

Space fullerenes

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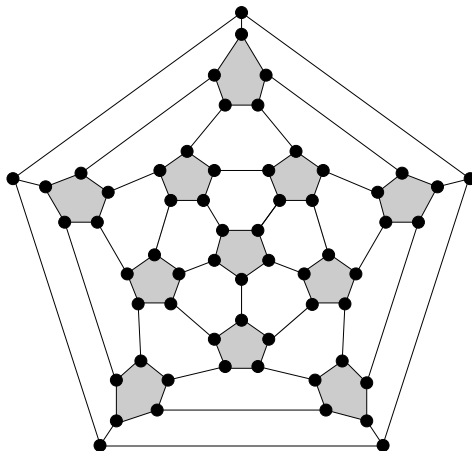
I. Introduction

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 $\text{Aut}(T)$ contains translations in three non-coplanar directions.
- T is **proper** if $\text{Aut}(T) = \text{Aut}(G)$ for its 1-skeleton (**net**) G , i.e. vertex-edge graph of T , realized in the 3-space $\mathbb{E}^3$.

Fullerenes

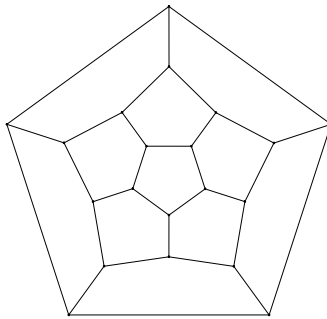
- A **fullerene** F_n is polyhedron with n 3-valent vertices and only **5-gonal** and **6-gonal** faces. So, $p_5=12$ and $p_6=\frac{n}{2}-10$.
- F_n exist for all even $n \geq 20$ except 22. Number of F_n is $1, 1, 1, 2, \dots, 1812, \dots$ for $n = 20, 24, 26, 28, \dots, 60, \dots$
Thurston, 1998, 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 $F_{60}(I_h)$:



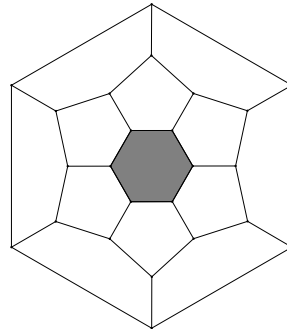
*Truncated
Icosahedron,
soccer ball,
Buckminsterfullerene*

Space fullerenes

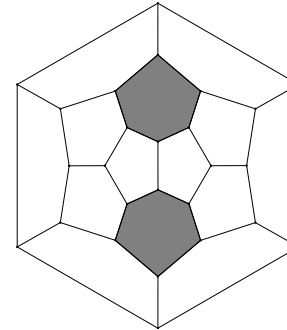
- **Frank-Kasper fullerenes** are all (four) fullerenes with **isolated hexagons**: $F_{20}(I_h)$, $F_{24}(D_{6d})$, $F_{26}(D_{3h})$, $F_{28}(T_d)$.



