Space fullerenes

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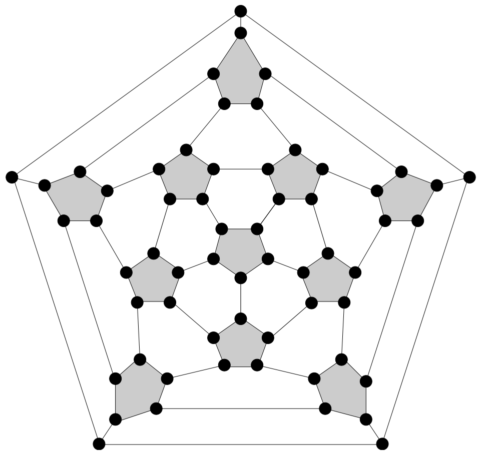
I. Introduction

Tilings

- 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 are polygons, not necessarily planar.
- Tiling T is face-to-face if each face belongs to =2 tiles.
- A tiling is simple if it is by *simple* (3-valent) polyhedra with 3 meeting in each edge and 4 in each vertex (both, 3 and 4, are minimal); so, vertices are 4-valent. Foam is simple tiling by bubbles.
- A tiling T is 3-periodic (or crystallographic) if $\mathrm{Aut}(T)$ contains translations in three non-coplanar directions.
- T is proper if $\mathrm{Aut}(T)$=$\mathrm{Aut}(G)$ for its 1-skeleton (net) G, i.e. vertex-edge graph of T, realized in the 3-space $\mathbb{E}^3$.

Fullerenes

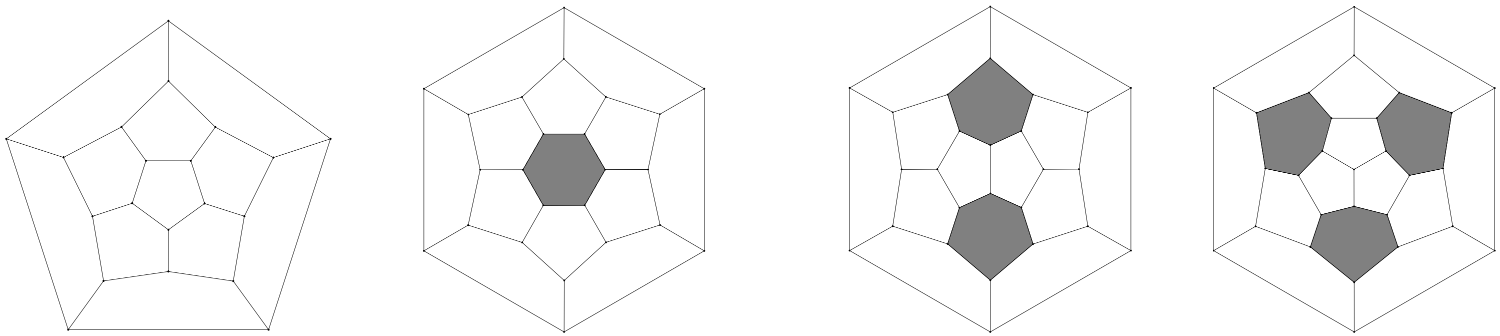
- A fullerene F_n is polyhedron with n 3-valent vertices and only 5-gonal and 6-gonal faces. So, p_5=12 and p_6=$\frac{n}{2}$-10.
- F_n exist for all even $n \geq 20$ except 22. Number of F_n is $1, 1, 1, 2, \dots, 1812, \dots$ for $n = 20, 24, 26, 28, \dots, 60, \dots$ Thurston,1998, implies that this number grows as n^9.
- There exist very efficient programs to enumerate them (FullGen by Brinkmann, CPF by Harmuth).
- Smallest fullerene with isolated pentagons is $F_{60}(I_h)$:



Truncated Icosahedron, soccer ball, Buckminsterfullerene

Space fullerenes

- Frank-Kasper fullerenes are all (four) fullerenes with isolated hexagons: $F_{20}(I_h)$, $F_{24}(D_{6d})$, $F_{26}(D_{3h})$, $F_{28}(T_d)$.



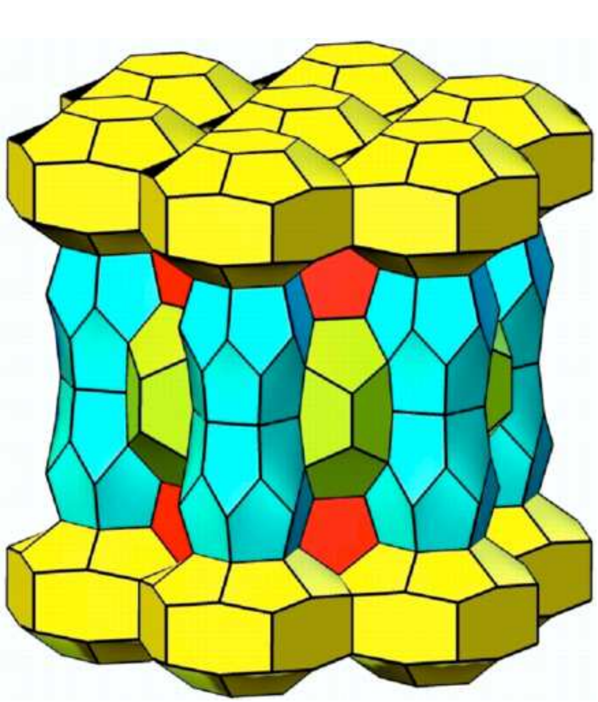
unique F_{20} unique F_{24} unique F_{26} one of 2 F_{28}

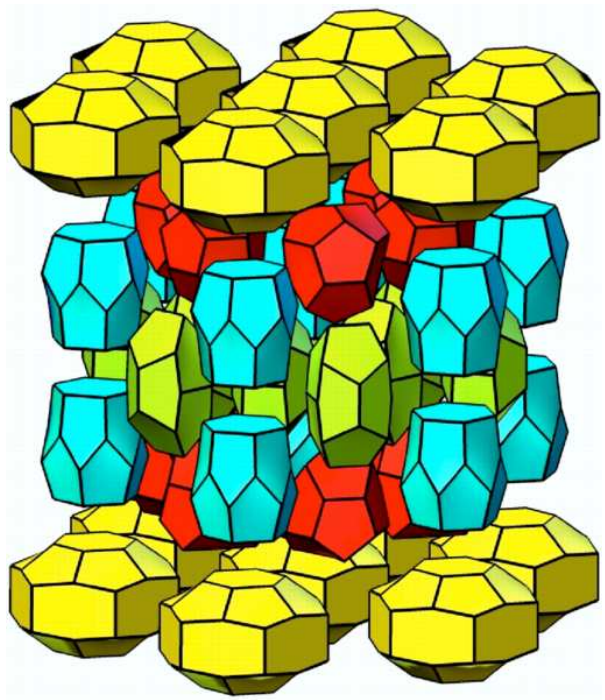
- Space fullerene: a simple 3-periodic tiling of $\mathbb{E}^3$ by fullerenes (possibly, non-congruent and curved faces).
- FK space fullerene: such tiling by Frank-Kasper fullerenes. Crystallographers usually consider their duals, introduced in Frank-Kasper, 1958, and called Frank-Kasper structures (or Frank-Kasper phases).

Deza-Shtogrin, 1999: only known non-FK space fullerene.

Non-FK space fullerene: is it unique?

This exception is the 4-valent 3-periodic tiling of $\mathbb{E}^3$ by F_{20}, F_{24} and its elongation $F_{36}(D_{6h})$ in ratio $7:2:1$.
So, new record: mean face-size ≈ 5.091<5.1 (C_{15}) and $\overline{f}$=13.2<13.29 (Rivier-Aste, 1996, conj. min.) <13.(3) (C_{15}).





Delgado, O'Keeffe: all space fullerenes with ≤ 7 orbits of vertices are 4 FK (A_{15}, C_{15}, Z, C_{14}) and this one (3,3,5,7,7).

Digression 1: on similar tilings

- Similar 4-valent 3-periodic tiling (also $P6/mmm$) is by F_{20}, F'_{20} (instead of F_{24}) and same F_{36} in ratio 3:2:1.

  F'_{20} is "twisted F_{20}": 6-ring alternating 4- and 6-gons having three 5-gons inside and three outside.

  It corresponds to metallic alloy $CaCu_5$, clathrate of type H, zeolite topology DOH, clathrasil Dodecasil D1H.

  Its unit cell has 34 vertices (H_2O in clathrate hydrate of type H and SiO_2 in DOH), $3+2$ dodecahedral cages (F_{20}, F'_{20}) and one F_{36} (the large guest, Ca in $CaCu_5$).
- Deza-Shtogrin, 2008, got infinity of only 1-periodic (so, non-crystallographic) 4-valent tilings by fullerenes (F_{20}, F_{24} and their elongations F_{30}, F_{36}) from their and any FK space fullerene with 6-fold axis and parallel miroir planes. Their *strip groups* are *pmmm* or *p2/m11*.

Digression 2: fullerene manifolds

d-fullerene: $(d\text{-}1)$-dimensional d-valent compact connected manifold, any 2-face is 5- or 6-gon. Any its face is polytopal i-fullerene, $i \leq d$; so, $d \in \{2, 3, 4, 5\}$ since (Kalai, 1990) any 5-polytope has a 3- or 4-gonal 2-face. Space fullerenes are euclidean 4-fullerenes. Their non-euclidean analogs are:

- Regular tilings of $\mathbb{S}^3$ by F_{20} (regular 120-cell) and of $\mathbb{H}^3$ by right-angled F_{24} (the *Löbell space* is its quotient).
- The *"greatest polyhex"*: convex hull, on a horosphere, of vertices of plane tiling 63 (regular honeycomb 633 in $\mathbb{H}^3$) It has only 6-gonal 2-faces; its fundamental domain is not compact but have a finite volume.
- The *"greatest polypent"*: tiling 5333 of $\mathbb{H}^4$ by 120-cell and (a finite 5-fullerene) its quotient by the symmetry group; (a compact 4-manifold tiled by finite number of 120-cells)

II. FK

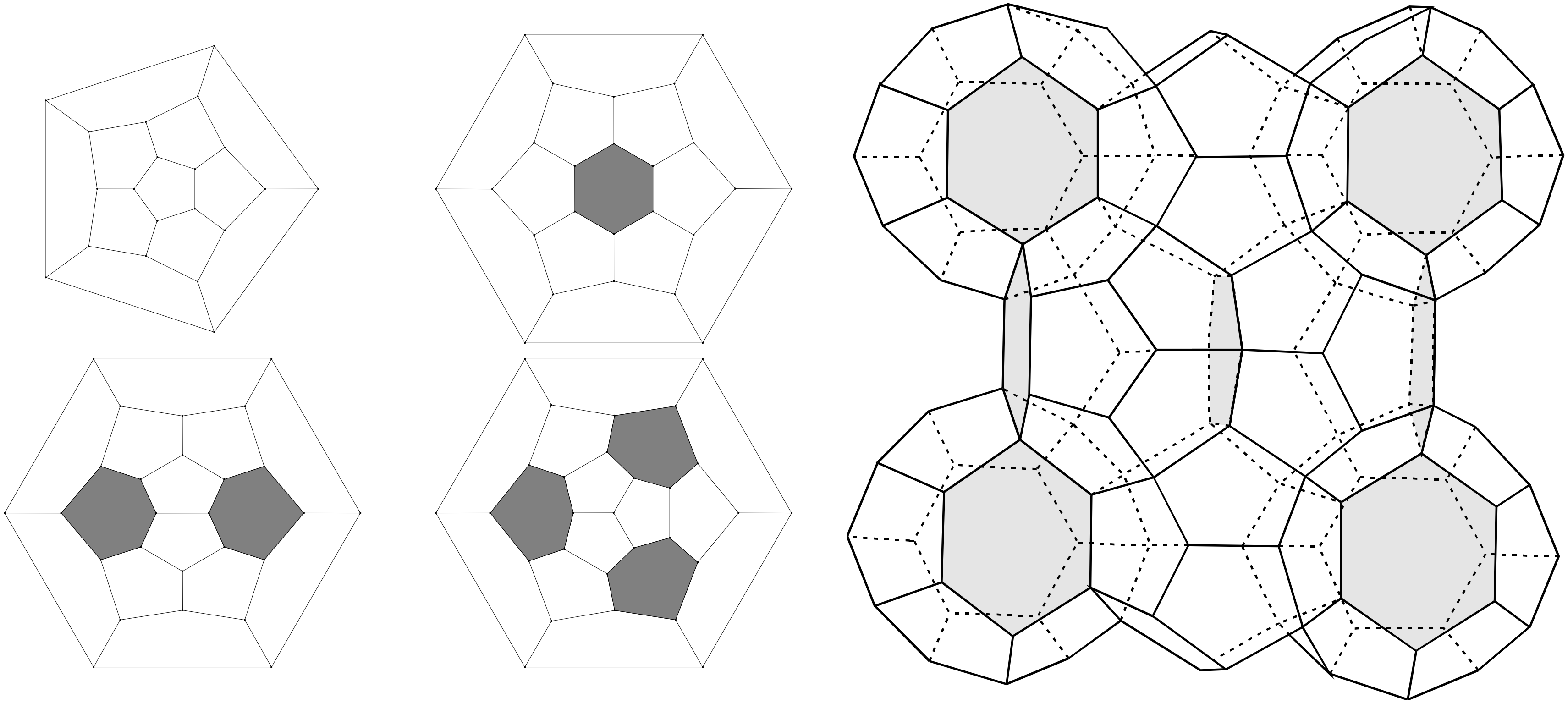
space fullerenes

Occurrence of FK space fullerenes

- In Metallurgy, as dual t.c.p. (tetrahedrally close-packed phases) of metallic alloys, where cells are atoms.
- Clathrates (compounds with one component, atomic or molecular, enclosed in framework of another), including
  - clathrate hydrates, where cells are solutes cavities, vertices are H_2O, edes are hydrogen bonds;
  - clathrasils (silicate materials with clathrate structure);
  - zeolites (hydrated microporous aluminosilicate minerals), where vertices are tetrahedra SiO_4 or $SiAlO_4$, cells are H_2O, edges are oxygen bridges.
- Soap froths (foams, liquid crystals).
- A_{15}: better than Kelvin's solution to his problem: bcc=A_3^* with minimised surface energy, i.e., tr.β_3 and edges are curved, so that faces meet at $120°$ and edges at $109.4°$.

Main problem: to find possible structures, they are very rare

FK space fullerenes; example A_{15}



Frank-Kasper polyhedra F_{20}, F_{24}, F_{26}, F_{28} with maximal symmetry I_h, D_{6d}, D_{3h}, T_d, respectively, are Voronoi cells surrounding atoms of a FK phase. Their duals: 12,14,15,16 coordination polyhedra. FK phase cells are almost regular tetrahedra; their edges, sharing 6 or 4 tetrahedra, are - or + disclination lines (defects) of local icosahedral order.

