
16	$P6_3/mmc$	40	13.400	(5, 2, 2, 1)	$(20_{12,2,6}, 8_{4^2}, 8_{4^2}, 4_4)$	$(8, 0, 4), 4\mathbb{Z}(0, 2, 0)$
17	$Imma$	20 × 2	13.400	(5, 2, 2, 1)	$(20_{4^3,8}, 8_8, 8_{4^2}, 4_4)$	$(0, 4, 2), 2\mathbb{Z}^2(2, 0, 0)$
18	$Cmcm$	20 × 2	13.400	(5, 2, 2, 1)	$(20_{4,8^2}, 8_8, 8_8, 4_4)$	$\mathbb{Z}/3\mathbb{Z}(4, 4, 2)$
19	$Pmna$	40	13.400	(5, 2, 2, 1)	$(20_{2^2,4^2,8}, 8_{4^2}, 8_{4^2}, 4_4)$	$(4, 8, 4), 2\mathbb{Z}^2(2, 0, 0)$
20	$Pmna$	40	13.400	(5, 2, 2, 1)	$(20_{2^2,4^4}, 8_{4^2}, 8_{4^2}, 4_4)$	$(8, 8, 4)$
21	$Pbam$	40	13.400	(5, 2, 2, 1)	$(20_{4^3,8}, 8_{4^2}, 8_{4^2}, 4_4)$	$(4, 8, 4), 2\mathbb{Z}^2(2, 0, 0)$
22	$Ima2$	20 × 2	13.400	(5, 2, 2, 1)	$(20_{4^3,8}, 8_{4^2}, 8_{4^2}, 4_4)$	$(2, 4, 2), \mathbb{Z}^2(2, 0, 0)$
23	$Pnma$	40	13.400	(5, 2, 2, 1)	$(20_{4^3,8}, 8_{4^2}, 8_{4^2}, 4_4)$	$\mathbb{Z}/3\mathbb{Z}(8, 8, 4)$
24	$Pmma$	40	13.400	(5, 2, 2, 1)	$(20_{2^2,4^2,8}, 8_{4^2}, 8_{2^2,4}, 4_4)$	$(4, 8, 4), 2\mathbb{Z}^2(2, 0, 0)$
25	$Pmc2_1$	40	13.400	(5, 2, 2, 1)	$(20_{2^6,4^2}, 8_{2^2,4}, 8_{2^4}, 4_{2^2})$	$(4, 8, 4), 2\mathbb{Z}^2(2, 0, 0)$
26	$Pmc2_1$	40	13.400	(5, 2, 2, 1)	$(20_{2^6,4^2}, 8_{2^2,4}, 8_{2^4}, 4_{2^2})$	$(4, 8, 4), 2\mathbb{Z}^2(2, 0, 0)$
27	$R\bar{3}m$	20 × 3	13.400	(5, 2, 2, 1)	$(30_{18,3,9}, 12_{6^2}, 12_{6^2}, 6_6)$	$(4, 0, 2), 2\mathbb{Z}(0, 2, 0)$
28	$P6_222$	60	13.400	(5, 2, 2, 1)	$(30_{12,6^3}, 12_{12}, 12_{6^2}, 6_6)$	$(12, 6, 6), 3\mathbb{Z}(0, 2, 0)$
29	$P3_221$	60	13.400	(5, 2, 2, 1)	$(30_{3^2,6^4}, 12_{6^2}, 12_{6^2}, 6_6)$	$(12, 12, 6)$
30	$Fmmm$	20 × 4	13.400	(5, 2, 2, 1)	$(40_{16^2,8}, 16_{16}, 16_{8^2}, 8_8)$	$\mathbb{Z}(0, 2, 0), \mathbb{Z}/2\mathbb{Z}(4, 2, 2)$
31	$Cmcm$	40 × 2	13.400	(5, 2, 2, 1)	$(40_{4^2,8^4}, 16_{8^2}, 16_{4^2,8}, 8_8)$	$(0, 8, 4), 4\mathbb{Z}^2(2, 0, 0)$
32	$Cmcm$	40 × 2	13.400	(5, 2, 2, 1)	$(40_{4^4,8^3}, 16_{8^2}, 16_{8^2}, 8_8)$	$(0, 8, 4), 4\mathbb{Z}^2(2, 0, 0)$
33	$Cmc2_1$	40 × 2	13.400	(5, 2, 2, 1)	$(40_{4^6,8^2}, 16_{4^2,8}, 16_{4^4}, 8_{4^2})$	$(4, 8, 4), 2\mathbb{Z}^2(2, 0, 0)$
34	$Cccm$	20 × 2	13.400	(5, 3, 0, 2)	$(20_{4,8^2}, 12_{4,8}, 0, 8_8)$	$(4, 0, 4), \mathbb{Z}^2(2, 0, 0)$
35	$Pmna$	40	13.400	(5, 3, 0, 2)	$(20_{2^2,4^4}, 12_{4^3}, 0, 8_{4^2})$	$(8, 0, 8), 2\mathbb{Z}^2(2, 0, 0)$
36	$Pmma$	40	13.400	(5, 3, 0, 2)	$(20_{2^4,4^3}, 12_{4^3}, 0, 8_{4^2})$	$(4, 0, 8), 2\mathbb{Z}^2(2, 0, 0), \mathbb{Z}^2(4, 0, 0)$
37	$Cmcm$	40 × 2	13.400	(10, 3, 6, 1)	$(40_{16,4^2,8^2}, 12_{4,8}, 24_{4^2,8^2}, 4_4)$	$(2, 8, 2), \mathbb{Z}(0, 4, 0), 2\mathbb{Z}^2(2, 0, 0)$
38	$Cmc2_1$	40 × 2	13.400	(10, 3, 6, 1)	$(40_{4^4,8^3}, 12_{4^3}, 24_{4^6}, 4_4)$	$(6, 12, 2)$