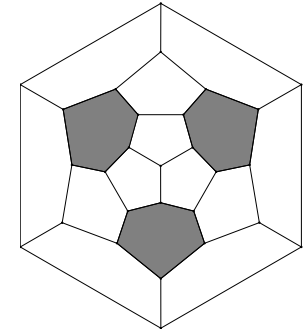
unique F_{20}



unique F_{24}



unique F_{26}

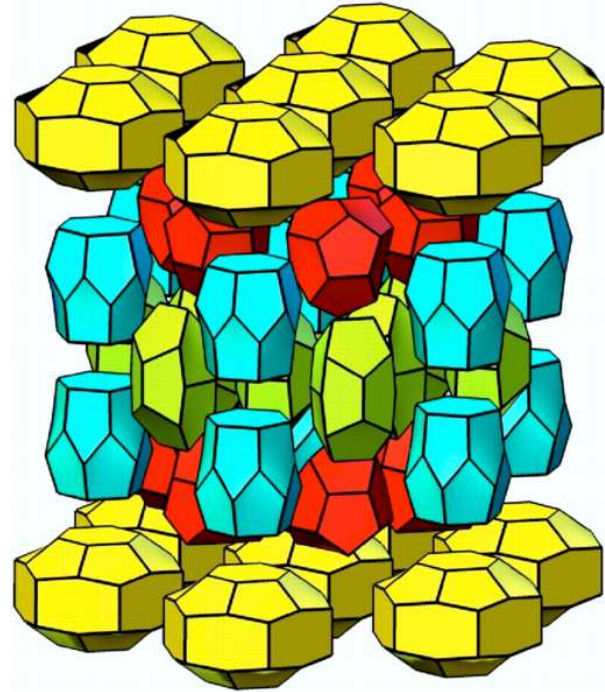
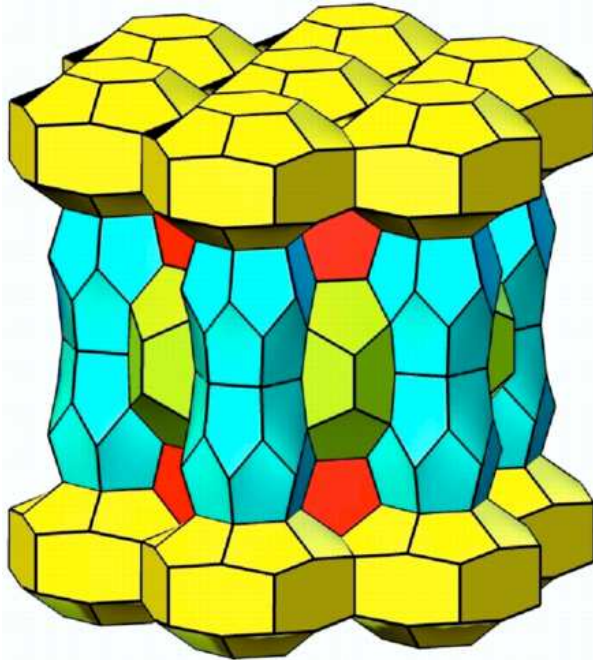


one of 2 F_{28}

- **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](#): 1st non-FK space fullerene, **MDS**.

Non-FK space fullerene MDS

Called now **MDS**, it 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. Its new records: mean face-size $\approx 5.091 < 5.1$ (C_{15}) and $\bar{f}=13.2 < 13.29$ (Rivier-Aste, 1996, conj. min.) $< 13.(3)$ (C_{15}).



Delgado, O'Keeffe, 2006: all space fullerenes with ≤ 7 vertex-orbits are 4 FK ($A_{15}, C_{15}, Z, C_{14}$) and MDS (3,3,5,7,7).

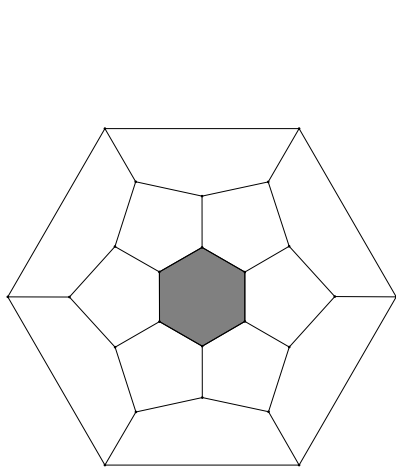
All known non-FK space fullerenes

name	$\bar{f}$ in cell	nr of v -orb.	20 I_h	24 D_{6d}	26 D_{3h}	28 T_d	28 D_2	30 C_{2v}	30 C_{2v}	36 D_{6h}	36 D_{3h}	40 T_d
MDS	13.20	7	7	2	0	0	0	0	0	1	0	0
ODH	13.40	10	9	10	0	0	0	0	0	1	0	0
ODG	13.26	10	12	5	0	1	0	0	0	0	0	1
ODL	13.(3)	11	8	6	0	0	0	0	0	0	1	0
ODJ	13.29	11	10	4	2	0	0	0	0	1	0	0
ODF	13.30	9	17	0	0	0	0	0	6	0	0	0
ODI	13.(3)	11	6	1	0	0	0	2	0	0	0	0
ODM	13.40	11	6	1	0	0	3	0	0	0	0	0