24 known primary FK space fullerenes

t.c.p.	clathrate exp.alloy	sp. group	$\overline{f}$	F_{20}:F_{24}:F_{26}:F_{28}	n	?
A_{15}	type I Cr_3Si	$Pm\bar{3}n$	13.50	1, 3, 0, 0	8	+
C_{15}	type II $MgCu_2$	$Fd\bar{3}m$	13.(3)	2, 0, 0, 1	24	+
C_{14}	type V $MgZn_2$	$P6_3/mmc$	13.(3)	2, 0, 0, 1	12	+
Z	type IV Zr_4Al_3	$P6/mmm$	13.43	3, 2, 2, 0	7	+
σ	type III $Cr_{46}Fe_{54}$	$P4_2/mnm$	13.47	5, 8, 2, 0	30	+
H	complex	$Cmmm$	13.47	5, 8, 2, 0	30	+
K	complex	$Pmmm$	13.46	14, 21,6,0	82	
F	complex	$P6/mmm$	13.46	9, 13, 4, 0	52	
J	complex	$Pmmm$	13.45	4, 5, 2, 0	22	
ν	$Mn_{81.5}Si_{8.5}$	$Immm$	13.44	37, 40, 10, 6	186	
δ	$MoNi$	$P2_12_12_1$	13.43	6, 5, 2, 1	56	+
P	$Mo_{42}Cr_{18}Ni_{40}$	$Pbnm$	13.43	6, 5, 2, 1	56	

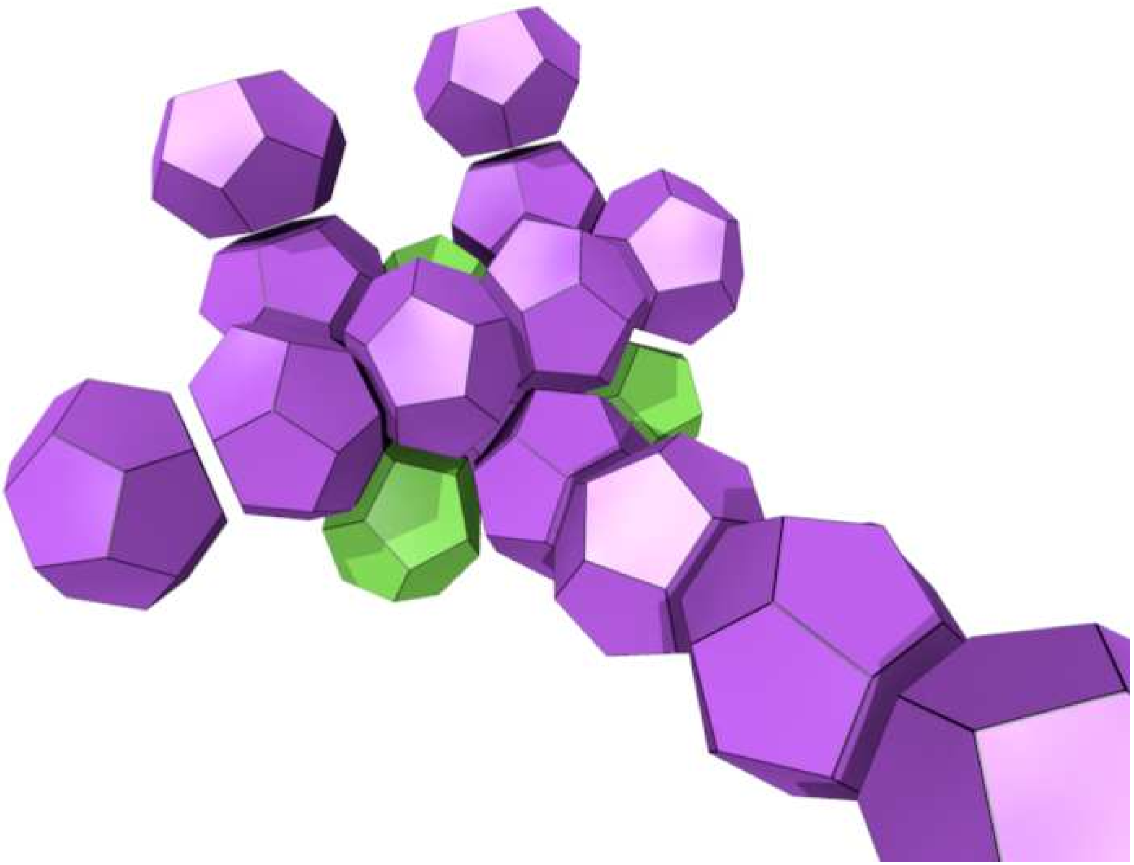
24 known primary FK space fullerenes

t.c.p.	exp. alloy	sp. group	$\overline{f}$	F_{20}:F_{24}:F_{26}:F_{28}	n	?
K^*	$Mn_{77}Fe_4Si_{19}$	$C2$	13.42	25,19, 4, 7	220	
R	$Mo_{31}Co_{51}Cr_{18}$	$R\overline{3}$	13.40	27, 12, 6, 8	159	
μ	W_6Fe_7	$R\overline{3}m$	13.38	7, 2, 2, 2	39	+
$-*$	K_7Cs_6	$P6_3/mmc$	13.38	7, 2, 2, 2	26	+
$p\sigma$	Th_6Cd_7	$Pbam$	13.38	7, 2, 2, 2	26	+
M	$Nb_{48}Ni_{39}Al_{13}$	$Pnam$	13.38	7, 2, 2, 2	52	
C	$V_2(Co,Si)_3$	$C2/m$	13.36	15, 2, 2, 6	50	
I	$Vi_{41}Ni_{36}Si_{23}$	Cc	13.37	11, 2, 2, 4	228	
T	$Mg_{32}(Zn,Al)_{49}$	$Im3$	13.36	49, 6, 6, 20	162	
SM	$Mg_{32}(Zn,Al)_{49}$	$Pm\overline{3}n$	13.36	49, 9, 0, 23	162	
X	$Mn_{45}Co_{40}Si_{15}$	$Pnmm$	13.35	23, 2, 2, 10	74	
$-$	Mg_4Zn_7	$C2/m$	13.35	35, 2, 2, 16	110	

27 structures excl. SM and adding Laves $2t$-layers, $2 \leq t \leq 5$.

FK space fullerene A_{15} (β-W phase)

Gravicenters of cells F_{20} (atoms Si in Cr_3Si) form the bcc network A_3^*. Unique with its fractional composition $(1, 3, 0, 0)$. Oceanic methane hydrate (with type I, i.e., A_{15}) contains 500-2500 Gt carbon; cf. ~ 230 for other natural gas sources.



Special space fullerenes A_{15} and C_{15}

Those extremal space fullerenes A_{15}, C_{15} correspond to

- clathrate hydrates of type I ($4Cl_2.7H_2O$) and II ($CHCl_3.17H_2O$);
- zeolite topologies MEP, MTN;
- clathrasils Melanophlogite, Dodecasil 3C;
- metallic alloys Cr_3Si (or β-tungsten W_3O), $MgCu_2$.

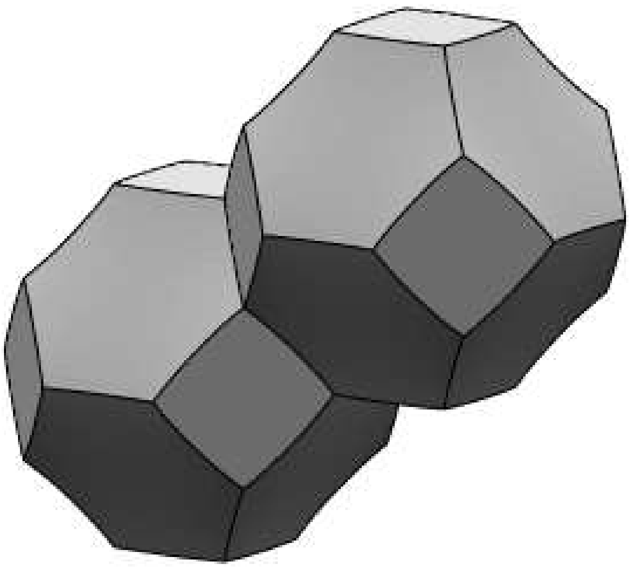
Their *unit cells* have, respectively, 46, 136 vertices and 8 (2 F_{20} and 6 F_{24}), 24 (16 F_{20} and 8 F_{28}) cells.

27 known FK structures have mean number $\overline{f}$ of faces per cell (mean coordination number) in $[13.(3)(C_{15}), 13.5(A_{15})]$ and their mean face-size is within $[5+\frac{1}{10}(C_{15}), 5+\frac{1}{9}(A_{15})]$.

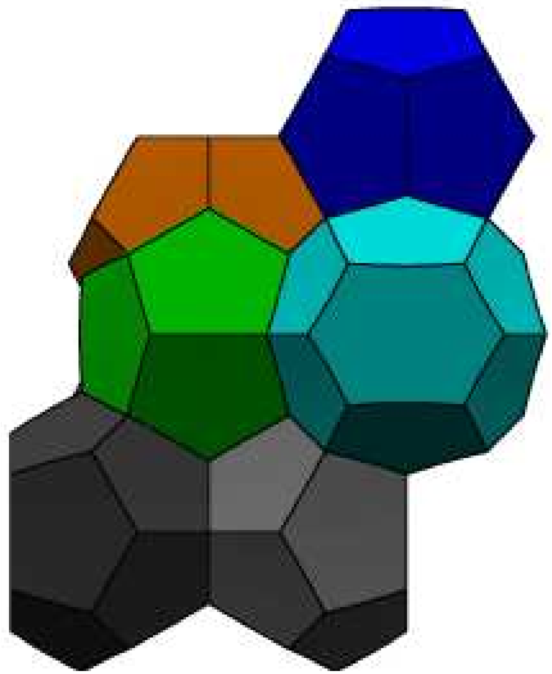
Closer to impossible 5 or $\overline{f}=12$ (120-*cell*, $\mathbb{S}^3$-tiling by F_{20}) means lower energy. Minimal $\overline{f}$ for *simple* (3, 4 tiles at each edge, vertex) $\mathbb{E}^3$-tiling by a *simple* polyhedron is 14 (tr.oct).

Weak Kelvin problem

Partition $\mathbb{E}^3$ into *equal volume* cells D of minimal surface area, i.e. maximal $IQ(D) = \frac{36\pi V^2}{A^3}$ (lowest energy foam). Kelvin's example has *congruent* cells. Almgren proposed to beat it by variational optimization over periodic structures.



Lord Kelvin, 1887: bcc=A_3^*
IQ(curved tr.Oct.) ≈ 0.757
IQ(tr.Oct.) ≈ 0.753



Weaire-Phelan, 1994: A_{15}
IQ(unit cell) ≈ 0.764
2 curved F_{20} and 6 F_{24}

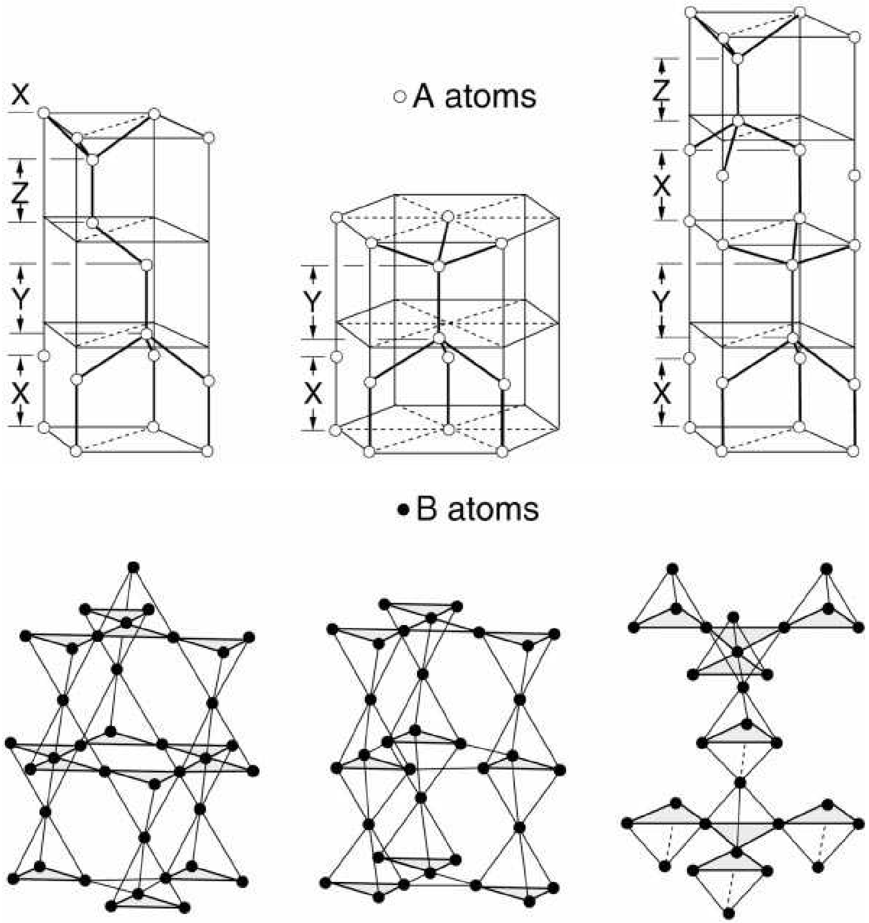
In $\mathbb{E}^2$, the best is (Hales, 2001) graphite $F_\infty = (6^3)$.

A_{15} at Olympic Games

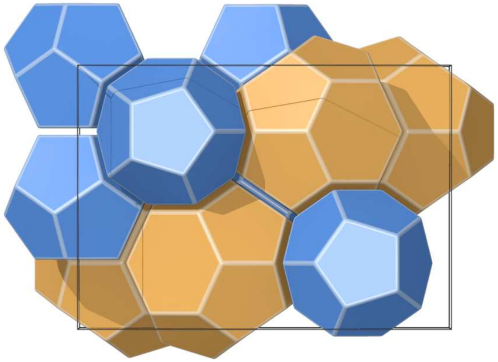
Weaire-Phelan partition is a variationally optimized version of the "main" space fullerene, A_{15}.
It is realized as a futurist swimming complex "Water Cube" (or "Building of Bubbles") at Beijing Olympic Games, 2008.

Laves phases: space fullerenes $(2,0,0,1)$

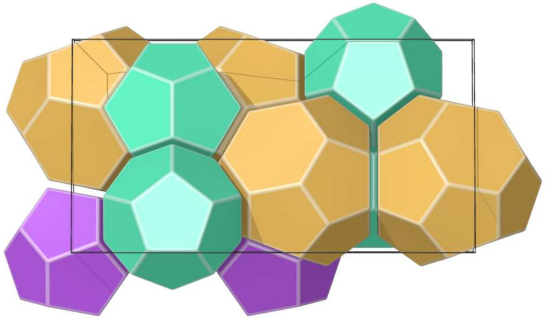
It is largest (> 1400) group of intermetallics; formula $\approx AB_2$.
Most crystallize as (cubic) C_{15} or (hexagonal) C_{14}, C_{36}.
Smaller B atoms: corner-linked tetrahedra B_4 regular in C_{15}
A atoms: interstices in B sub-lattice, or F_{28} gravicenters. In C_{15}, C_{14} A form diamond network and its hexagonal variant.



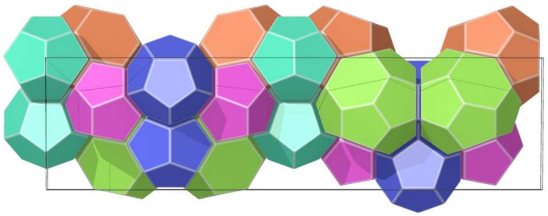
Five Laves phases found among 84



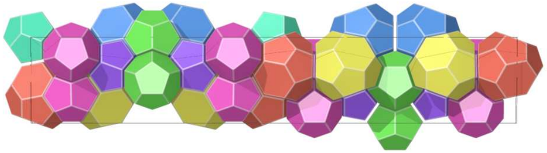
C_{15} ($MgCu_2$ 3-*layer*)



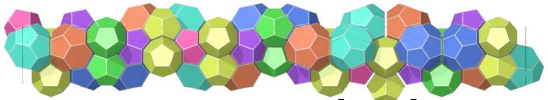
C_{14} ($MgZn_2$ 2-*layer*)



C_{36} ($MgNi_2$ 4-*layer* stack), $P6_3/mmc$



$MgNi_2$-55 mol% $MgCu_2$ (6-*layer* stack), $P6_3/mmc$



$MgZn_2$+0.07$MgAg_2$ (9-*layer* stack), $R\bar{3}m$

A continuum of stackings (math.) but energy limitations.

More on Laves phases

- All FK-structures with $x_{26} = x_{24} = 0$ are Laves phases.
- Laves phases are structures defined by stacking layers of F_{28} together with two choices at every step.
  Thus a symbol $(a_i)_{-\infty \le i \le \infty}$ with $a_i{=}\pm 1$ describes them.
  Frank & Kasper, 1959 generalized this construction to sequence with $a_i = 0, \pm 1$.
- *Laves phases are formed* between elements A and B with ideal (in closest packing by hard spheres) atomic diameter ratio r_A/r_B= $\sqrt{3/2} \approx 1.225$ but real ratio is in $[1.05 - 1.68]$. Packing efficiency (atom-occupied unit cell fraction) is 0.72.
- *Over 900 binary and ternary* Laves phases are known including C_{14} (131+263), C_{15} (219+272), C_{36} (17+14).
  About 22 million chemical substances are known; the crystal structure of $\approx 400,000$ of them is determined.