39	$C222_1$	40 × 2	13.400	(10, 3, 6, 1)	$(40_{4^2,8^4}, 12_{4,8}, 24_{8^3}, 4_4)$	$(6, 12, 2)$
40	$P\bar{4}m2$	20	13.400	(10, 5, 2, 3)	$(10_{2,4^2}, 5_{1,4}, 2_2, 3_{1,2})$	$(1, 2, 3), 2\mathbb{Z}^2(2, 0, 0)$
41	$Pmn2_1$	40	13.400	(10, 5, 2, 3)	$(20_{2^6,4^2}, 10_{2^3,4}, 4_{2^2}, 6_{2^3})$	$(6, 4, 6), 2\mathbb{Z}^2(2, 0, 0)$
42	$Pmn2_1$	40	13.400	(10, 5, 2, 3)	$(20_{2^6,4^2}, 10_{2^3,4}, 4_{2^2}, 6_{2^3})$	$(6, 4, 6), 2\mathbb{Z}^2(2, 0, 0)$
43	$Pmc2_1$	40	13.400	(10, 5, 2, 3)	$(20_{2^6,4^2}, 10_{2^3,4}, 4_{2^2}, 6_{2^3})$	$(6, 4, 6), 2\mathbb{Z}^2(2, 0, 0)$
44	$Cmc2_1$	40 × 2	13.400	(10, 5, 2, 3)	$(40_{4^6,8^2}, 20_{4^3,8}, 8_{4^2}, 12_{4^3})$	$(6, 4, 6), 2\mathbb{Z}^2(2, 0, 0)$
45	$Cmc2_1$	40 × 2	13.400	(10, 5, 2, 3)	$(40_{4^6,8^2}, 20_{4^3,8}, 8_{4^2}, 12_{4^3})$	$(6, 4, 6), 2\mathbb{Z}^2(2, 0, 0)$
46	$I4_1/amd$	34 × 2	13.411	(8, 4, 4, 1)	$(32_{16,8^2}, 16_{16}, 16_{8^2}, 4_4)$	$(0, 8, 2), 4\mathbb{Z}^2(2, 0, 0)$
47	$I4_1/amd$	34 × 2	13.411	(8, 4, 4, 1)	$(32_{16^2}, 16_{16}, 16_{16}, 4_4)$	$(0, 8, 0), \mathbb{Z}/3\mathbb{Z}(8, 0, 2)$
48	$I4_1/amd$	34 × 2	13.411	(8, 5, 2, 2)	$(32_{16,8^2}, 20_{16,4}, 8_8, 8_8)$	$(2, 4, 4), 4\mathbb{Z}^2(2, 0, 0)$
49	$I4_122$	34 × 2	13.411	(8, 5, 2, 2)	$(32_{16,8^2}, 20_{16,4}, 8_8, 8_8)$	$(2, 4, 0), (8, 0, 4)$
50	$Cmma$	14 × 2	13.428	(3, 3, 0, 1)	$(12_{4,8}, 12_{4,8}, 0, 4_4)$	$\mathbb{Z}/2\mathbb{Z}(4, 0, 2), \mathbb{Z}^2(2, 0, 0)$
51	$Pmna$	28	13.428	(3, 3, 0, 1)	$(12_{2^2,4^2}, 12_{4^3}, 0, 4_4)$	$(8, 0, 4), 2\mathbb{Z}^2(2, 0, 0)$
52	$Cmcm$	28 × 2	13.428	(3, 3, 0, 1)	$(24_{4^2,8^2}, 24_{8^3}, 0, 8_8)$	$(4, 0, 4), 2\mathbb{Z}^2(2, 0, 0), \mathbb{Z}^2(4, 0, 0)$
53	$P4_2/mmc$	36	13.444	(7, 7, 4, 0)	$(14_{2,4,8}, 14_{2,4,8}, 8_{4^2}, 0)$	$(2, 8, 0), 6\mathbb{Z}^2(2, 0, 0)$
54	$P4_2/mmc$	36	13.444	(7, 8, 2, 1)	$(14_{2,4,8}, 16_{4^2,8}, 4_4, 2_2)$	$(4, 4, 2), 6\mathbb{Z}^2(2, 0, 0)$
55	$P4_32_12$	60	13.466	(7, 4, 2, 2)	$(28_{4,8^3}, 16_{8^2}, 8_8, 8_8)$	$4\mathbb{Z}(4, 2, 2)$
56	$I4_1/amd$	38 × 2	13.473	(6, 11, 2, 0)	$(24_{8^3}, 44_{16^2,4,8}, 8_8, 0)$	$(6, 4, 0), 8\mathbb{Z}^2(2, 0, 0)$
57	$P4_2/mnm$	32	13.500	(3, 3, 2, 0)	$(12_{4,8}, 12_{4,8}, 8_{4^2}, 0)$	$2\mathbb{Z}(0, 2, 0), 2\mathbb{Z}^2(6, 2, 0)$
58	$P4_2/mnm$	18	13.555	(3, 4, 2, 0)	$(6_{2,4}, 8_8, 4_4, 0)$	$2\mathbb{Z}^2(4, 2, 0)$
59	$Pccn$	36	13.555	(3, 4, 2, 0)	$(12_{4,8}, 16_{4^2,8}, 8_8, 0)$	$2\mathbb{Z}(8, 4, 0)$
60	$P6_422$	54	13.555	(3, 4, 2, 0)	$(18_{3^2,6^2}, 24_{12^2}, 12_{6^2}, 0)$	$3\mathbb{Z} \times \mathbb{Z}/3\mathbb{Z}(4, 2, 0), 3\mathbb{Z}^2(4, 2, 0)$