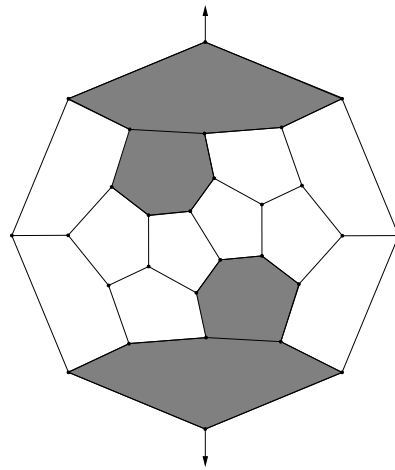
7 new 3-periodic non-FK space fullerenes (all with at most 11 vertex orbits) are given from 2010 on RCSR (Reticular Chemistry Structure Resource) database (O'Keeffe et al.) as *clathrates*, *simple tilings*. So, five new putative tiles, in addition to four Frank-Kasper ones and $F_{36}(D_{6h})$.

Fullerenes occurring in $\mathbb{E}^3$ - and $\mathbb{S}^3$ -tilings

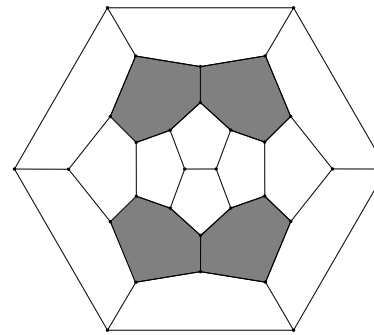
In all known (Deza-Shtogrin, 1999) 4-valent tilings of $\mathbb{S}^3$ by fullerenes (fullerene 4-polytopes), putative tiles (besides 4 Frank-Kasper ones, $F_{36}(D_{6h})$) are $F_{30}(D_{5h})$, $F_{32}(D_{3h})$ below.