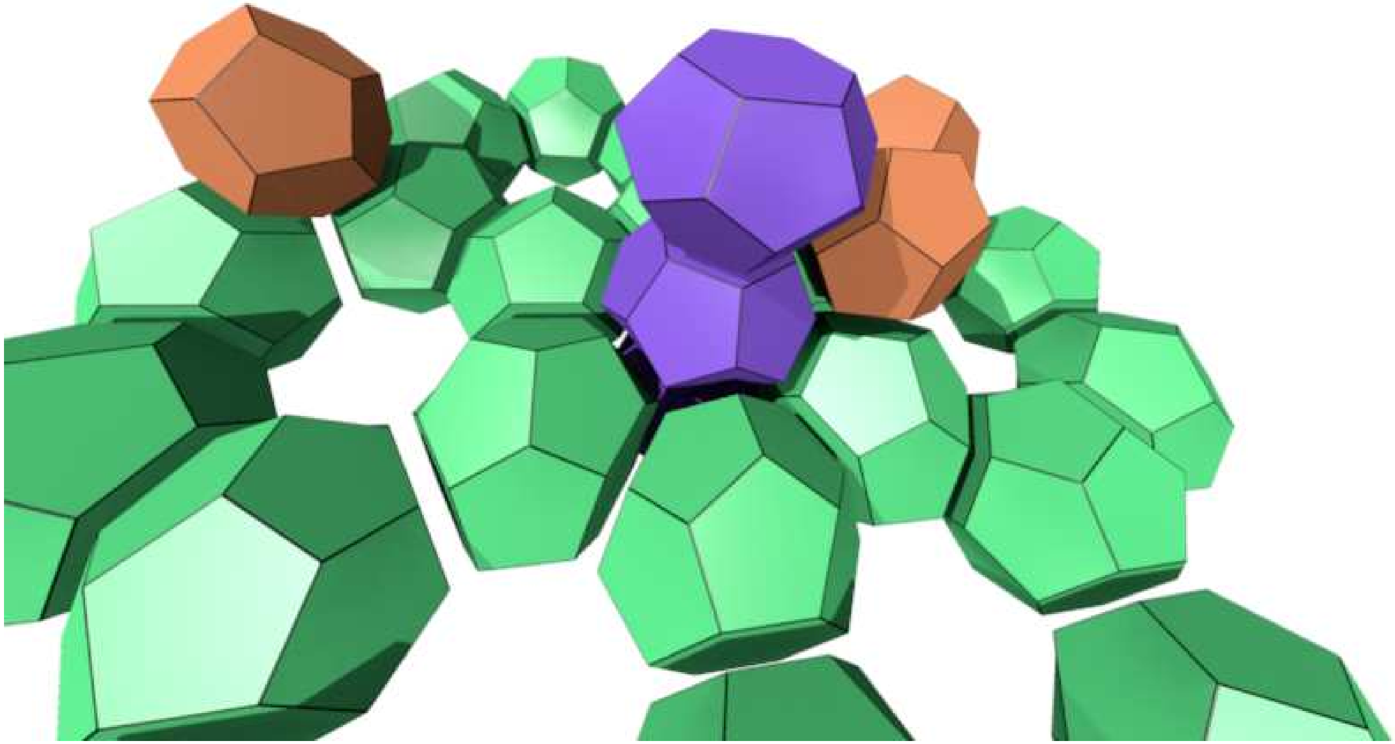
Digression: layers in Laves phases

Smaller B atoms form single kagome $3.6.3.6$ net.
A atoms are in 2 nets 3^6 above and below; they form triple layers: 2 types differing by reflection. Triple and single layers form main layers of 4 atomic planes: 6 types.
A continuum of math. possible stackings but by energetic reasons only shortest are found in real systems.

Komura-al., 1962-1977, found 6-, 8-, 9-, 10-, 16-, 21-layer stackings in Mg-based ternary Laves phases:
2-layer XY'(C_{14}), 3- XYZ (C_{15}), 4- XY'X'Z (C_{36}), 6- XYZX'Z'Y'
8- XY'XY'X'ZX'Z, 9- XY'XYZ'YZX'Z, 10- XYZ'YZX'Z'YZ'Y'.
Unit cell size of t-layer is 6t for t=2,4,6,8,9,10 and 24 for t=3.

Krypyakevich-Melnik, 1974: 14-layer $LiMg_7Zn_{13}$, $P6_3/mmc$.
Kitano-al., 1998: likeliest 12-layer $(Ti_{0.95}V_{0.05})Co_2$ has XYZXY'X'Z'YZX'Z'Y' (or 4323 in Zhdanov symbol), $P\bar{3}m1$.

FK space fullerene Z



Z is also not unique one with its fraction $(3, 2, 2, 0)$.
It corresponds also to clathrate of type III, say, $Br_2.86H_2O$.

III. Results of our computation

Computer enumeration

Dutour-Deza-Delgado, 2009 found 84 FK structures (incl. 13 among 27 known) with $N \leq 20$ fullerenes in reduced (i.e. by a Bieberbach group) fundamental domain.

# 20	# 24	# 26	# 28	fraction	N(nr. of)	n(known structure)
4	5	2	0	known	11(1)	not J-complex
8	0	0	4	known	12(1)	24(4-layer C_{36})
7	2	2	2	known	13(5)	26(–*), 26($p\sigma$), 39(μ), not M
6	6	0	2	new	14(3)	-
6	5	2	1	known	14(6)	56(δ), not P
6	4	4	0	known	14(4)	7(Z)
7	4	2	2	conterexample	15(1)	-
5	8	2	0	known	15(2)	30(σ), 30(H-complex)
9	2	2	3	new	16(1)	-
6	6	4	0	conterexample	16(1)	-
4	12	0	0	known	16(1)	8(A_{15})

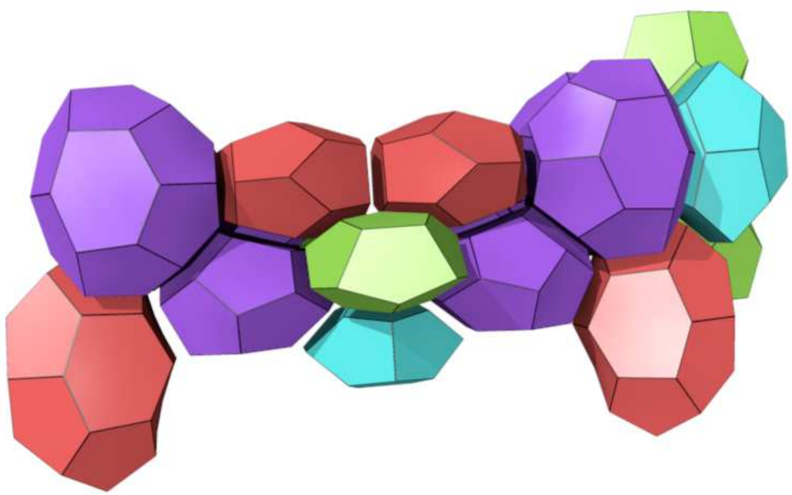
Computer enumeration

# 20	# 24	# 26	# 28	fraction	N(nr.of)	n(known structure)
8	5	2	2	new	17(2)	-
8	4	4	1	new	17(2)	-
12	0	0	6	known	18(4)	12(C_{14}),24(C_{15}),36(6-*layer*),54(9-*layer*)
7	8	2	1	new	18(1)	-
7	7	4	0	new	18(1)	-
6	8	4	0	conterexp.	18(3)	-
11	2	2	4	new	19(11)	-
11	1	4	3	new	19(1)	-
6	11	2	0	new	19(1)	-
10	6	0	4	new	20(3)	-
10	5	2	3	new	20(6)	-
10	4	4	2	new	20(20)	-
10	3	6	1	new	20(3)	-

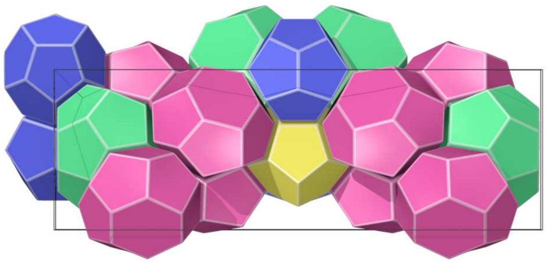
Conterexamples to 2 old conjectures

Any 4-vector, say, $(x_{20}, x_{24}, x_{26}, x_{28})$, is a linear combination $a_0(1,0,0,0)$+$a_1(1,3,0,0)A_{15}$+$a_2(3,2,2,0)$ Z+$a_3(2,0,0,1)C_{15}$ with $a_0 = x_{20}$- $\frac{x_{24}}{3}$-$\frac{7x_{26}}{6}$-$2x_{28}$ and a_1= $\frac{x_{24}-x_{26}}{3}$, a_2=$\frac{x_{26}}{2}$, a_3=x_{28}.

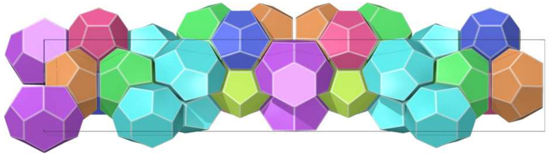
- Yarmolyuk-Krypyakevich, 1974: $a_0 = 0$ for FK fractions. So, $5.1 \leq \overline{q} \leq 5.(1)$, $13.(3) \leq \overline{f} \leq 13.5$; equalities iff C_{15}, A_{15}
- Conterexamples: $(7,4,2,2)$, $(6,6,4,0)$, $(6,8,4,0)$ (below). Mean face-sizes $\overline{q}$: ≈ 5.1089, $5.(1)$(A_{15}), ≈ 5.1148. Mean numbers of faces per cell $\overline{f}$: $13.4(6)$, 13.5($A15$), $13.(5)$ disproving Nelson-Spaepen, 1989: $\overline{q} \leq 5.(1)$, $\overline{f} \leq 13.5$.



All found conterexamples



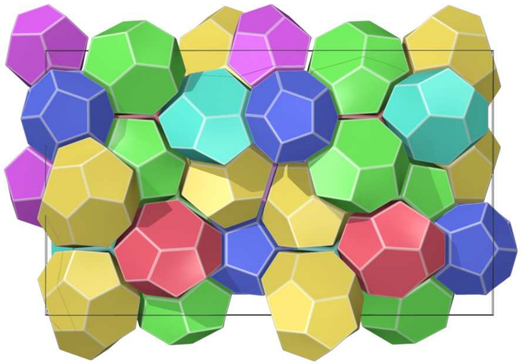
Nr. 18 (6, 8, 4, 0)



Nr. 40 (6, 6, 4, 0)

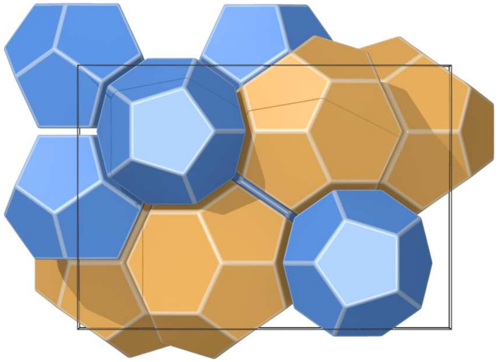
Nr. 62 (6, 8, 4, 0)

Nr. 1 (7, 4, 2, 2)

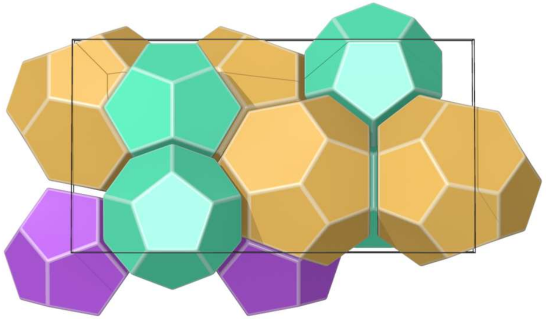


Nr. 63 (6, 8, 4, 0)

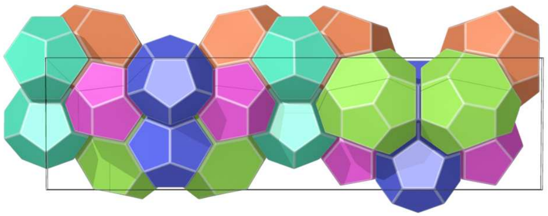
All found with known fraction (2,0,0,1)



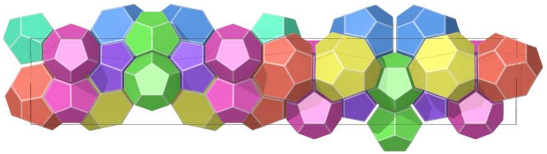
C_{15} ($MgCu_2$ 3-*layer*)



C_{14} ($MgZn_2$ 2-*layer*)



C_{36} ($MgNi_2$ 4-*layer* stacking)

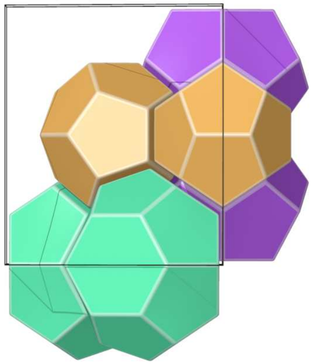


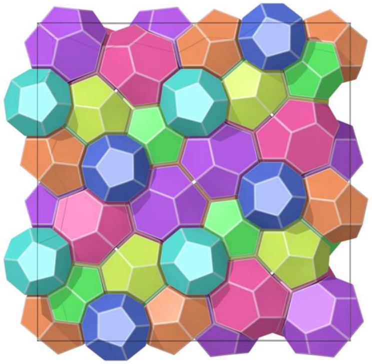
$MgNi_2$-55 mol% $MgCu_2$ (6-*layer* stacking)

$MgZn_2$+0.07 $MgAg_2$ (9-*layer* stacking)

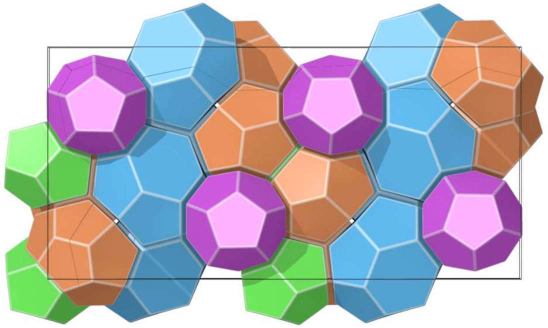
Laves-Friauf phases: a continuum of such stacking variants.