The vectors $v_{120} = (1, 0, 0, 0)$, $v_{A15} = (1, 3, 0, 0)$, $v_Z = (3, 2, 2, 0)$, $v_{C15} = (2, 0, 0, 1)$ being linearly independent, any vector x [let us denote it $(x_{20}, x_{24}, x_{26}, x_{28})$] is a linear combination $a_0 v_{120} + a_1 v_{A15} + a_2 v_Z + a_3 v_{C15}$. In these terms, the Yarmolyuk–Kripyakevich conjecture is equivalent to saying that if x is the fraction sequence of the FK phase then $a_0 = 0$, or, equivalently, $6x_{20} - 2x_{24} - 7x_{26} - 12x_{28} = 0$.

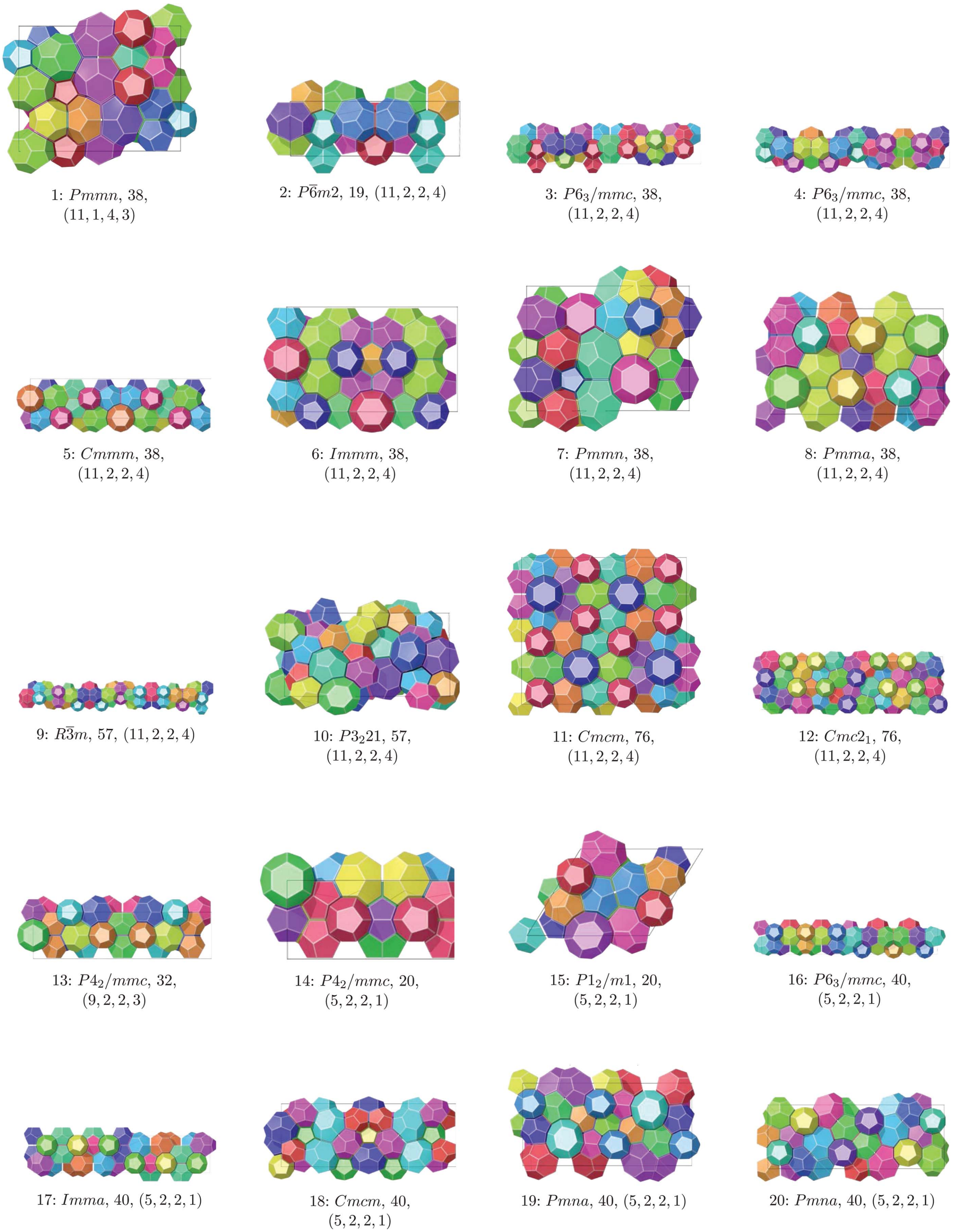
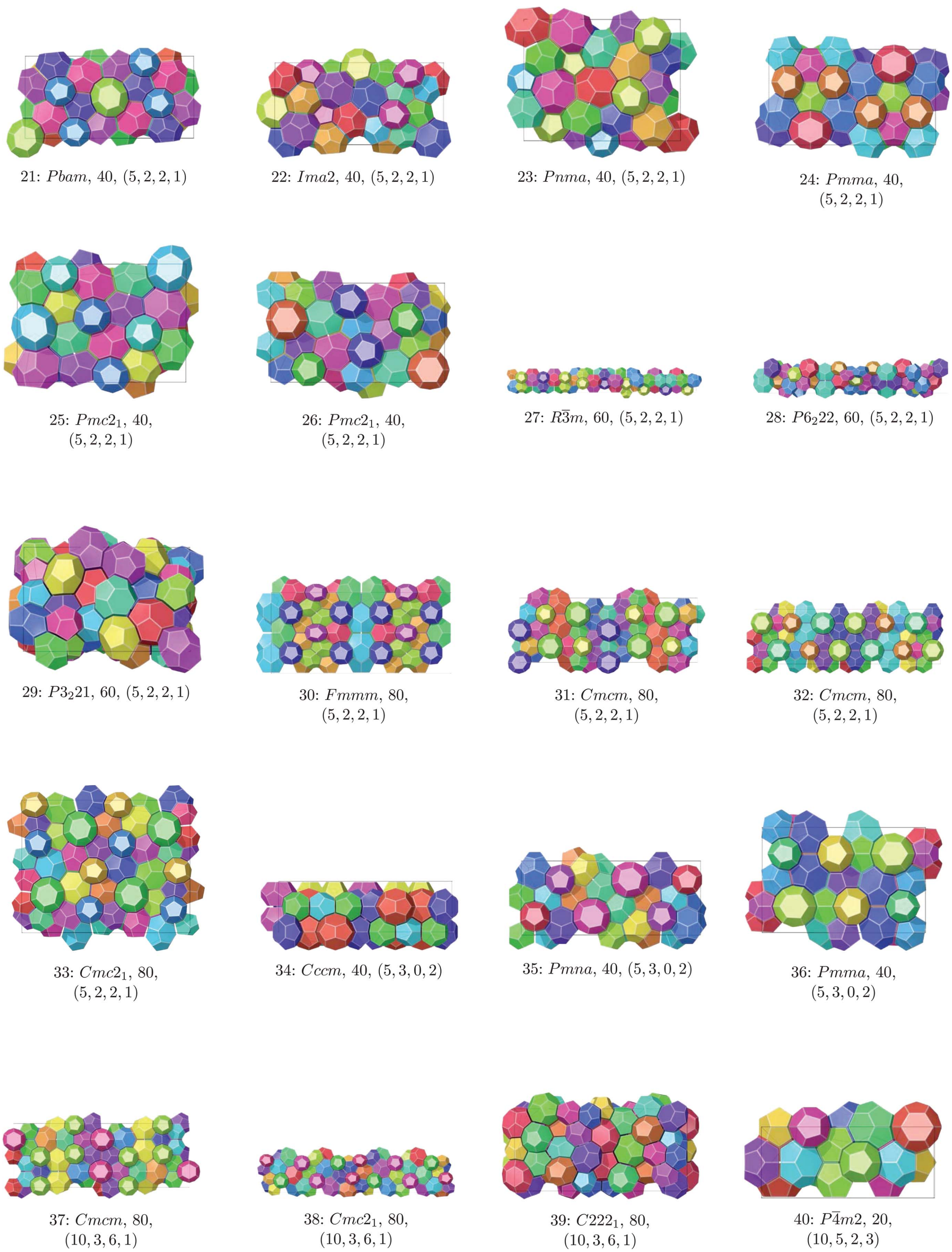