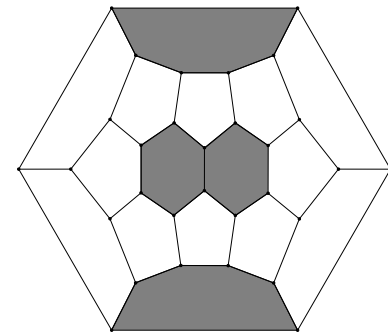
24, D_{6d}



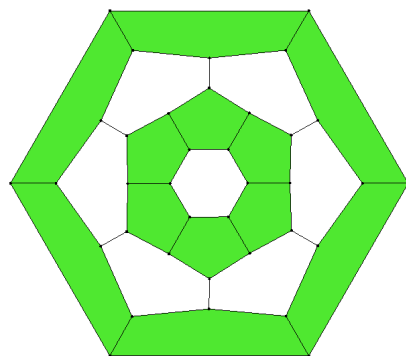
28, D_2



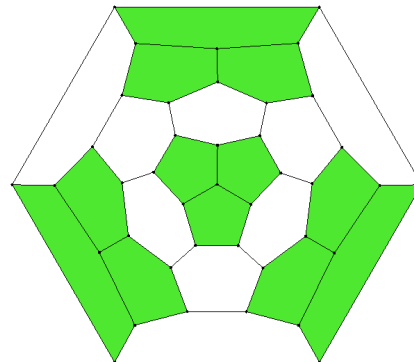
30, D_{2d}



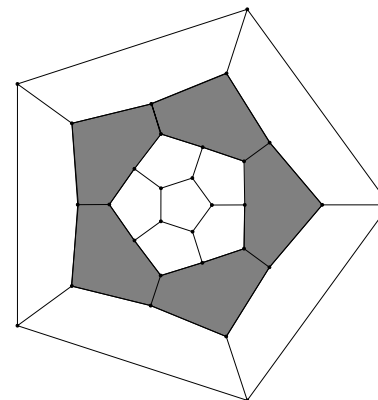
30, C_{2v}



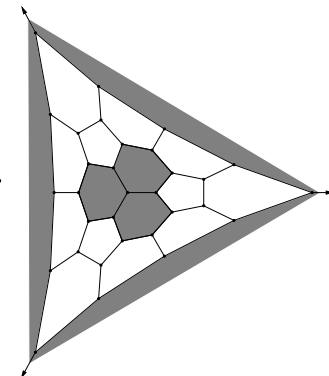
36, D_{6h}



40, T_d



30, D_{5h}



32, D_{3h}

FK space fullerenes given on RCSR

name	t.c.p.	$\bar{f}$	v	20	24	26	$_{28}T_d$
ODK	Nr.58	13.(5)	11	3	4	2	0
MEP	A_{15}	13.50	3	1	3	0	0
SIG	σ	13.47	17	5	8	2	0
ZRA-d	Z	13.43	5	3	2	2	0
MUR	μ	13.38	13	7	2	2	2
MUH	K_7Cs_6	13.38	13	7	2	2	2
TEI	T	13.36	27	49	6	6	20
TEP	SM	13.36	28	49	9	0	23
MTN	C_{15}	13.(3)	3	2	0	0	1
MGZ-X-d	C_{14}	13.(3)	7	2	0	0	1

Above structures are given on RCSR as nets of *clathrates*, *simple tilings*. ODK is our Nr. 58. It and TEP coming from *Sadoc-Mosseri construction* are not physical.

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** 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 mirror planes. Their *strip groups* are $pmmm$ or $p2/m11$.

Digression 2: fullerene manifolds

d -fullerene: $(d-1)$ -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 4-fullerenes in $\mathbb{H}^3$. 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

Crystalline and icosahedral orders

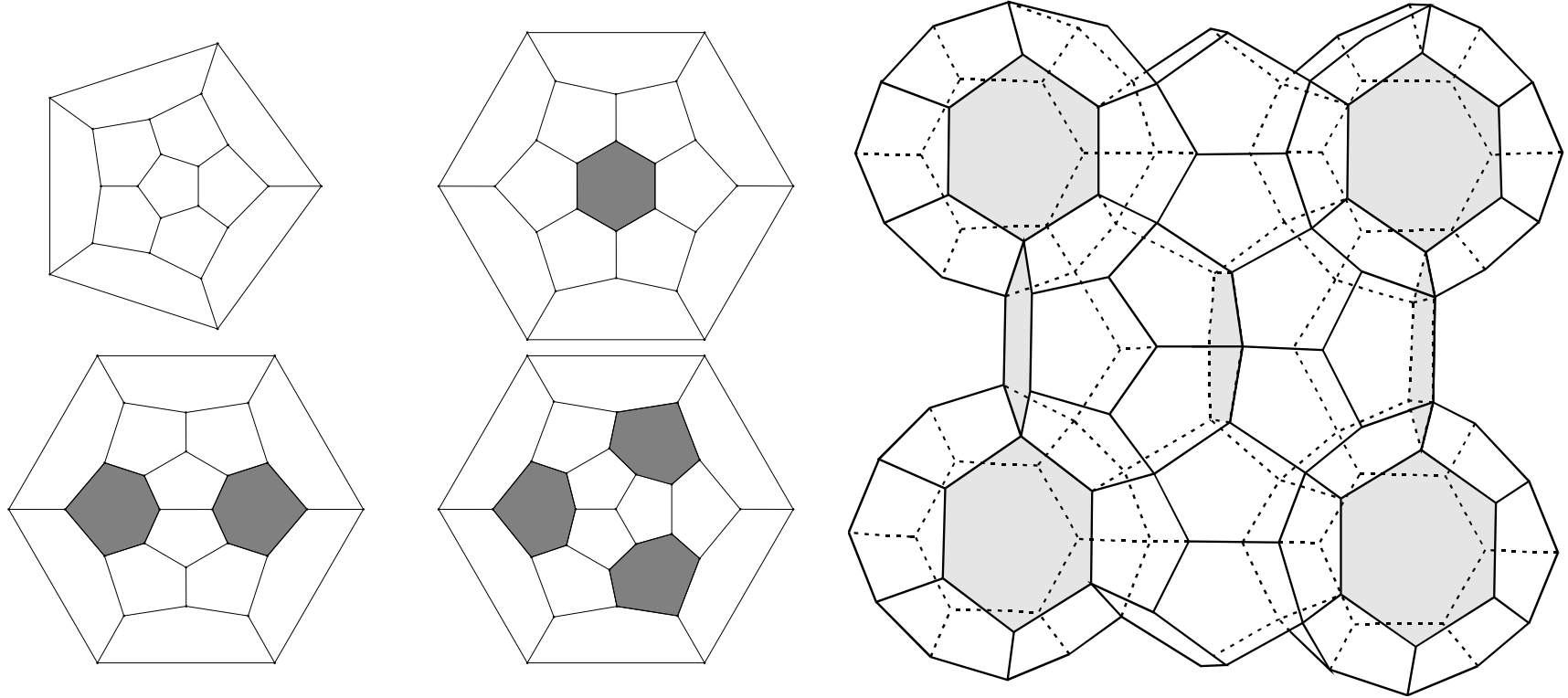
- **Crystals**: from basic units by symm. operations, incl. translations, excl. order 5 rotations (cryst. restriction).
- **Quasicrystals, fullerene-like, icosahedral packings**: order 5 rotations instead of translations.
- **Frank, 1952**: liquids are characterized by icosahedral coordination, preventing easy crystallisation into close packed structures. **Frank-Kasper phases**: 1958-1959.
- **Sheng-Luo-Alamgir-Bai-Ma, 2006**: 4 FK polyhedra predominate among coordination and Voronoi polyhedra of non-crystalline metallic materials.
- Bulk metallic *glass* (non-crystalline solid material) formers tend to local icosahedral chemical ordering (LIO). The frustration between this short-range and crystalline long-range orderings controls fragility and glass or quasicrystal forming ability of these liquids.