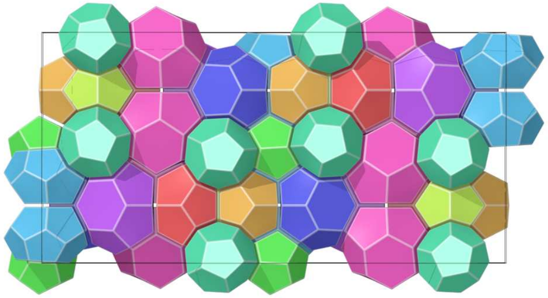
All found with known fraction (3,2,2,0)





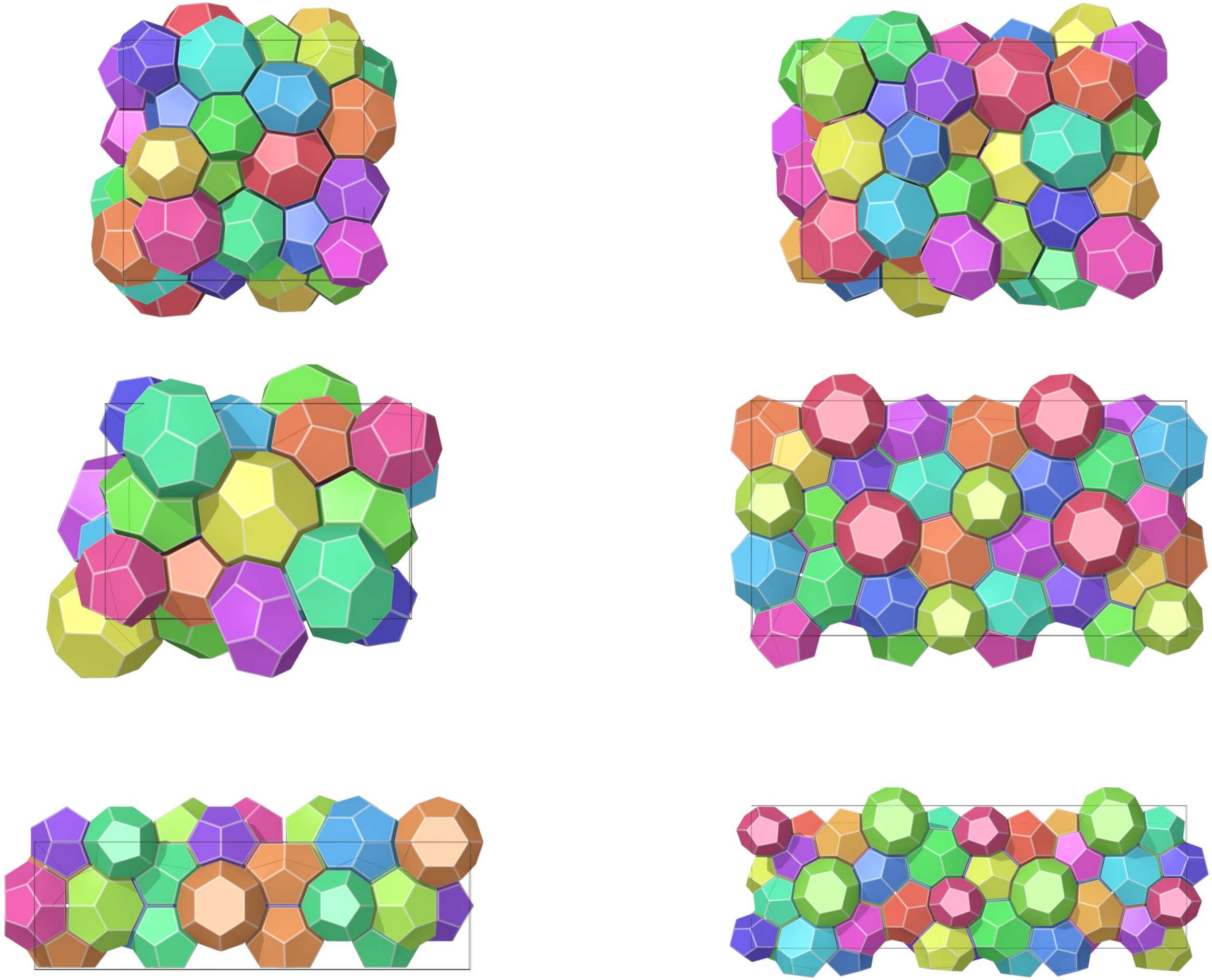
Z





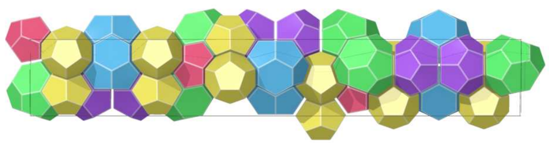
One structure, Z, is known.

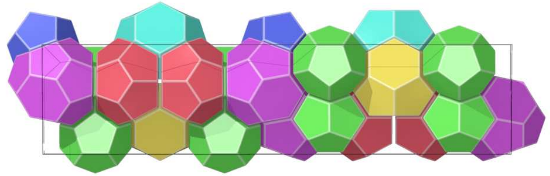
All found with known fraction (6,5,2,1)

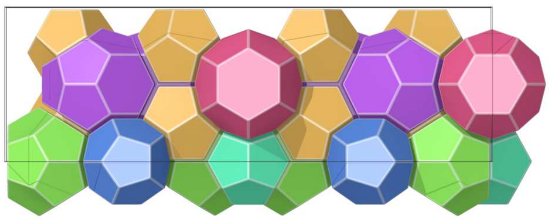


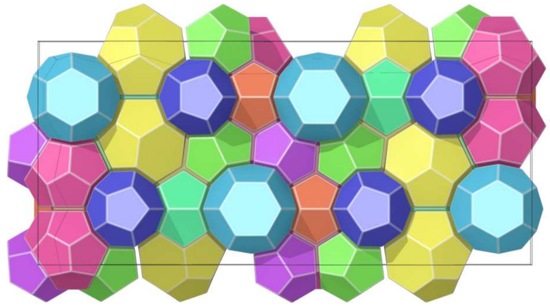
1st structure is δ: the only known other one, P, is not here.

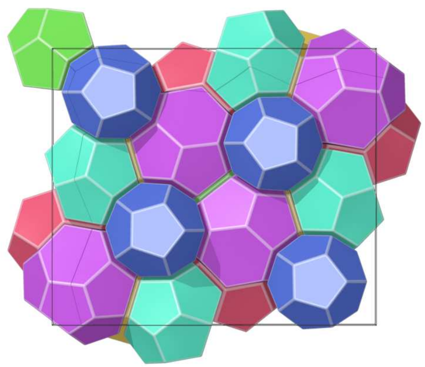
All found with known fraction (7,2,2,2)





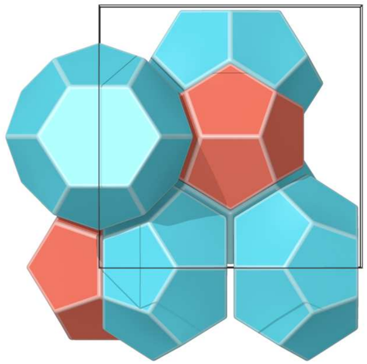




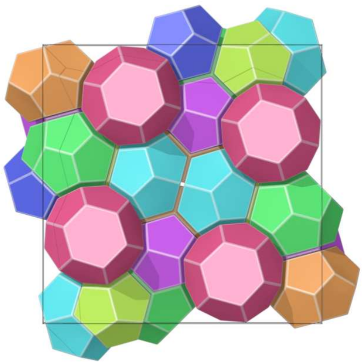


1st, 2nd, 5th are μ, –$^* = (K_7Cs_6)$, $p\delta$; remaining M is out.

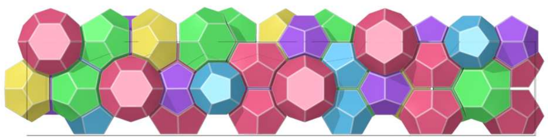
Others found with known fractions



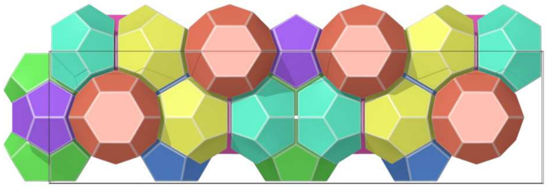
(1,3,0,0) A_{15}



(5,8,2,0) σ

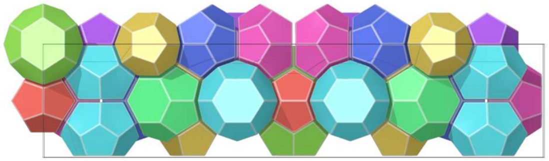


(4,5,2,0) not J

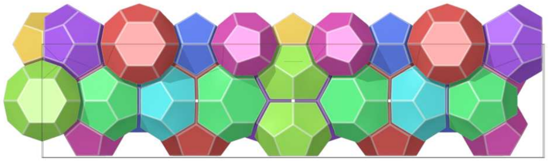


(5,8,2,0) H-complex

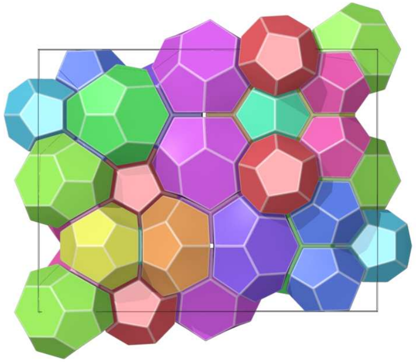
Unique found with their new fraction



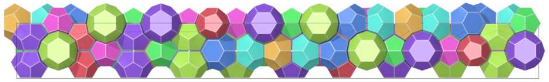
(7, 8, 2, 1)



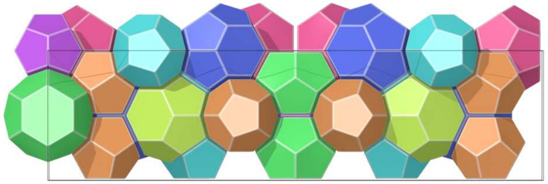
(7, 7, 4, 0)



(11, 1, 4, 3)

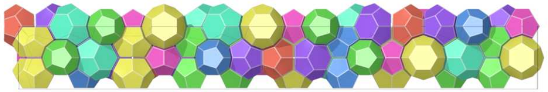


(6, 11, 2, 0)

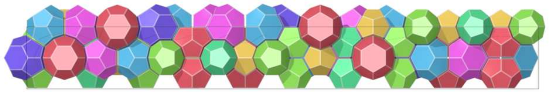


(9, 2, 2, 3)

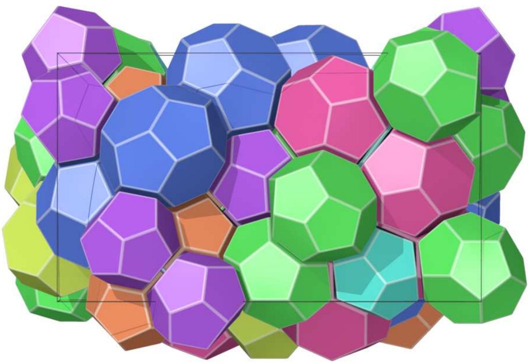
All found with 2 other new fractions



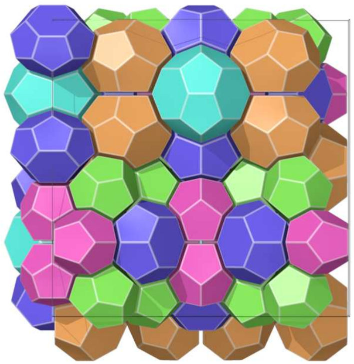
(8,5,2,2)



(8,4,4,1)

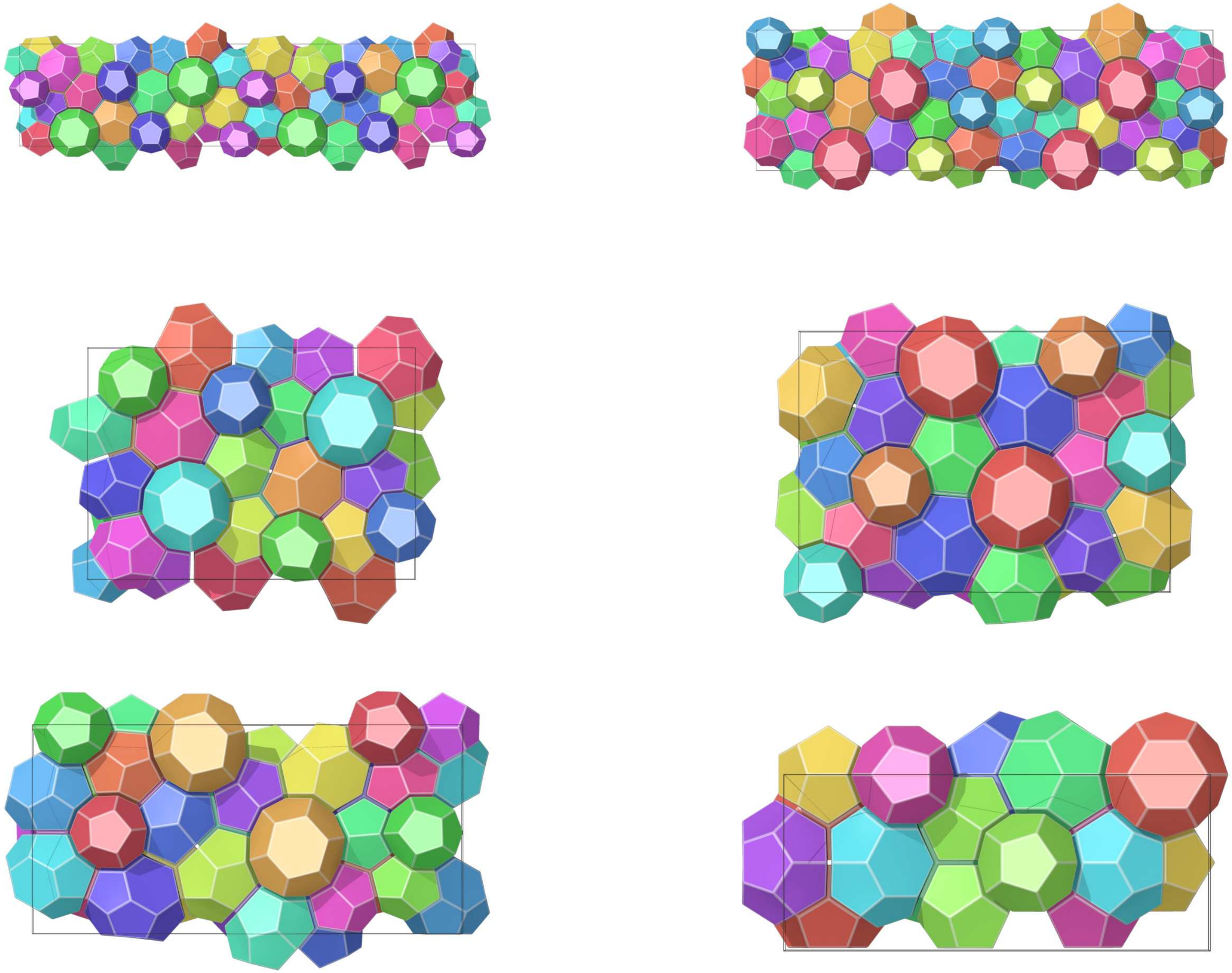


(8,5,2,2)



(8,4,4,1)

All found with new fraction (10,5,2,3)



Birdview on computation

- Let n and N be the sizes (number of fullerenes) in usual and reduced fundamental domains, i.e., unit cells up to the symmetry group and its Bieberbach subgroup.
- For $N \leq 14$, we got 20 structures in 15 computing days. Going from N to N+1, running time multiplies by ≈ 2.3. But further, it became large scale parallel computation. The last case N=20 took 1 month on ≈ 200 processors.
- We found 84 structures with $N \leq 20$: respectively, $1, 1, 5, 13, 3, 3, 4, 9, 13, 32$ of them for $N = 11, \dots, 20$.
- 71 among 84 structures are new, i.e., not in the list of 24 known ones. Among 23 found fractional compositions, 16 are new (not in the list of 18 known ones) including 3 disproving conjecture of Yarmolyuk-Kripyakevich, 1974.

IV. Combinatorial encoding and topological recognition problem

Flags and flag operators

- A pure cell n-complex $\mathcal{C}$ in $\mathbb{E}^n$ is a set $\{C_i\}$ of convex polytopes (cells) such that every face of a cell is a cell, the intersection of any two cells is their common face and any inclusion maximal cell has dimension n.
- It is closed (or has no boundary) if any $(n-1)$-cell is contained in two n-dimensional cells.
- A flag is an sequence $F_{n_0} \subset F_{n_1} \subset \cdots \subset F_{n_r}$ of cells of dimension $n_0, \dots, n_r$. $(n_0, \dots, n_r)$ is the type of the flag.
- A flag is complete if its type is $(0, \dots, n)$. Denote by $\mathcal{F}(\mathcal{C})$ the set of complete flags of $\mathcal{C}$.
- If $f = (F_0, \dots, F_n)$ is a complete flag and $0 \leq i \leq n$, then the flag $\sigma_i(f)$ differs from f only in the dimension i. A cell complex $\mathcal{C}$ is defined by the action of σ_i on $\mathcal{F}(\mathcal{C})$.
- The problem is that $\mathcal{F}(\mathcal{C})$ may be infinite or too large.