Figure 7
Other new space fullerenes.



21: $Pbam$, 40, $(5, 2, 2, 1)$

22: $Ima2$, 40, $(5, 2, 2, 1)$

23: $Pnma$, 40, $(5, 2, 2, 1)$

24: $Pmma$, 40, $(5, 2, 2, 1)$

25: $Pmc2_1$, 40, $(5, 2, 2, 1)$

26: $Pmc2_1$, 40, $(5, 2, 2, 1)$

27: $R\overline{3}m$, 60, $(5, 2, 2, 1)$

28: $P6_222$, 60, $(5, 2, 2, 1)$

29: $P3_221$, 60, $(5, 2, 2, 1)$

30: $Fmmm$, 80, $(5, 2, 2, 1)$

31: $Cmcm$, 80, $(5, 2, 2, 1)$

32: $Cmcm$, 80, $(5, 2, 2, 1)$

33: $Cmc2_1$, 80, $(5, 2, 2, 1)$

34: $Cccm$, 40, $(5, 3, 0, 2)$

35: $Pmna$, 40, $(5, 3, 0, 2)$

36: $Pmma$, 40, $(5, 3, 0, 2)$

37: $Cmcm$, 80, $(10, 3, 6, 1)$

38: $Cmc2_1$, 80, $(10, 3, 6, 1)$

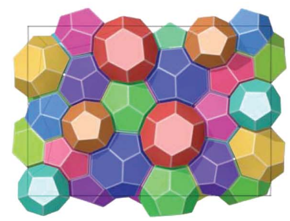
39: $C222_1$, 80, $(10, 3, 6, 1)$

40: $P\overline{4}m2$, 20, $(10, 5, 2, 3)$

Figure 7 (continued)