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 , edges 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., $tr.\beta_3$ 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	$\bar{f}$	$F_{20}:F_{24}:F_{26}:F_{28}$	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	$\bar{f}$	$F_{20}:F_{24}:F_{26}:F_{28}$	n	?
K^*	$Mn_{77}Fe_4Si_{19}$	$C2$	13.42	25,19, 4, 7	220	
R	$Mo_{31}Co_{51}Cr_{18}$	$R\bar{3}$	13.40	27, 12, 6, 8	159	
μ	W_6Fe_7	$R\bar{3}m$	13.38	7, 2, 2, 2	39	+
$\neg*$	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	$Mg_{32}(Zn, Al)_{49}$	$Im\bar{3}$	13.36	49, 6, 6, 20	162	
SM	$Mg_{32}(Zn, Al)_{49}$	$Pm\bar{3}n$	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 fullerenes given as nets

name	t.c.p.	$\bar{f}$	v	20	24	26	$_{28}T_d$
ODK	Nr.58	13.(5)	11	3	4	2	0
MEP	A_{15}	13.50	3	1	3	0	0
SIG	σ	13.47	17	5	8	2	0
ZRA-d	Z	13.43	5	3	2	2	0
MUR	μ	13.38	13	7	2	2	2
MUH	$K_7C_{s_6}$	13.38	13	7	2	2	2
TEI	T	13.36	27	49	6	6	20
TEP	SM	13.36	28	49	9	0	23
MTN	C_{15}	13.(3)	3	2	0	0	1
MGZ-X-d	C_{14}	13.(3)	7	2	0	0	1

Above structures are given on RCSR database ([O'Keeffe et al.](#)) as *clathrates*, *simple tilings*. ODK is our Nr. 58. It and TEP (*Sadoc-Mosseri construction*) are not physical.

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), $MgCu_2$.

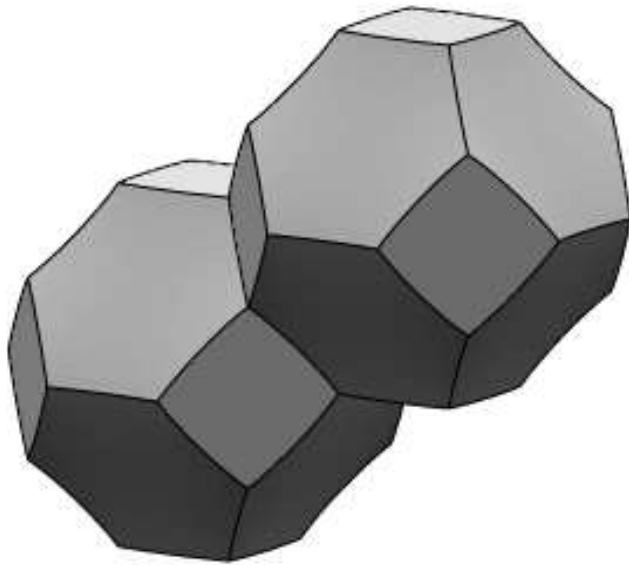
Their *unit cells* have, respectively, 46, 136 vertices and 8 (2 F_{20} and 6 F_{24}), 24 (16 F_{20} and 8 F_{28}) cells.