Digression on a non-existence case

- Given a type T of flag and a closed cell complex $\mathcal{C}$, the cell complex $\mathcal{C}(T)$ is kaleidoscope (or Wythoff) construction, Grassmann (or shadow) geometry.
- For example, if $T=\{0\}$, then $\mathcal{C}(T)=\mathcal{C}$ (identity); $\mathcal{C}(\{n\}), \mathcal{C}(\{1\}), \mathcal{C}(\{0,1\})$ and $\mathcal{C}(\{0,\dots,n\}$ are dual, median, truncated and order complexes of $\mathcal{C}$.
- Does there exist space fullerene with all fullerene tiles (maximal cells) being $F_{60}(I_h)$ (soccerballs)?
  The answer: such objects are $\mathcal{C}(\{0,1\})$, where $\mathcal{C}$ is the Coxeter geometry with diagram $(5,3,5)$ (regular tiling of $\mathbb{H}^3$ by $F_{20}(I_h)$ with vertex figure $F^*_{20}(I_h)$).
  So, it not exists as a space fullerene or as a polytope (in $\mathbb{E}^3$ or on $\mathbb{S}^3$) but it exists in the hyperbolic space $\mathbb{H}^3$.
  A. Pasini, *Four-dimensional football, fullerenes and diagram geometry*, Discrete Math. **238** (2001) 115–130

Delaney symbol

- Suppose $\mathcal{C}$ is a cell complex, with a group G acting on it. Delaney symbol of $\mathcal{C}$ with respect to G is a comb. object (say, a finite connected "colored" graph) containing:
  - The orbits O_k of complete flags under G,
  - The action of σ_i on those orbits for $0 \leq i \leq n$.
  - For every orbit O_k and $f \in O_k$, $\inf m : (\sigma_i \sigma_j)^m(f)$=$f$ is independent of f and denoted $m_{i,j}(k)$.

  The quotient $\mathcal{C}/G$ is an orbifold (orbit space).
- If $G = \mathrm{Aut}(\mathcal{C})$, we speak simply of Delaney symbol of $\mathcal{C}$.
- Theorem: If $\mathcal{C} = \mathbb{E}^3$ (or any simply connected manifold), then it is entirely described by its Delaney symbol.
  A.W.M. Dress, *Presentations of discrete groups, acting on simply connected manifolds ... a systematic approach*, Advances in Math. **63-2** (1987) 196–212.

The inverse recognition problem

- Suppose we have a Delaney symbol $\mathcal{D}$, i.e. the data of permutations $(\sigma_i)_{0\leq i\leq n}$ and the matrices $m_{ij}(k)$.

  We want to know what is the universal cover manifold $\mathcal{C}$ (especially, if it is Euclidean space $\mathbb{E}^n$).

- If we have only 1 orbit of flags, then the Delaney symbol is a Coxeter-Dynkin diagram and the decision problem is related to the eigenvalues of the Coxeter matrix.
- If $n = 2$, then we can associate a curvature $c(\mathcal{D})$ to the Delaney symbol and the sign determines whether $\mathcal{C}$ is a sphere, euclidean plane or hyperbolic plane.
- In our case $n = 3$, the problem is related to hard questions in 3-dimensional topology. But the software Gavrog/3dt by Delgado can actually decide them.

Functionalities of Gavrog/3dt

- Test for euclidicity of Delaney symbols, that is recognize when $\mathcal{C}$ is Euclidean space.
- Find minimal Delaney symbols (representation with smallest fundamental domain and maximal group of symmetry) and test for isomorphism among them.
- Compute the space group of crystallographic structure.
- Create pictures,, i.e. get metric information, from Delaney symbols.
- All this depends on difficult questions of 3-dimensional topology, some unsolved. This means that in theory the program does not always works, but in practice it does.

  O. Delgado Friedrichs, *Euclidicity criteria*, PhD thesis and *3dt-Systre*, `http://gavrog.sourceforge.net`

V. Combinatorial enumeration problem: dead ends and exits

Enumeration size reduction

- The full computer enumeration of FK space fullerenes is impossible, since infinite sequence of structures, parametrized by infinite words, are known.

  A complete description by mathematical argument is elusive too, since the known structures are quite varied.
- A subproblem - determine 3-periodic tilings with $\leq n$ cells in fundamental domain - is still infinite since slight move of vertices preserves some tilings.

  There is a continuum, 1, 0 of affinely non-equivalent tilings with fractions $(2, 0, 0, 1)$, $(1, 3, 0, 0)$, $(1, 0, 0, 0)$ resp.
- All periodic tilings can be described combinatorially by Delaney symbol. It was used by O'Keeffe and Delgado for enumeration, up to n orbits under G (automorphism group of the tiling coming in the end of computation). But we choose other method using that adjacencies between cells describe completely the structure.

Proposed enumeration method

- Instead we enumerate something intermediate between infinite tilings and Delaney symbol using all symmetries: quotient manifold of $\mathbb{E}^3$-tilings by a *good* group of their combinatorial symmetries, i.e., orientable closed 3-manifolds with N maximal cells, no one self-adjacent.
- Also, since Frank-Kasper fullerenes are 3-connected (so, at most 1 plane realization), no need to consider full flags (F_0, F_1, F_2, F_3). We simply used, as vertices, vertex-cell pairs $(v = F_0, C = F_3)$ with $v \in C$.
- Partial tiling: agglomeration of tiles, possibly, with holes. Thus, the method is to add tiles in all possibilities and to consider adding tiles in all possible ways.
- The programming is more complicate than for the Delaney symbol method, but there is a gain in speed, since we know exactly which maximal cells occur.

Two program limitations

- Crystallographic structure is obtained as universal cover We test if universal covering of quotient is $\mathbb{E}^3$ using 3dt.
- We assume that quotient manifold is orientable and no cell in it is self-adjacent (but two cells can be adjacent on several faces). It increased speed but can (unlikely) exclude some structures with ≤ 20 cells in fund. domain
- Self-adjacency is excluded replacing automorphism group by its Bieberbach subgroup. Bieberbach group is a *torsion-free* (without elements of finite order, i.e. all elements have trivial stabilizers) crystallographic group.
- In fact, no Bieberbach automorphism stabilizes a cell. Neither it stabilizes a face (since else, its barycenter becomes a fixed point). So, no cell is self-adjacent, and the quotient is a tiling of fullerenes.

Crystallographic groups

- The isometry group of $\mathbb{E}^n$ consists of transformations $x \to xA + b$ with $b \in \mathbb{E}^n$ and $A \in O(n)$ (ortogonal group).
- Its subgroup G is called n-dim. crystallographic group if it is discrete and its orbit space $\mathbb{E}^n/G$ is compact.

  A space group is such group for n=3, a *crystal*; there are 219, up to affine equivalence; 230 counting reflections.
- Orbit space $\mathbb{E}^n/G$ is compact flat Riemannian manifold; they are in bijection with Bieberbach groups.
- Fundamental domain of G is any set $A \subset \mathbb{E}^n$ containing a system S of G-orbit representatves with $\overline{S} = A$.
- Bieberbach, 1912: the translational part $L = G \cap \mathbb{E}^n$ is a latttice ($L \simeq \mathbb{Z}^n$) and the point group $G/\mathbb{Z}^n$ of G is finite.

Flat compact 3-manifolds

- n-manifold M^n is a topological space *locally* (i.e., any point has such neighborhood) homeomorphic to $\mathbb{E}^n$. It is flat if its curvature is zero everywhere, i.e., if it is locally *isometric* to $\mathbb{E}^n$. If flat M^n is compact, then $M^n \simeq \mathbb{E}^n/G$, where G, the fund. group $\pi_1(\mathbb{E}^n/G)$ of M^n, is a Bieberbach group.
- The holonomy group (with respect to the Levi-Civita connection) of $\mathbb{E}^n/G$ is $G/L \simeq G/\mathbb{Z}^n$ (the point group).
- $\mathbb{Z}^n$ is a Bieberbach group, and $\mathbb{E}^n/\mathbb{Z}^n$ is n-torus $\prod_1^n \mathbb{S}^1$. All compact flat manifolds are finitely covered by tori.
- In $\mathbb{E}^2$, only 2 such flat manifolds: torus and Klein bottle.
- In $\mathbb{E}^3$, there are 6 orientable and 4 non-orientable ones.

All flat compact 3-manifolds

- Up to affine equivalence, there are (Hantsche-Wendt, 1934) 10 such manifolds: quotients T^3/F with group $F \subset SL(3,\mathbb{Z})$ being cyclic of order $1, 2, 3, 4, 6$ or $Z_2 \times Z_2$.
- There is one orientable manifold for each such F and 2 non-orientable ones with $F = Z_2$ and 2 with $Z_2 \times Z_2$.
- For the same F, the difference is in generators: besides 3 independent translations t_a, t_b, t_c for fixed basis a, b, c, it is 1 or 2 affine maps $u \to v + A(u)$ for given translation t_v and 3×3 matrix A with respect to the basis a, b, c.
- 9 manifolds are torus (5) $T^2 \times [0,1]/(x,y,0) \sim (\phi(x,y),1)$ or Klein bottle (4) $K^2 \times [0,1]/(x,y,0) \sim (\phi(x,y),1)$ *bundles* over $\mathbb{S}^1$, for some homeomorphisms $\phi(x,y) : T^2 \to T^2$ or $K^2 \to K^2$. Among them are $T^3 = T^2 \times \mathbb{S}^1$ and $K^2 \times \mathbb{S}^1$.
- Orientable *Hantsche-Wendt manifold* $T^3/(Z_2 \times Z_2)$ is the union of 2 copies of orientable twisted bundle over K^2.

Digression on all compact 3-manifolds

Perelman, 2003 (in arXiv:math.DG/0307245) proved the Thurston's, 1982 Geometrization Conjecture: any compact 3-manifold M is a (ess. unique) connected sum of following eight types of *prime* (non-decomposable) 3-manifolds: $\mathbb{S}^3$, $\mathbb{E}^3$, $\mathbb{H}^3$, $\mathbb{S}^2 \times \mathbb{R}^1$, $\mathbb{H}^2 \times \mathbb{R}^1$ and 3 left-invariant Riemannian metrics $\tilde{SL}(2, \mathbb{R})$, Nil, Sol (on this special linear group, the nilpotent Heisenberg group, the Poincaré-Lorentz group).

It implies that any 3-manifold with trivial fundamental group is homeomorphic to $\mathbb{S}^3$, i.e., the Poincaré, 1900 Conjecture (one of 7 "Millenium Problems", US$\$1,000,000$ worth).

Hamilton: is metric on M converges, under Ricci "heat" flow, to a metric of one of 8? But, on a way, metric often became ∞ (*singularities*). Perelman characterized all singularities and related them with underlying topological structures.

The algorithm: simple tree search

- Partial tiling: agglomeration of tiles, possibly, with holes.
- Computing all possibilities, we add all possible tiles, in all ways, one by one. All options are seen sequentially.
- So, one need to store in memory only previous choices, i.e. if a structure is made of maximal cells $C_1, \dots, C_N$, then we store only:

$$\begin{array}{c}\{C_1\}\\ \{C_1, C_2\}\\ \{C_1, C_2, C_3\}\\ \vdots\\ \{C_1, C_2, \dots, C_N\}\end{array}$$

- There are two basic movement in the tree: go deeper or go to the next choice (at the same or lower depth).

VI. Special constructions

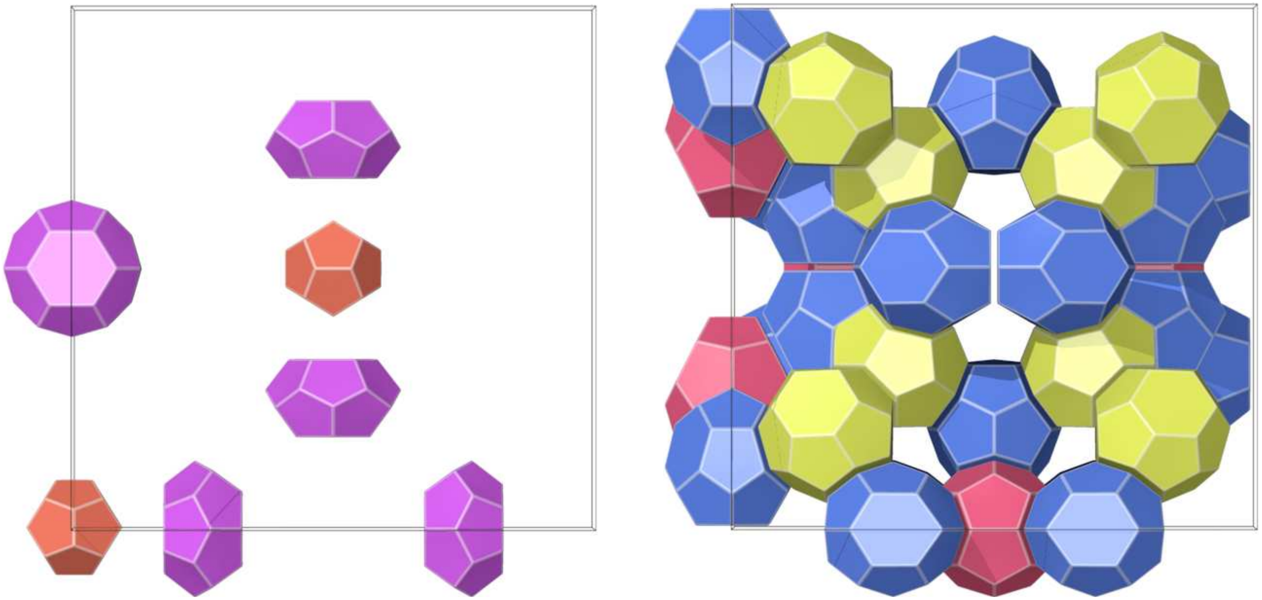
Sadoc-Mosseri inflation

- Given a space fullerene $\mathcal{T}$ by cells P, define the *inflation* $IFM(\mathcal{T})$ to be the simple tiling such that
  - Every cell P has a shrunken copy P' of P in interior.
  - On every vertex of P a F_{28} has been put.
  - On every m-gonal face of P', a F_{20} or F_{26} is put (if $m = 5$ or 6, respectively) which is contained in P.
- Thus, if $\mathcal{T}$ is a space fraction with fraction $(x_{20}, x_{24}, x_{26}, x_{28})$, then its inflation $IFM(\mathcal{T})$ is a space fraction with fraction $(x'_{20}, x'_{24}, x'_{26}, x'_{28})$, where

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

Sadoc-Mosseri inflation

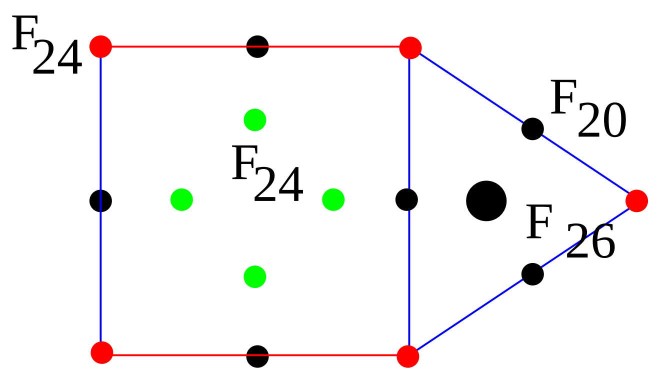
- The inflation of A_{15}: its shrunken cells and generated fullerenes F_{28}.



- Resulting space fullerene SM has fraction $(49, 9, 0, 23)$; cf. physical space fullerene T with fraction $(49, 6, 6, 20)$ and equal number 162 of cells in fundamental domain.