41: $Pmn2_1$, 40, $(10, 5, 2, 3)$

42: $Pmn2_1$, 40, $(10, 5, 2, 3)$

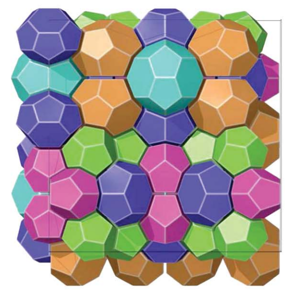


43: $Pmc2_1$, 40, $(10, 5, 2, 3)$

44: $Cmc2_1$, 80, $(10, 5, 2, 3)$

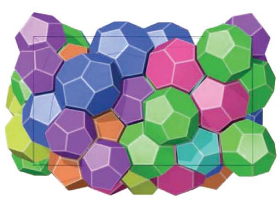
45: $Cmc2_1$, 80, $(10, 5, 2, 3)$

46: $I4_1/amd$, 68, $(8, 4, 4, 1)$

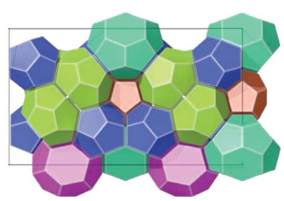


47: $I4_1/amd$, 68, $(8, 4, 4, 1)$

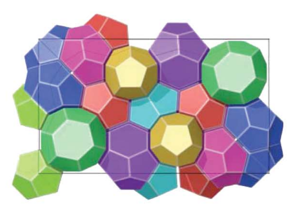
48: $I4_1/amd$, 68, $(8, 5, 2, 2)$



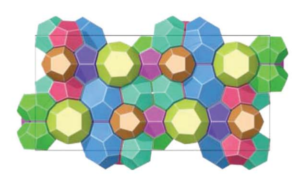
49: $I4_122$, 68, $(8, 5, 2, 2)$



50: $Cmma$, 28, $(3, 3, 0, 1)$

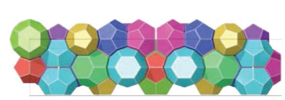


51: $Pmna$, 28, $(3, 3, 0, 1)$



52: $Cmcm$, 56, $(3, 3, 0, 1)$

53: $P4_2/mmc$, 36, $(7, 7, 4, 0)$

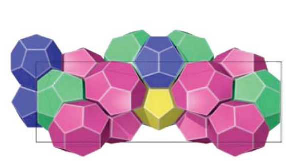


54: $P4_2/mmc$, 36, $(7, 8, 2, 1)$

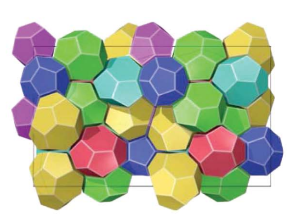
55: $P4_32_12$, 60, $(7, 4, 2, 2)$

56: $I4_1/amd$, 76, $(6, 11, 2, 0)$

57: $P4_2/mnm$, 32, $(3, 3, 2, 0)$



58: $P4_2/mnm$, 18, $(3, 4, 2, 0)$



59: $Pccn$, 36, $(3, 4, 2, 0)$

60: $P6_422$, 54, $(3, 4, 2, 0)$

Figure 7 (continued)

Now, if a fraction sequence satisfies the Yarmolyuk–Kripyakevich conjecture, then

$$\frac{x_{24}}{3}+x_{26}+\frac{5x_{28}}{3}\le x_{20}\le\frac{x_{24}}{2}+\frac{5x_{26}}{4}+2x_{28}$$

holds, *i.e.* the mean face size $\overline{q}$ belongs to [5.1, 5.(1)]. Furthermore, the equality cases are realized uniquely by Laves and A_{15} phases (in lower and upper bounds, respectively).

The fractions (7, 4, 2, 2), (3, 3, 2, 0), (3, 4, 2, 0) (see Table 3) are counterexamples to the Yarmolyuk–Kripyakevich rule. They are of mean face number $\sim$5.1089, 5.(1) or $\sim$5.1148, *i.e.* within the range [5.1, 5.(1)], outside of it, or exactly on the border. So, three structures with fraction (3, 4, 2, 0) are counterexamples to a weakening of the Yarmolyuk–Kripyakevich conjecture (Nelson & Spaepen, 1989) that $\overline{q}\le 5.(1)$, or, equivalently, that $\overline{f}\le 13.5$. Note that the fraction (3, 3, 2, 0) is uniquely found with $\overline{f}$ = 13.5 besides (1, 3, 0, 0) of A_{15}.

The value 110 for phase *K* in Table 1 differs from *N* = 220 in Shoemaker & Shoemaker (1986), where a superstructure was considered. We also give different correct groups for structures *M* and *P*.