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

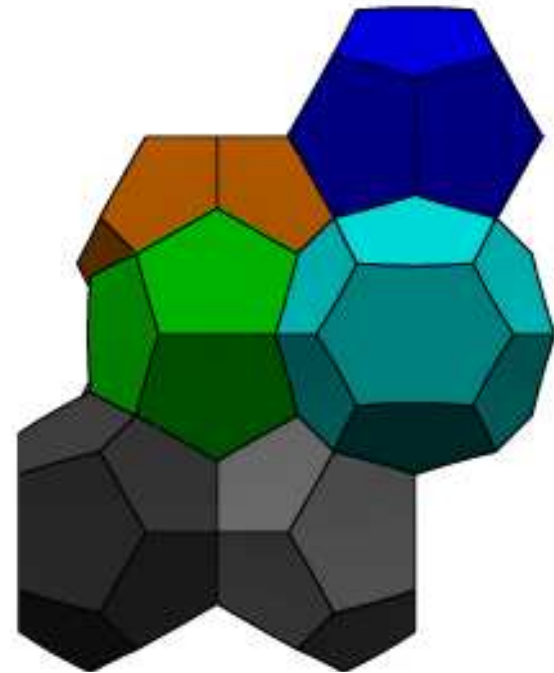
Closer to impossible 5 or $\bar{f} = 12$ (120-cell, S^3 -tiling by F_{20}) means lower energy. Minimal $\bar{f}$ for *simple* (3, 4 tiles at each edge, vertex) $\mathbb{E}^3$ -tiling by a *simple* polyhedron is 14 (tr.oct).

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 tiling: best known *monohedral*. Almgren: beat it by variational optimization (*Evolver*) over periodic structures.



Lord Kelvin, 1887: $\text{bcc} = A_3^*$
 $IQ(\text{curved tr.Oct.}) \approx 0.757$
 $IQ(\text{tr.Oct.}) \approx 0.753$



Weaire-Phelan, 1994: A_{15}
 $IQ(\text{unit cell}) \approx 0.764$
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.



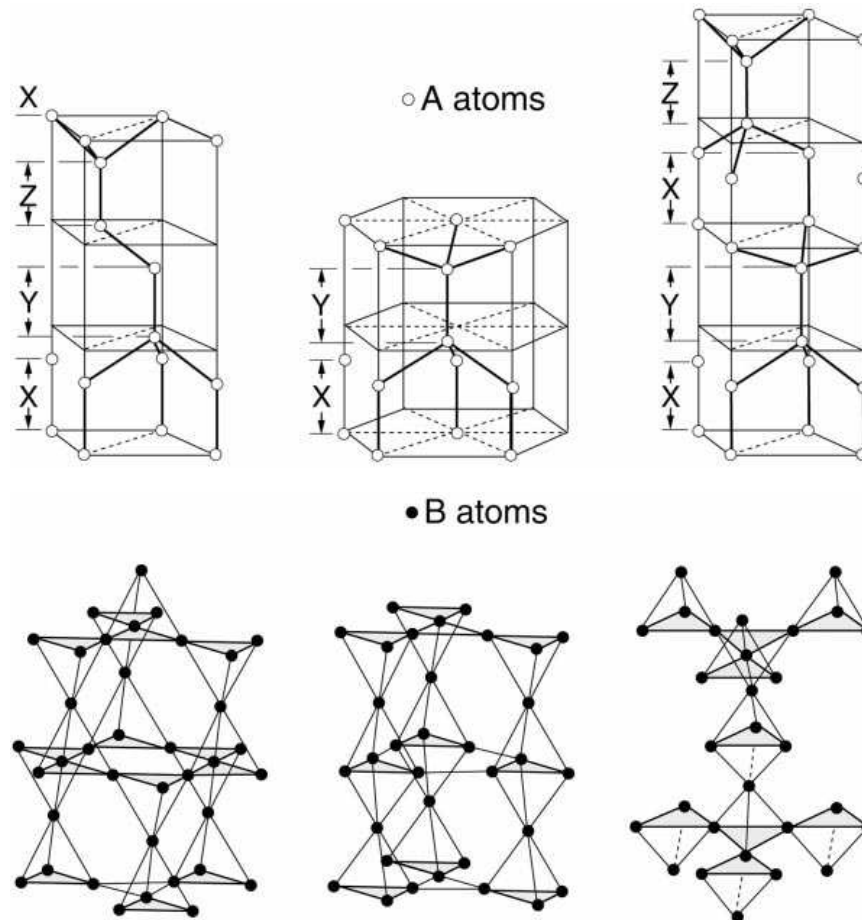
Laves phases: space fullerenes (2, 0, 0, 1)