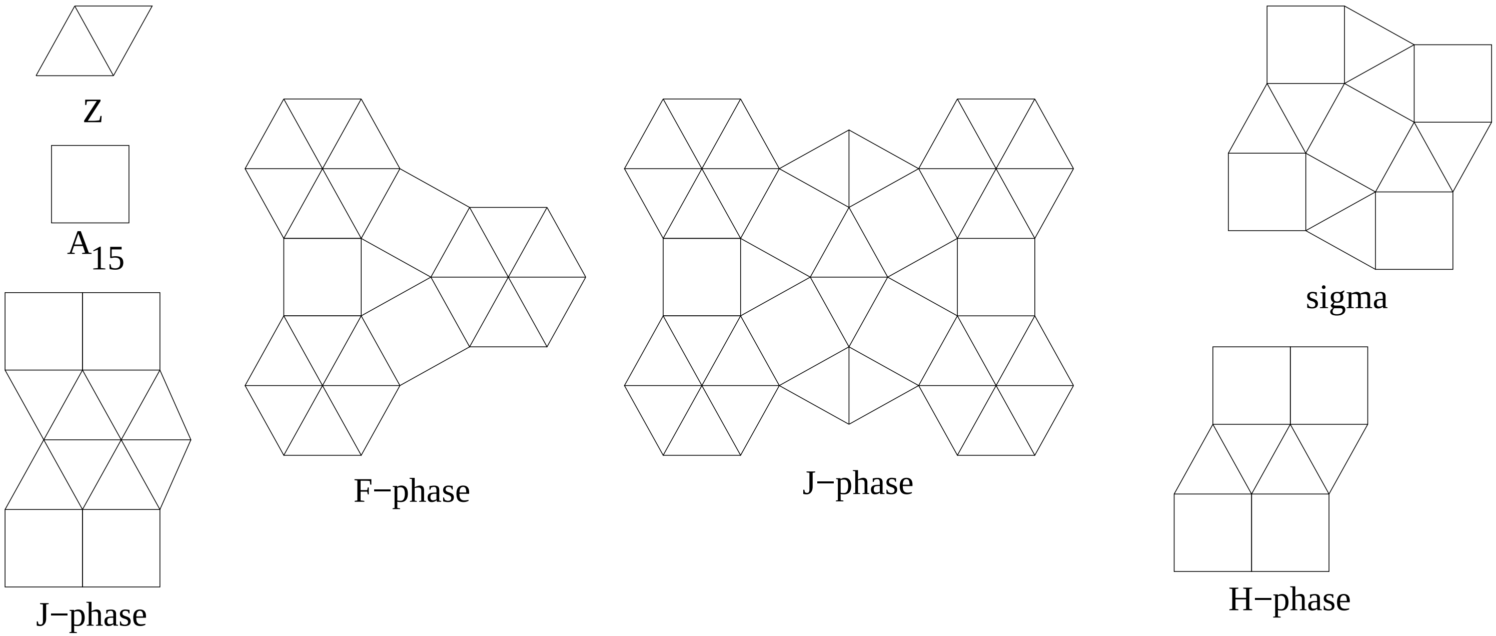
Frank-Kasper-Sullivan construction

- This construction is first described in Frank & Kasper, 1959 but a better reference is J.M. Sullivan, 2000: *New tetrahedrally closed-packed structures*.
- Take a tiling of the plane by regular 3- and 4-gons and define from it a space fullerene with $x_{28} = 0$.
- Graph edges are assigned red or blue color so that
  - triangles are monochromatic and
  - colors alternate around a square.
- Local structure is



Frank-Kasper-Sullivan construction

- The construction explains a number of structures:

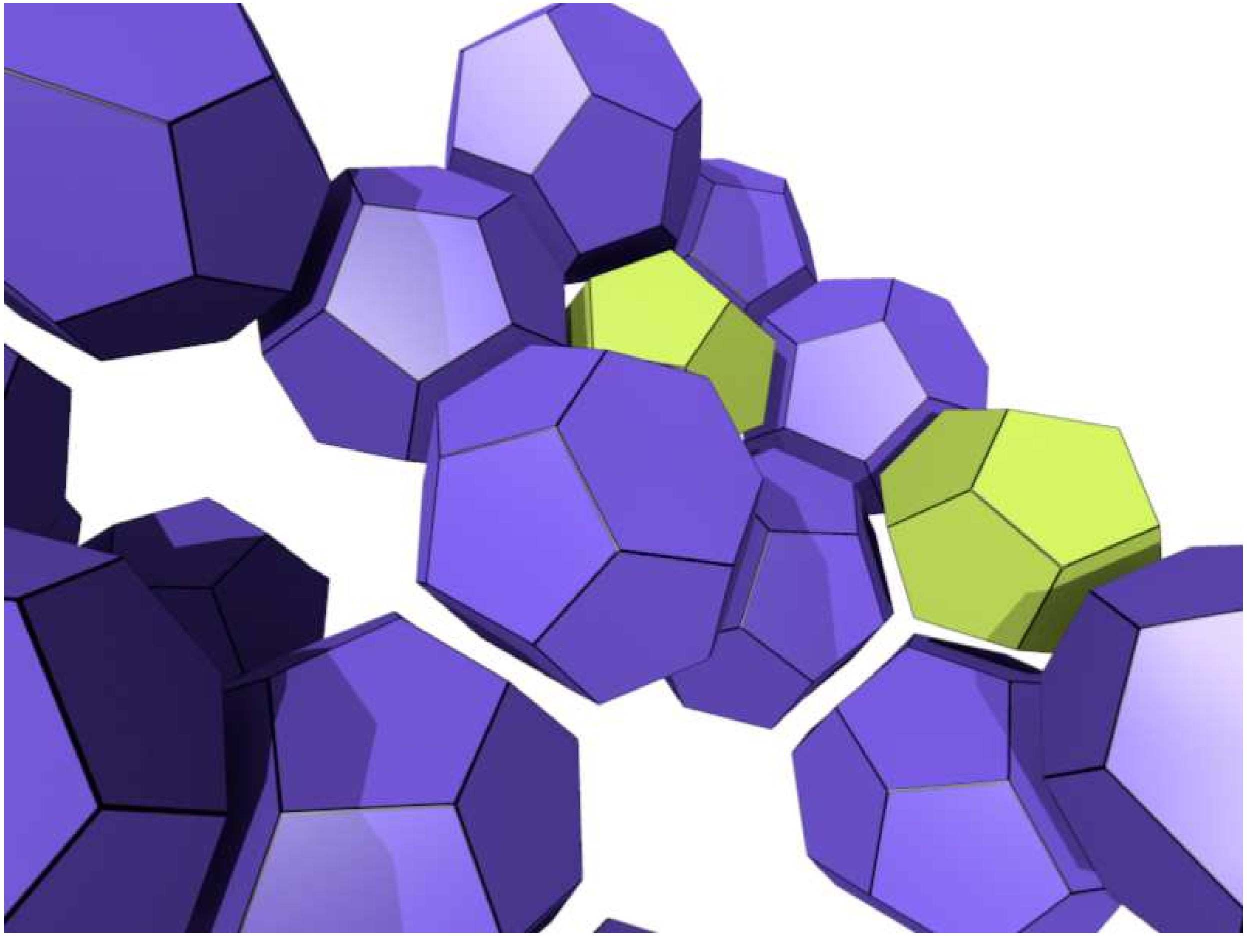


- Actually, a structure with $x_{28} = 0$ is physically realized if and only if it is obtained by this construction.

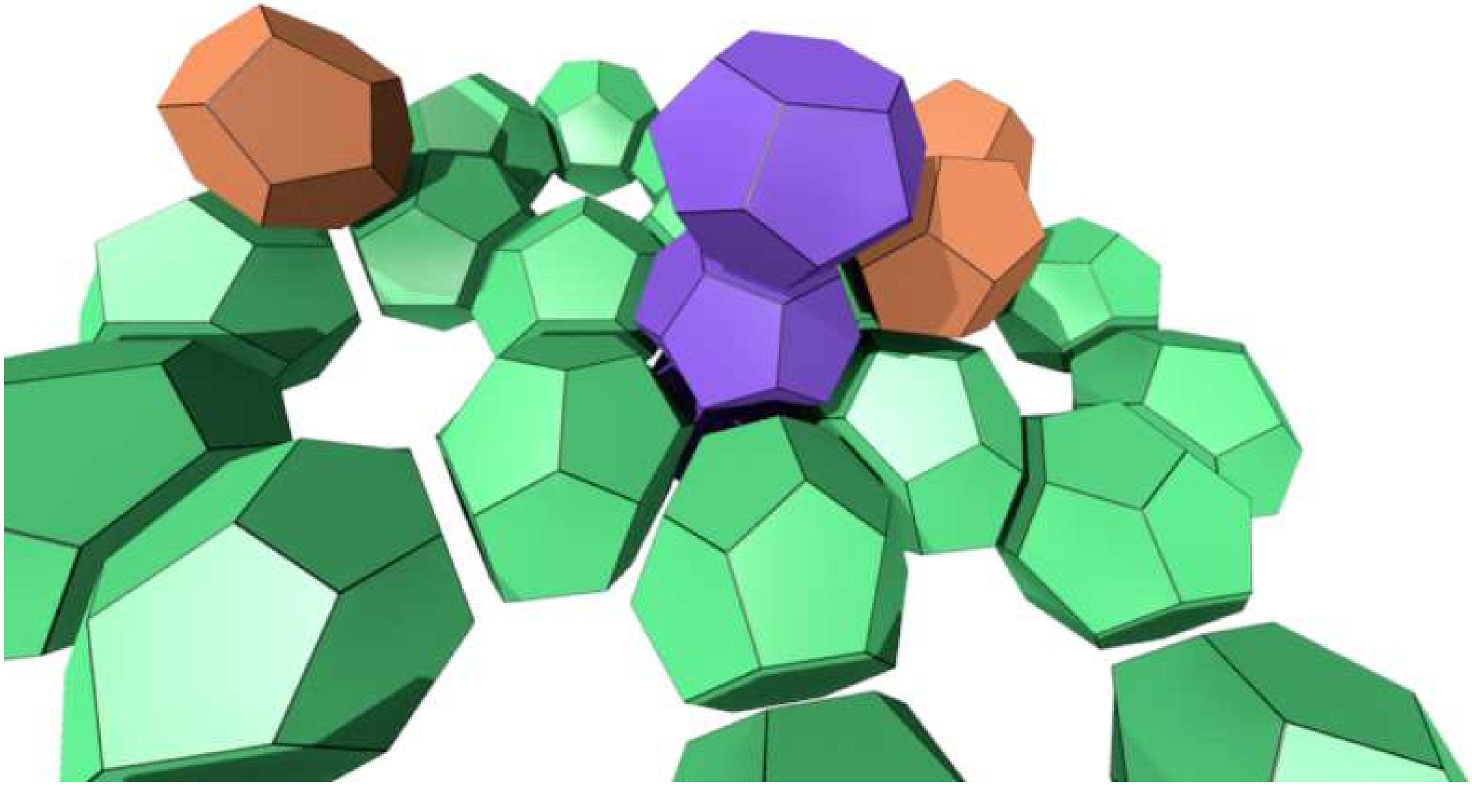
VII. Closer look on obtained structures

C_{15}, one of 5 found with $(2,0,0,1)$

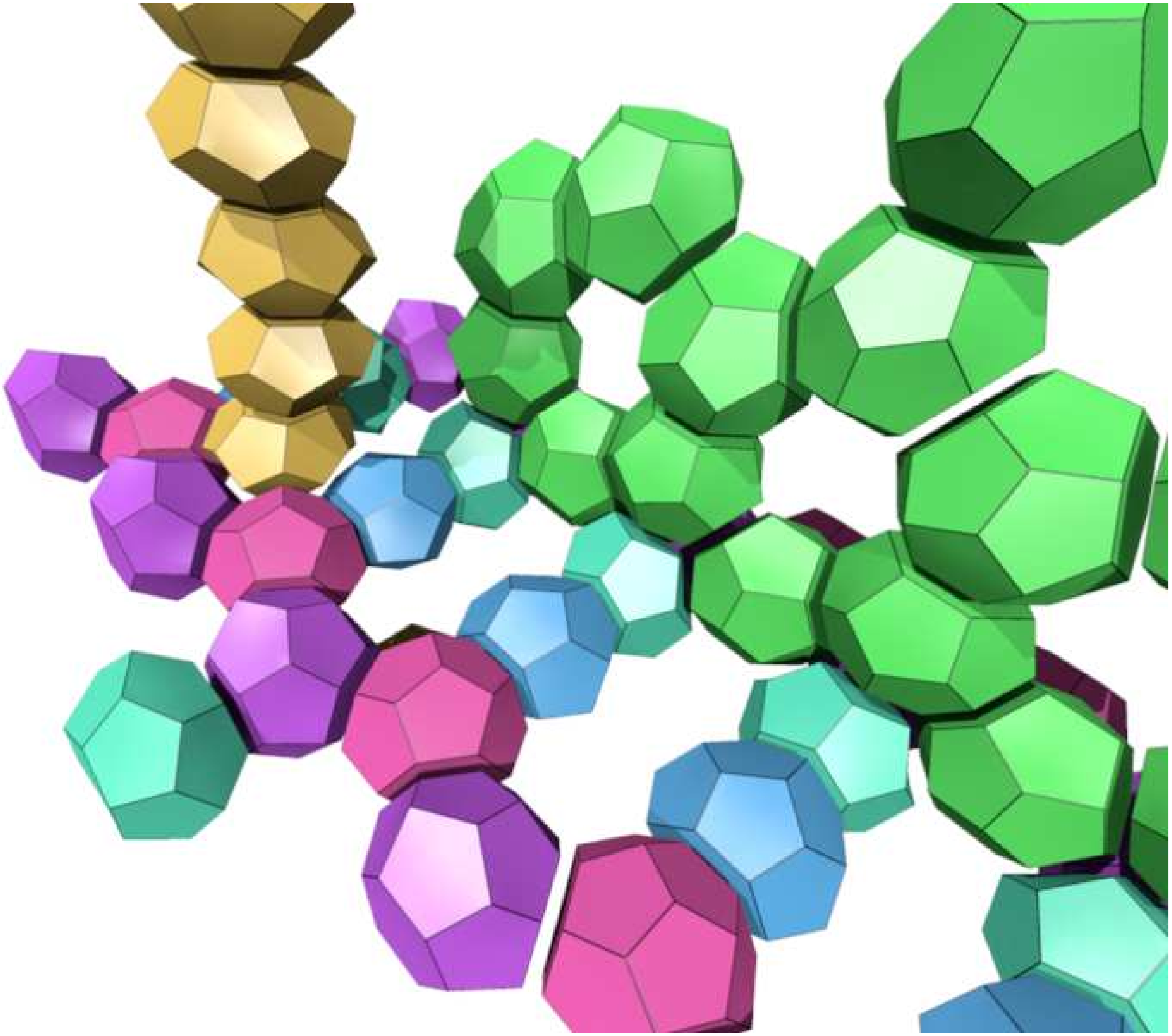
Cubic C_{15}: gravicenters of cells F_{28} (larger atoms A in AB_2) form diamond network (centered fcc). In hexagonal C_{14} they form "hexagonal diamond" (lonsdaleite found in meteorites). There is a continuum of $(2,0,0,1)$-structures.