Two of 16 obtained new fractions, (3, 3, 0, 1) and (5, 3, 0, 2) (see Table 3), are counterexamples to the condition given by Hellner & Pearson (1986) that $x_{28}, x_{24} > 0$ implies $x_{26} > 0$. On a positive note, none of the obtained 23 fractions (seven known and 16 new ones) violated the lower bounds of Nelson & Spaepen's (1989) conjecture: $\overline{q}\ge 5.1$, *i.e.* $\overline{f}\ge 13.(3)$. Also, we always have $x_{20} > 0$ and $x_{20}\ge \max(x_{24}/3, 3x_{26}/2, 2x_{28})$. For all 23 fractions found, except (2, 0, 0, 1), it holds that $x_{24} > 0$.

There are 27 known physical FK space fullerenes (see, for example, Rivier & Aste, 1996). Some reported FK phases were not included in the listing because of incompleteness of defining data on them: the C_1 phase (Wang *et al.*, 1986) and four Laves phases, namely, 16-, 21-layers (Komura & Kitano, 1977), 12-layers (Kitano *et al.*, 1998) and rhombohedral (Dwight & Kimball, 1974). We attribute name *mz* to the structures of Mg_4Zn_7 which were previously unnamed. The structure **odk** in the RCSR database corresponds to structure number 58 in Table 3.

It is interesting that, among all obtained space fullerenes with x_{28} = 0, those which are described in terms of hexagonal t.c.p. structures, *i.e.* from the Frank, Kasper and Sullivan construction, are exactly those which are physically realized.

The list of known physical space fullerenes is given in Table 1 and Fig. 5. The list of new space fullerenes whose fraction sequences are known is given in Table 2 and Fig. 6. The list of new space fullerenes with new fraction sequences is given in Table 3 and Fig. 7. A .cgd text file description of the new structures is available as two supplementary files.[2] The crystallographic fundamental domain is obtained by putting together *m* copies of the mathematical fundamental domain (which tile the space under translation of the space group). We give the number *N* of cells in the mathematical fundamental domain if $m = 1$ and $N\times m$ if $m > 1$. We give the decomposition of the set of cells in the mathematical fundamental domain into orbits under the space group. The major skeleton is computed for all space fullerenes given in the tables. Vertices corresponding to F_{20} are discarded since they are isolated. The partial fractions (x_{24}, x_{26}, x_{28}) of the connected components are given, together with the number of components of this type if finite. If a $\mathbb{Z}$ is put as prefix, then there exists a translation vector *v* of the space group such that all translations give distinct components of the major skeleton. If a $\mathbb{Z}/p\mathbb{Z}$ is put as prefix, then there is a translation of vector *v* of the space group such that the translations by $0, v, \ldots, (p-1)v$ are all distinct but the translation under pv is a symmetry of this component of the major skeleton. *A priori*, it is possible to have $\mathcal{T}_1$ and $\mathcal{T}_2$ non-isomorphic and Maj($\mathcal{T}_1$) isomorphic to Maj($\mathcal{T}_2$) but we did not find a single example of such pairs in the list of previously known and obtained space fullerenes. One possibility, which we have not considered for the enumeration process, is to build first the major skeleton or a component of it and then consider the addition of F_{20} in all possible ways. Based on all the known structures it seems reasonable to conjecture that any 3-periodic space fullerene has at least one dodecahedron in its structure and that its average coordination number and mean face size are larger than those of the DS space fullerene.

Another problem that we did not consider is whether or not the generated FK space fullerenes have faces that are contained in affine planes. Some of the obtained FK space fullerenes are very different from the known physical structures, for example, by having no apparent layering. It might be interesting to search for more infinite series of FK space fullerenes.

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[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: EO5006). Services for accessing these data are described at the back of the journal.

References

Alvarez, S. (2006). *Dalton Trans.* **17**, 2045–2051.
Delgado-Friedrichs, O. (1990). PhD thesis, Bielefeld University, Germany.
Delgado-Friedrichs, O. (2000*a*). *3dt*, http://www.gavrog.org/.
Delgado-Friedrichs, O. (2000*b*). *Discrete Comput. Geom.* **24**, 279–292.
Delgado-Friedrichs, O., Dress, A. & Huson, D. (1995). *Sém. Lothar. Combin.* **34**, B34*a*.
Delgado-Friedrichs, O. & O'Keeffe, M. (2006). *Acta Cryst.* A**62**, 228–229.
Delgado-Friedrichs, O. & O'Keeffe, M. (2007). *Acta Cryst.* A**63**, 344–347.
Delgado-Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2006). *Acta Cryst.* A**62**, 350–355.
Deza, M. & Shtogrin, M. I. (1999). *Southeast Asian Bull. Math.* **23**, 9–18.
Deza, M. & Shtogrin, M. I. (2009). *Russian Math. Surveys*, **64**, 139–141.
Dress, A. W. M. (1987). *Adv. Math.* **63**, 196–212.
Dwight, A. E. & Kimball, C. W. (1974). *Acta Cryst.* B**30**, 2791–2793.