It is largest (> 1400) group of intermetallics; formula $\approx AB_2$.

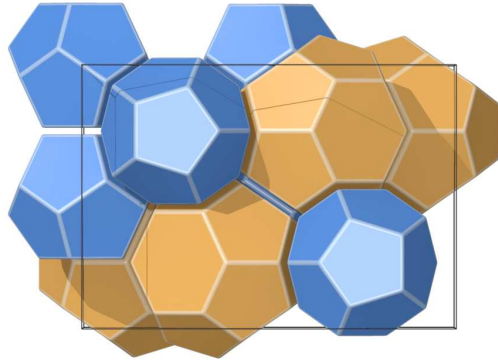
Most crystallize as (cubic) C_{15} or (hexagonal) C_{14} , C_{36} .

Smaller B atoms: corner-linked tetrahedra B_4 regular in C_{15}

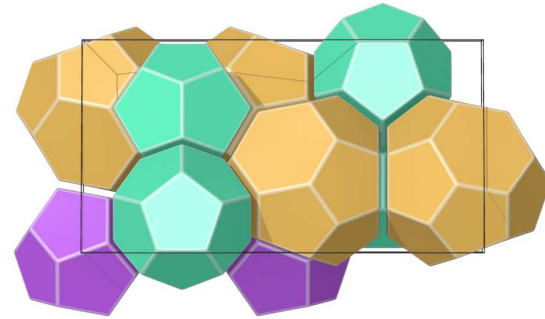
A atoms: interstices in B sub-lattice, or F_{28} gravicenters. In C_{15} , C_{14} A form diamond network and its hexagonal variant.



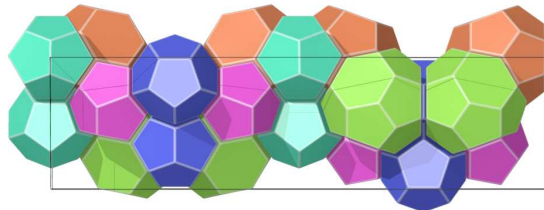
Five Laves phases found among 84



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), $P6_3/mmc$



$MgZn_2+0.07MgAg_2$ (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 $(a_i)_{-\infty \leq i \leq \infty}$ 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- $XYZ'YZX'Z'YZ'Y'$.