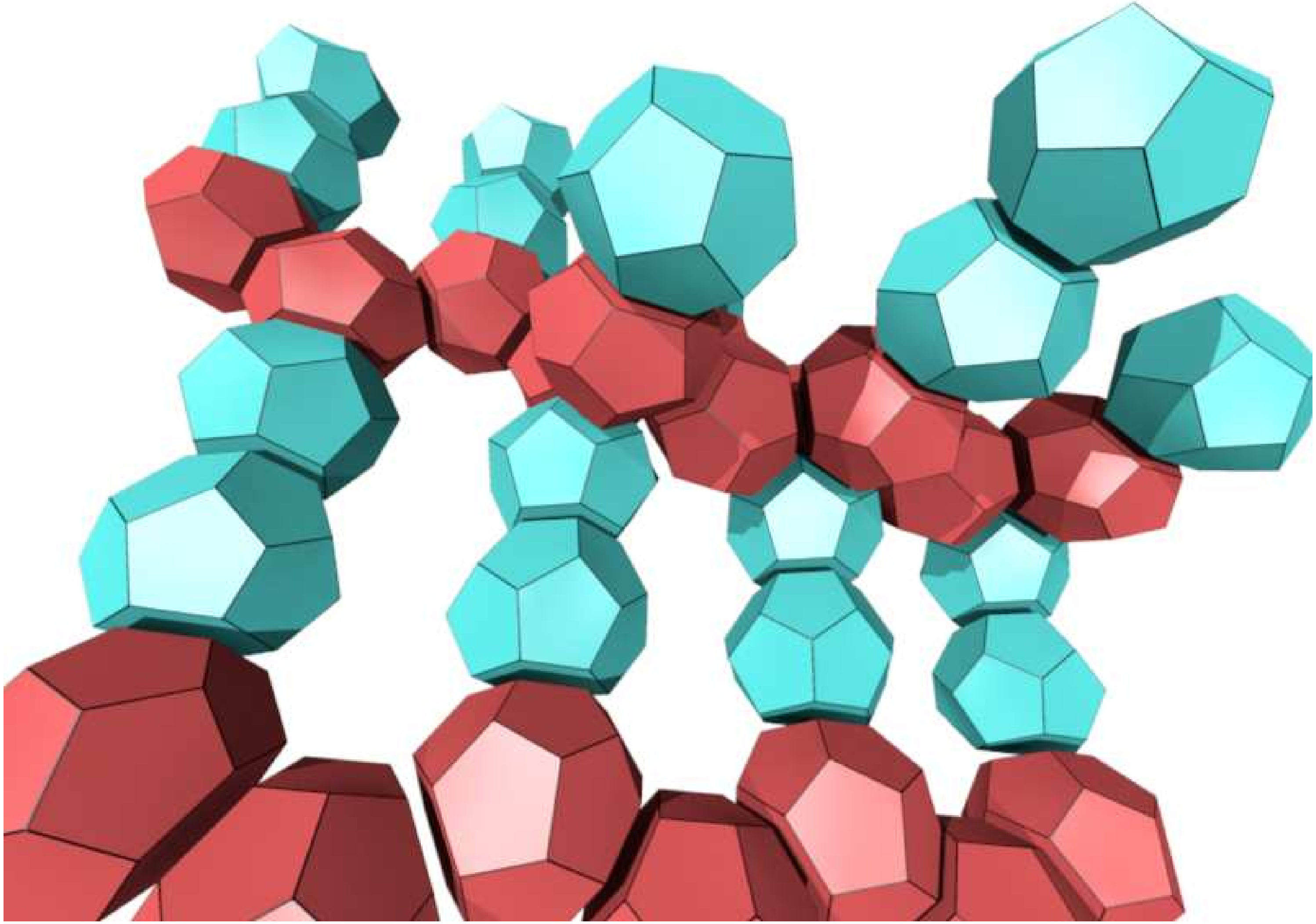
Z, one of 4 found with $(3, 2, 2, 0)$



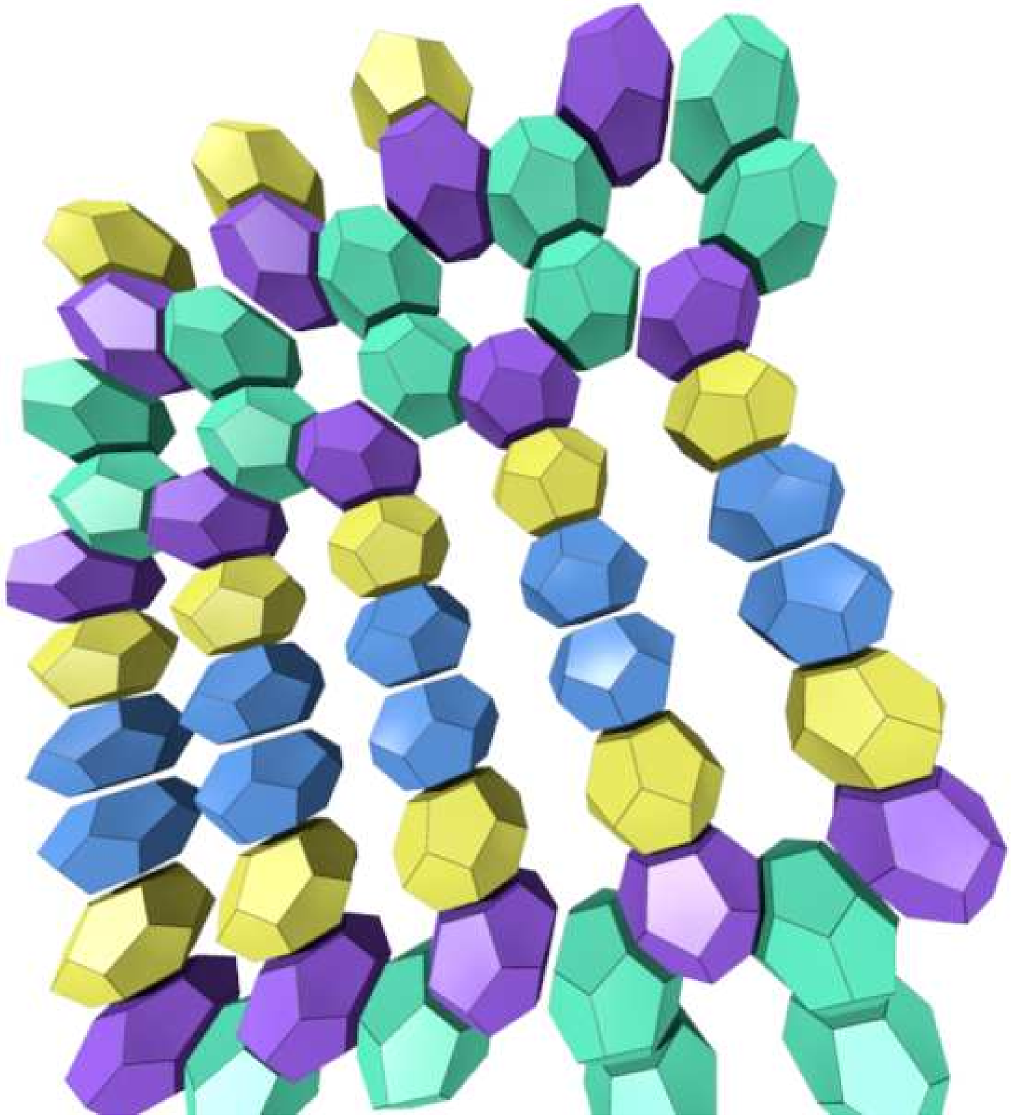
2nd found structure $(3, 2, 2, 0)$



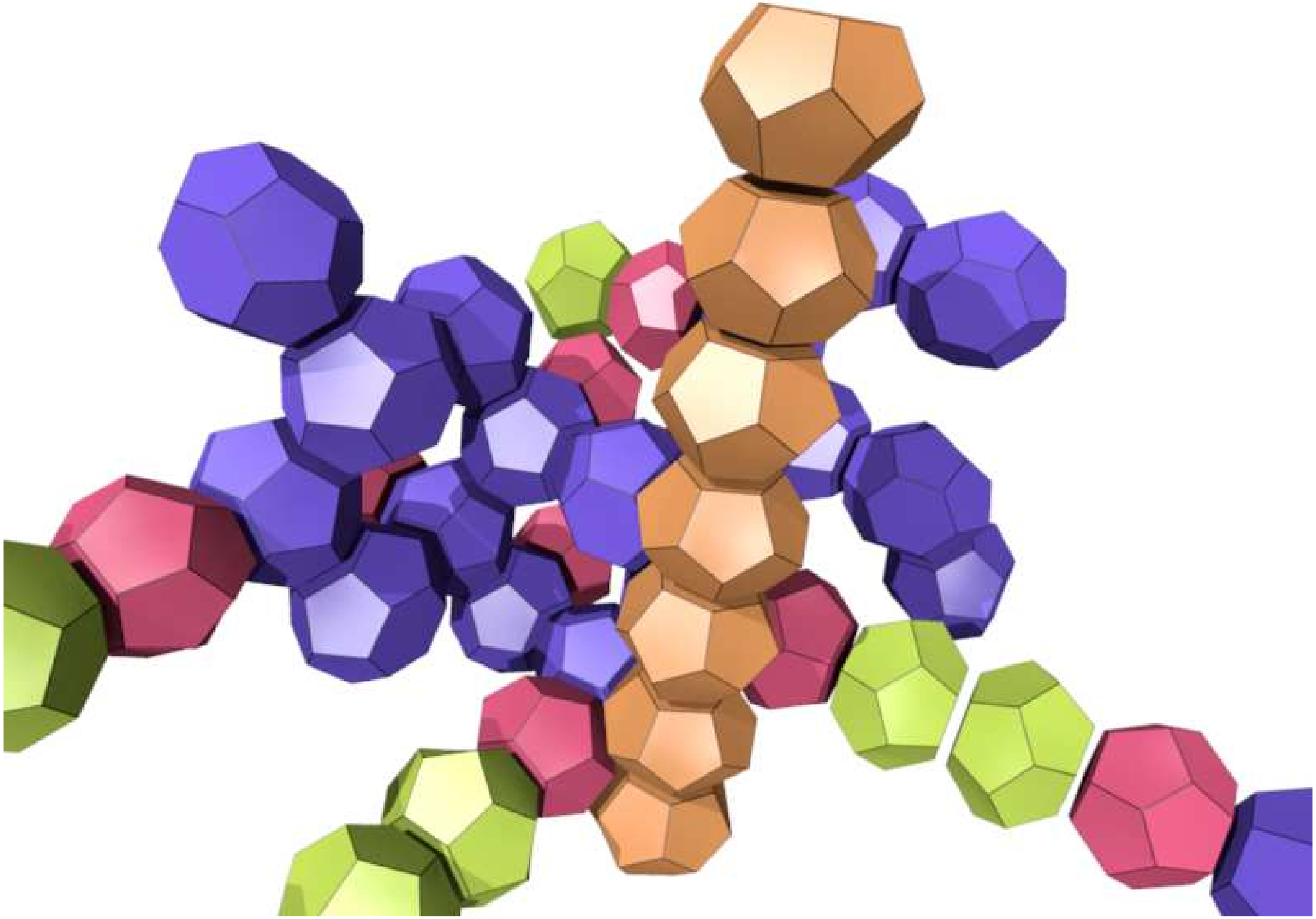
3rd found structure $(3, 2, 2, 0)$



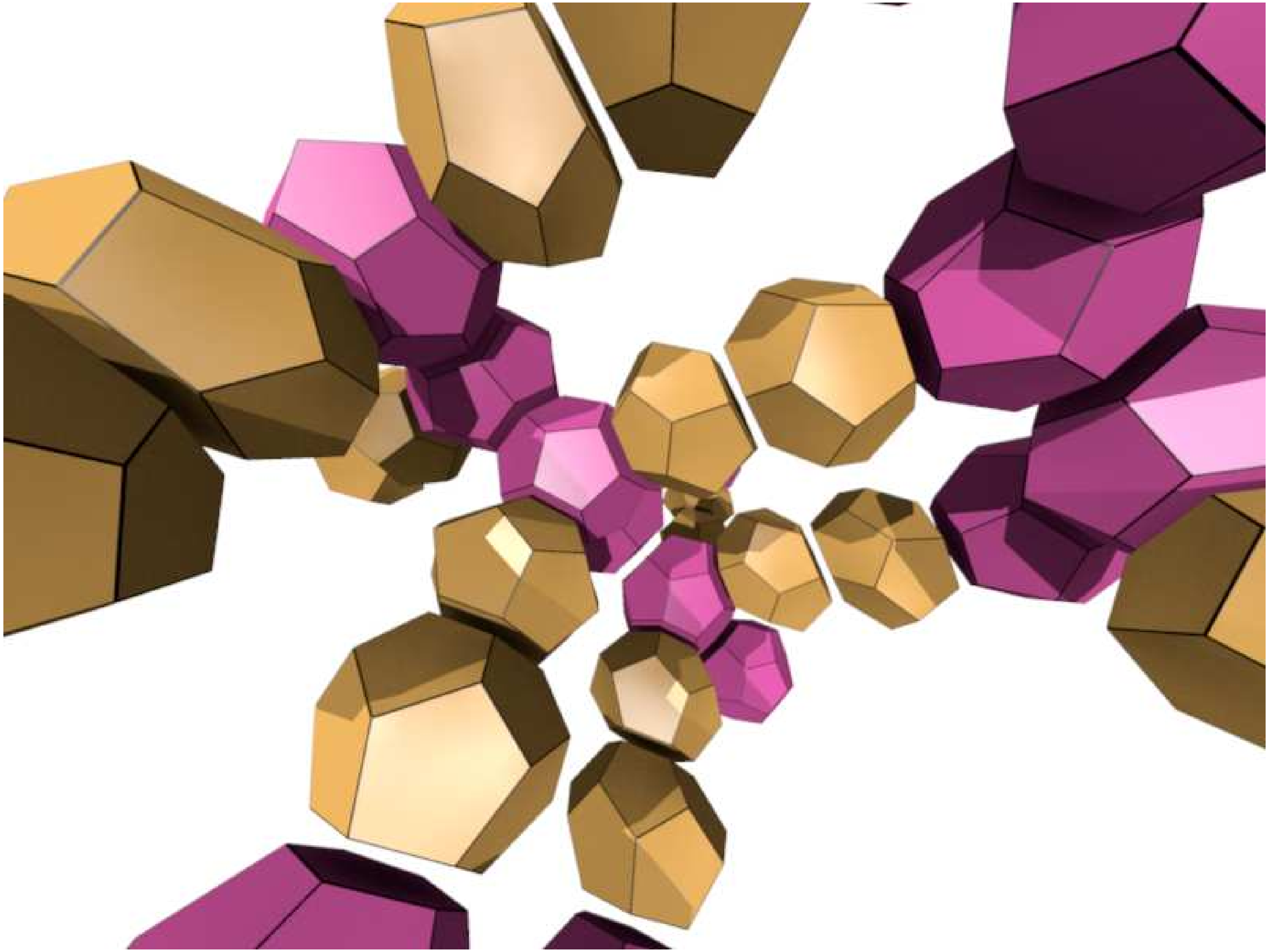
4th found structure $(3, 2, 2, 0)$



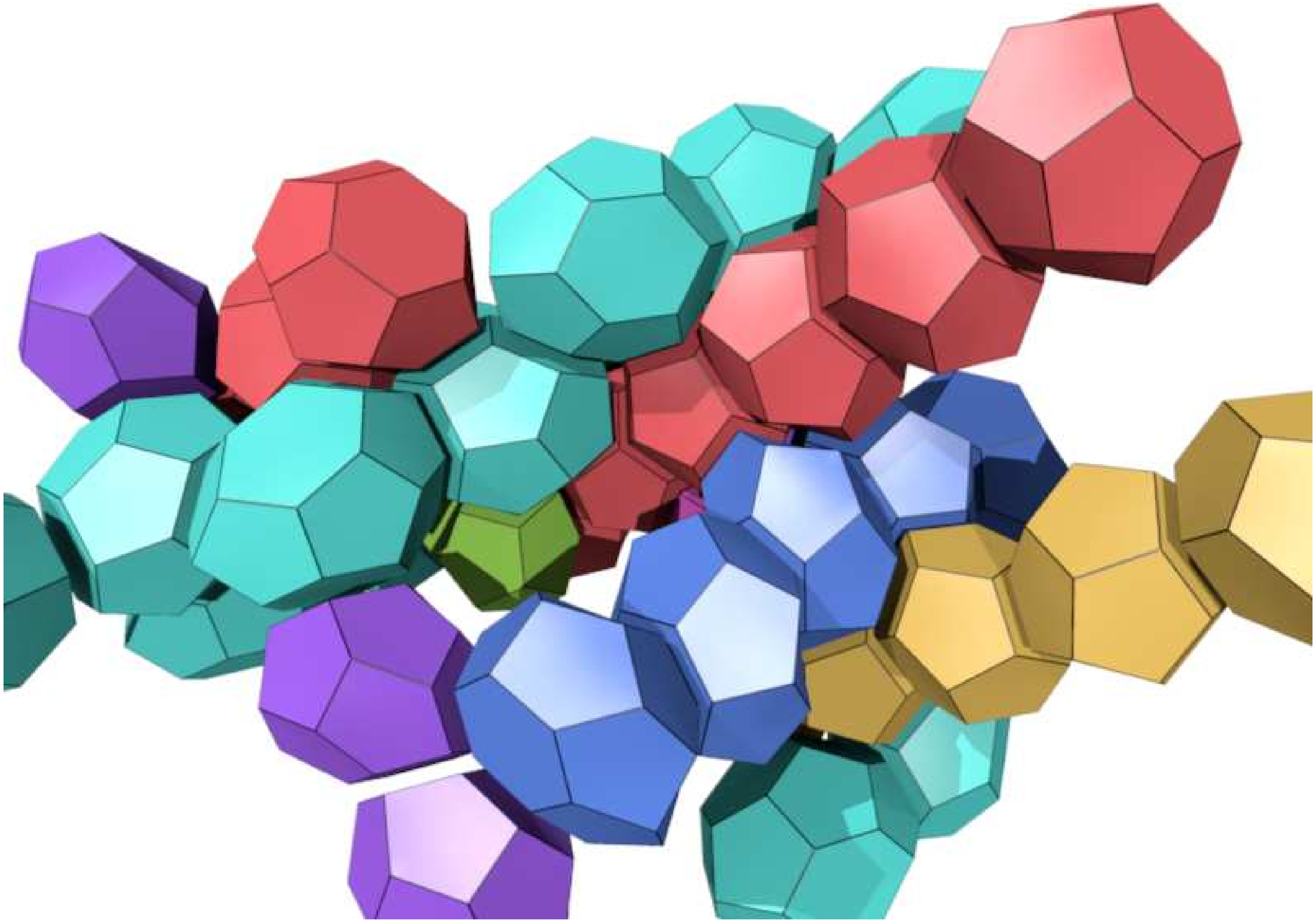
One of 3 found structures $(3, 3, 0, 1)$