Fowler, P. W. & Manolopoulos, D. E. (1995). *An Atlas of Fullerenes.* Oxford University Press.

Frank, F. C. (1952). *Proc. R. Soc. London Ser. A*, **215**, 43–46.

Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184–190.

Frank, F. C. & Kasper, J. S. (1959). *Acta Cryst.* **12**, 483–499.

Gabrielli, R. (2009). *Philos. Mag. Lett.* **89**, 483–491.

Hellner, E. & Pearson, W. B. (1986). *J. Solid State Chem.* **70**, 241–248.

Jeffrey, G. A. (1984). *Inclusion Compounds*, Vol. 1, edited by J. L. Atwood, J. E. D. Davies and D. D. MacNicol, pp. 135–182. New York: Academic Press.

Kitano, Y., Akitoh, S.-I., Mitarai, M., Ohnishi, K., Kitasaka, K., Noguchi, K. & Numata, M. (1998). *Microsc. Res. Tech.* **40**, 277–283.

Komura, Y. & Kitano, Y. (1977). *Acta Cryst.* B**33**, 2496–2501.

Kripyakevich, P. I. (1970). *Kristallografiya*, **15**, 690.

Kuo, K. H., Ye, H. Q. & Li, D. X. (1986). *J. Mater. Sci.* **21**, 2597–2622.

Lord, E. A., MacKay, A. L. & Ranganathan, S. (2006). *New Geometries for New Materials.* Cambridge University Press.

Meier, W. M. & Olson, D. H. (1992). *Atlas of Zeolite Structure Types*, 3rd ed. London: Butterworths.

Nelson, D. R. & Spaepen, F. (1989). *Solid State Phys.* **42**, 1–90.

O'Keeffe, M. & Hyde, B. G. (1996). *Crystal Structures I: Patterns and Symmetry.* Washington: Mineralogical Society of America.

O'Keeffe, M., Peskov, M. A., Ramsden, S. J. & Yaghi, O. M. (2008). *Acc. Chem. Res.* **41**, 1782–1789.

Pearson, W. B. & Shoemaker, C. B. (1969). *Acta Cryst.* B**25**, 1178–1183.

Rivier, N. & Aste, T. (1996). *Forma*, **11**, 223–231.

Sadoc, J. F. & Mosseri, R. (1985). *J. Phys.* **46**, 1809–1826.

Sadoc, J. F. & Mosseri, R. (1999). *Geometric Frustation.* Cambridge University Press.

Samson, S. (1968). *Structural Chemistry and Molecular Biology*, pp. 688–717. San Francisco: W. H. Freeman.

Sheng, H., Luo, W., Alamgir, F., Bai, J. & Ma, E. (2006). *Nature (London)*, **439**, 419–425.

Shoemaker, C. B. & Shoemaker, D. P. (1968). *Developments in the Structural Chemistry of Alloy Phases*, pp. 107–139. New York: Plenum.

Shoemaker, C. B. & Shoemaker, D. P. (1972). *Acta Cryst.* B**28**, 2957–2965.

Shoemaker, D. P. & Shoemaker, C. B. (1986). *Acta Cryst.* B**42**, 3–11.

Sloan, E. D. & Koh, C. (2007). *Clathrate Hydrates of Natural Gases*, 3rd ed. New York: M. Dekker.

Sullivan, J. M. (2000). *Proc. Eurofoam (Delft)*, pp. 111–119.

Thoma, D. L. (2001). *Intermetallic Laves Phases, Encyclopedia of Materials: Science and Technology*. USA: Elsevier.

Thurston, W. P. (1998). *Geometry and Topology Monographs 1, The Epstein Birthday Schrift*, pp. 511–549.

Vesnin, A. Y. (1989). *Math. Notes*, **49**, 575–577.

Wang, D. N., Ye, H. Q. & Kuo, K. H. (1986). *Acta Cryst.* B**42**, 21–25.

Weaire, D. & Phelan, R. (1994). *Philos. Mag. Lett.* **69**, 107–110.

Yarmolyuk, Y. P. & Kripyakevich, P. I. (1974). *Sov. Phys. Crystallogr.* **19**, 334–337.