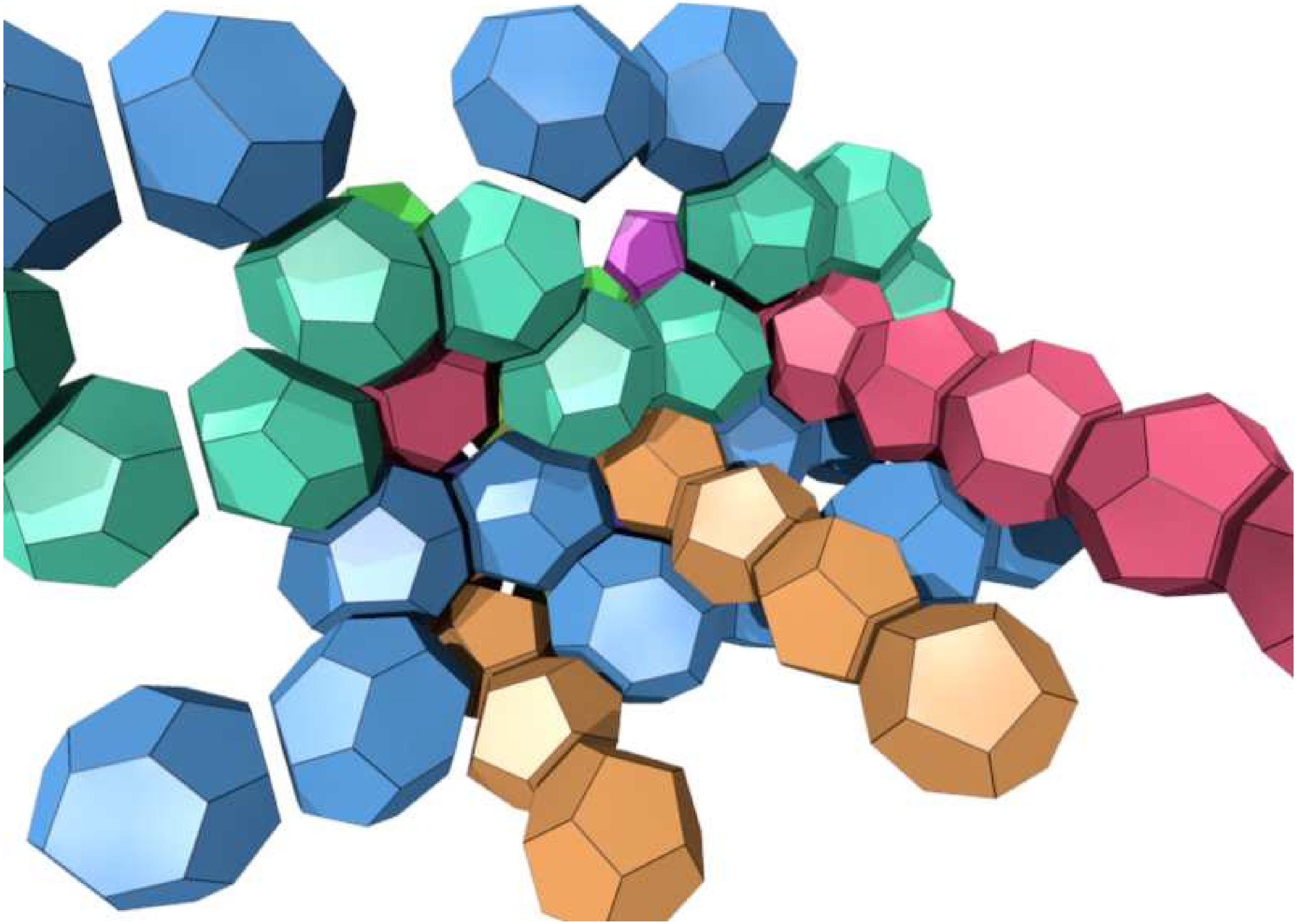
2nd found structure with $(3,3,0,1)$



3rd found structure with $(3, 3, 0, 1)$

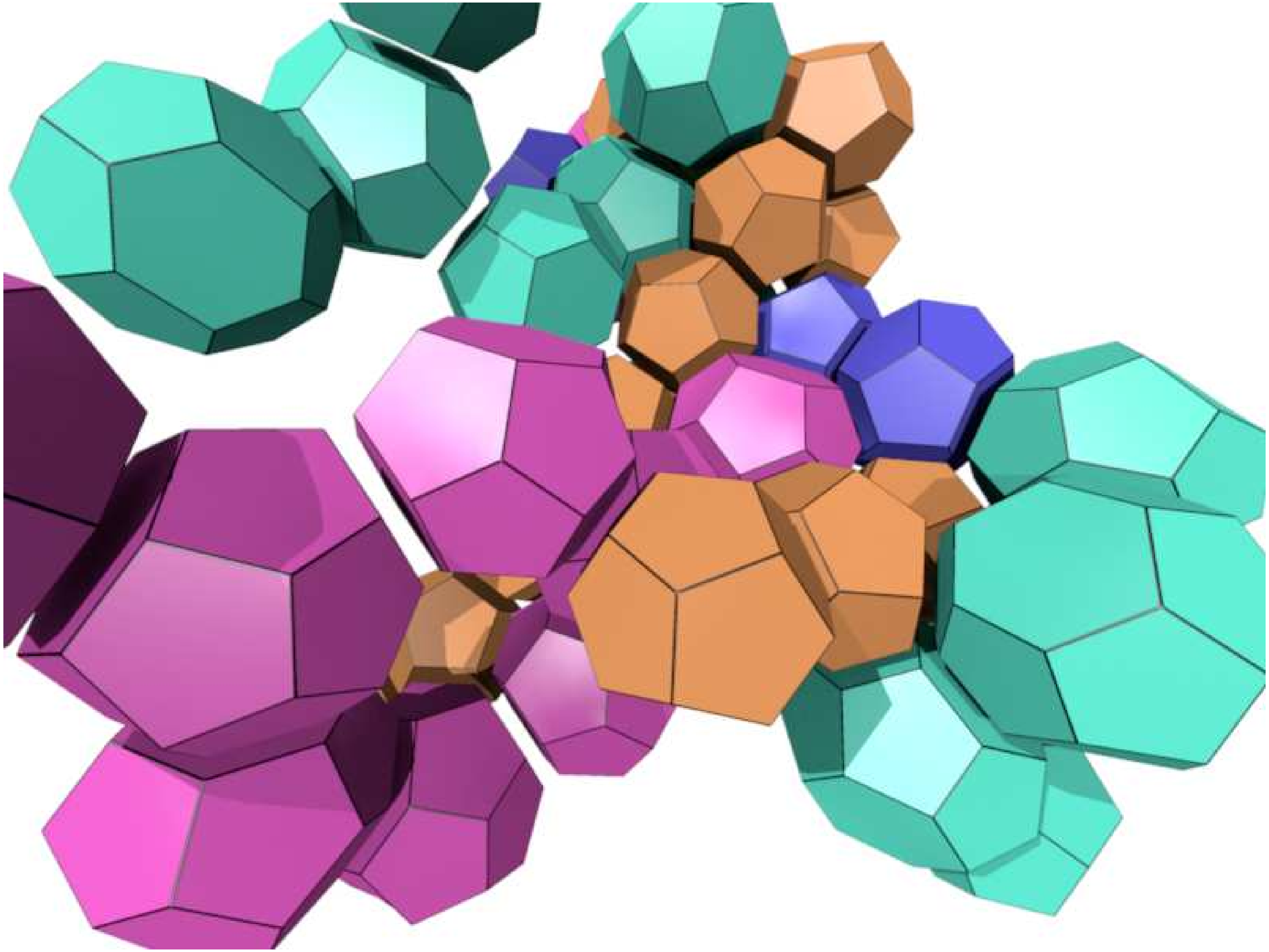


One of 5 found structures $(7, 2, 2, 2)$



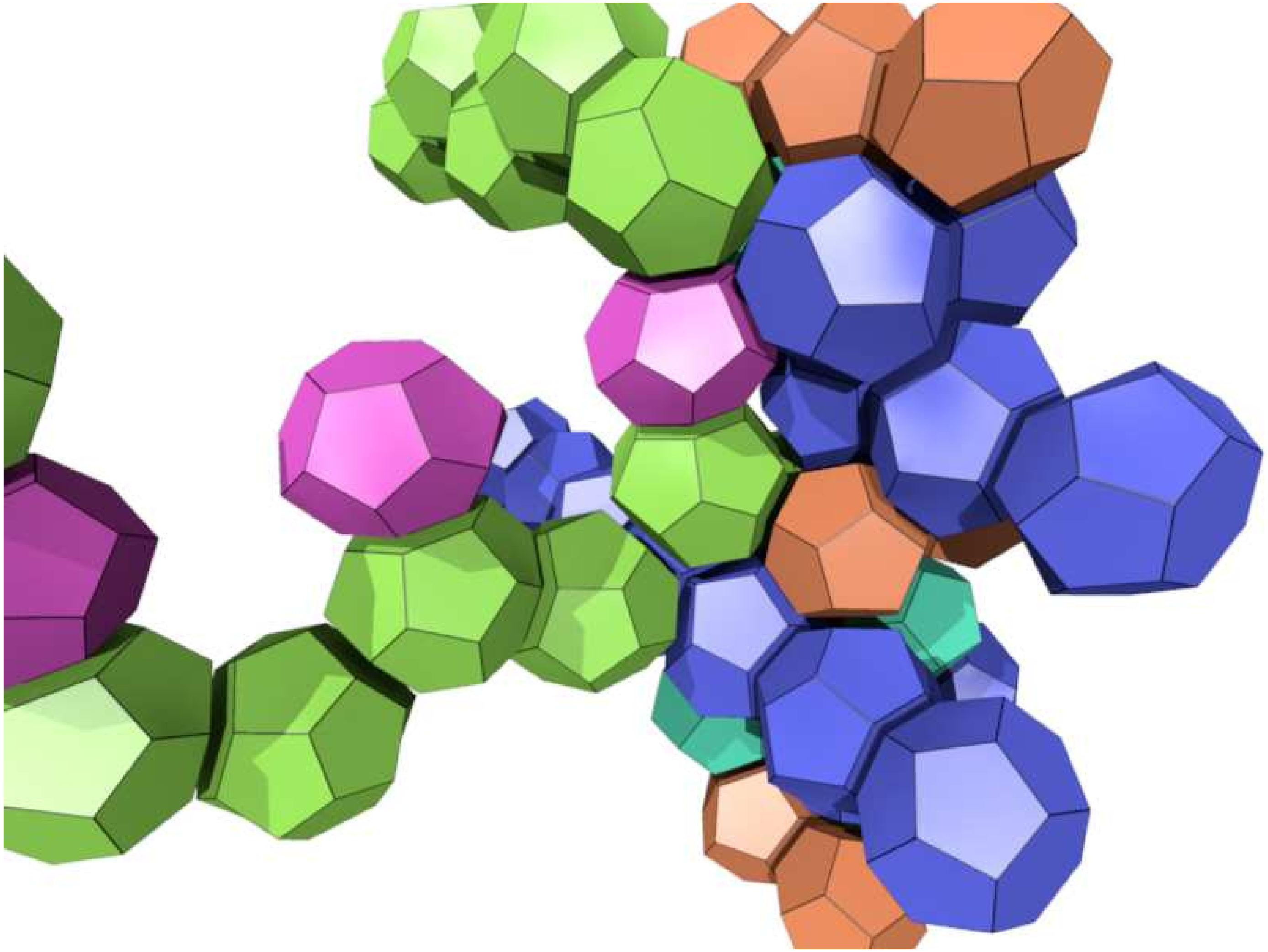
It is a mix of C_{15} and A_{15} in layers.

Another found structure $(7, 2, 2, 2)$



It is a mix of Z and C_{15} in layers.

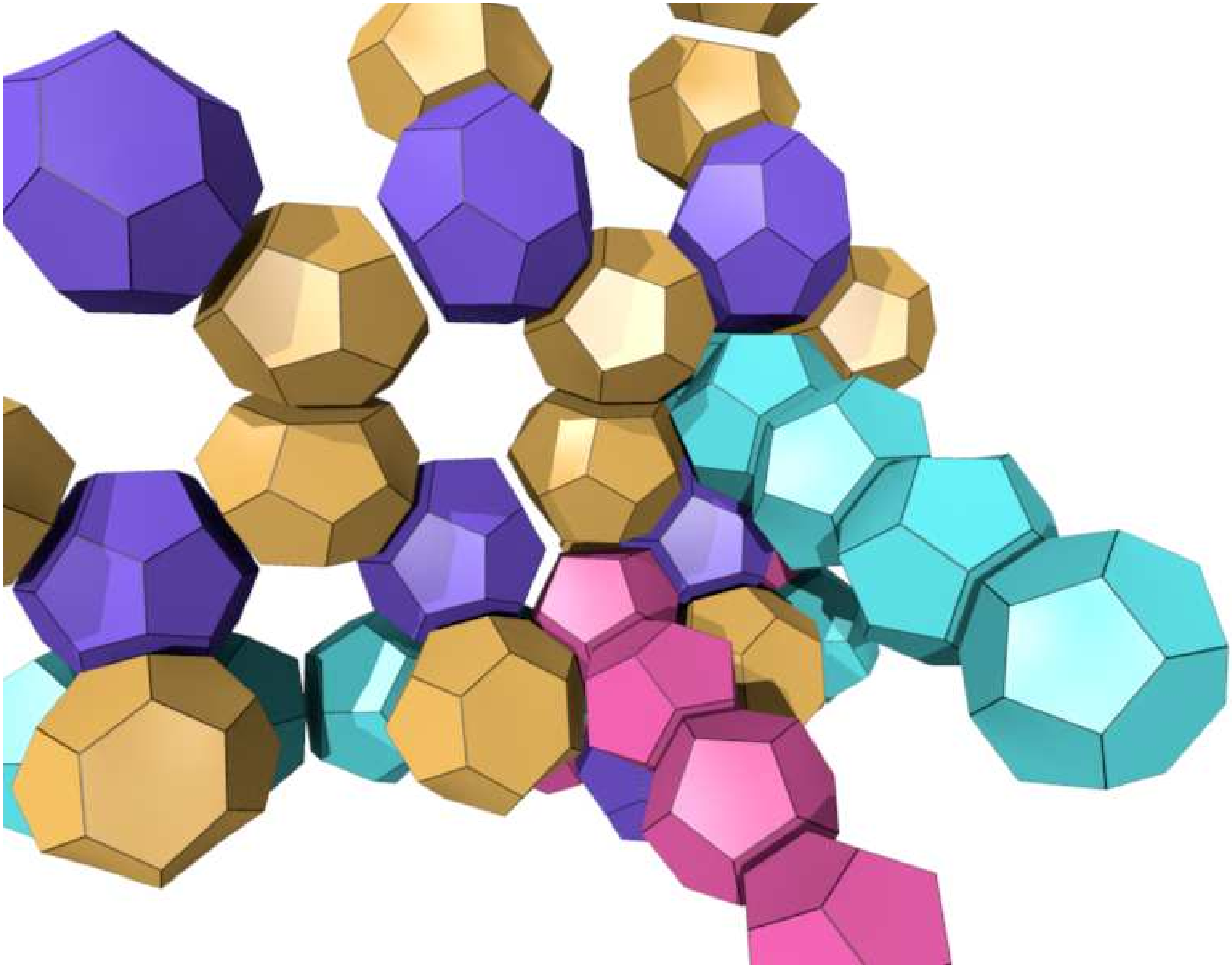
Unique found structure $(4,5,2,0)$



It is a mix of Z and A_{15} in layers. Its N=11 is smallest found.

It is not J complex (the only known one $(4,5,2,0)$) with n=22.

One of 20 found structures $(5, 2, 2, 1)$



Conclusion

- Frank, 1952: liquids are characterized by icosahedral coordination, preventng easy crystallisation into close packed structures. Frank-Kasper phases: 1958-1959.
- Sheng-Luo-Alamgir-Bai-Ma, 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.
- We found all 84 structure types of dual Frank-Kasper phases (called space fullerenes or hypothetical clathrates) with up to 20 Frank-Kasper polyhedra in Bieberbach unit cell. 13 of them are among 27 known.
- So, a new challenge to practical Crystallography and Chemistry is to check the existence of compounds having one of 71 new geometrical structures.