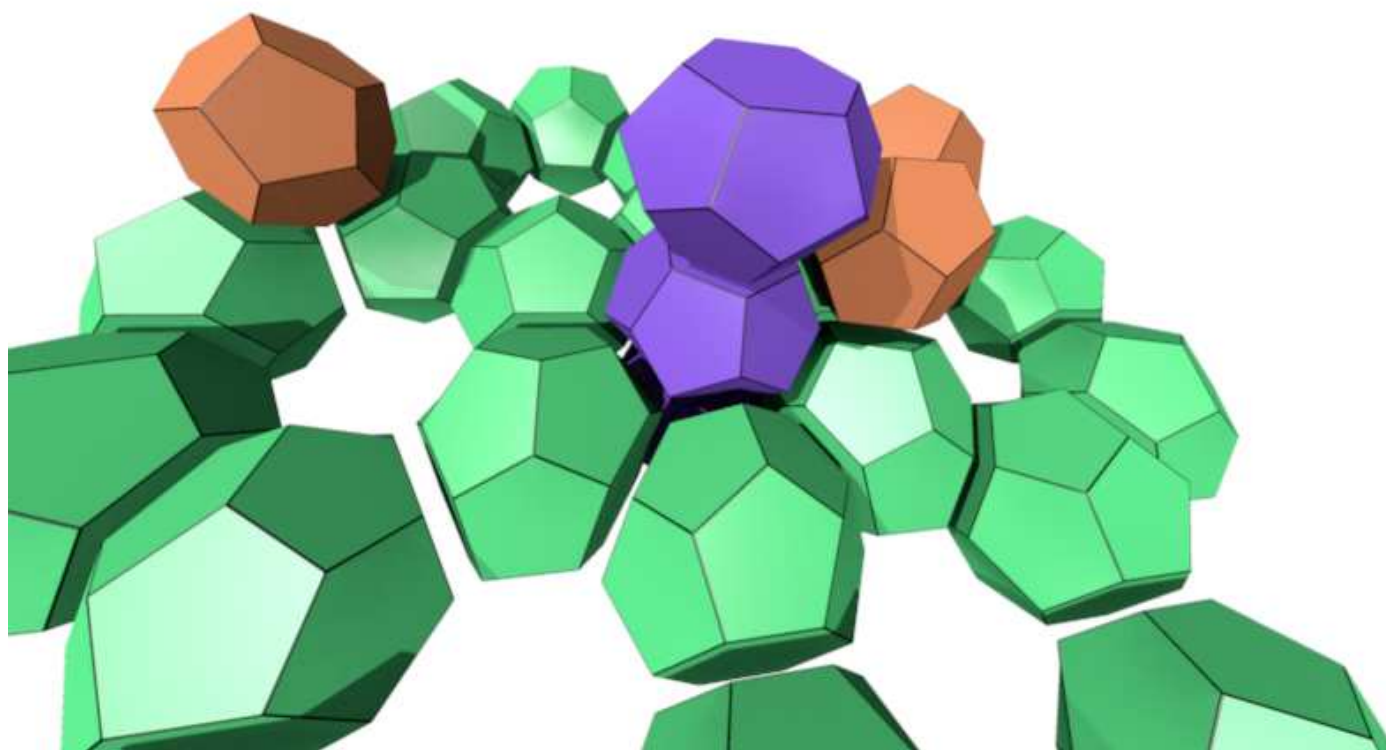
Unit cell size of t-layer is $6t$ for $t=2,4,6,8,9,10$ and 24 for $t=3$.

Krpyakevich-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, $Br_{2.86}H_2O$.

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	counterexample	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	counterexample	16(1)	-
4	12	0	0	known	16(1)	8(A_{15})

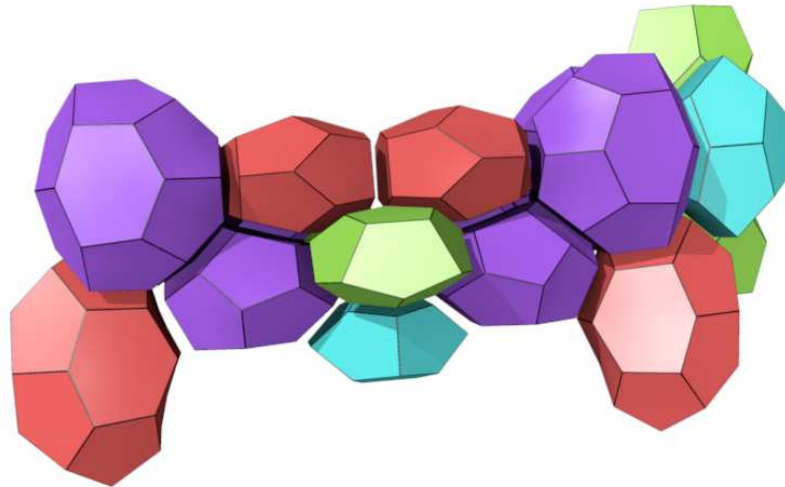
Computer enumeration

# 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)	-

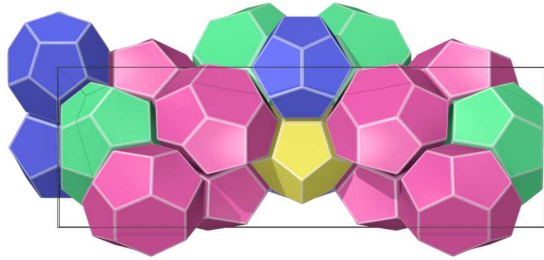
Counterexamples to 2 old conjectures

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



All found counterexamples



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



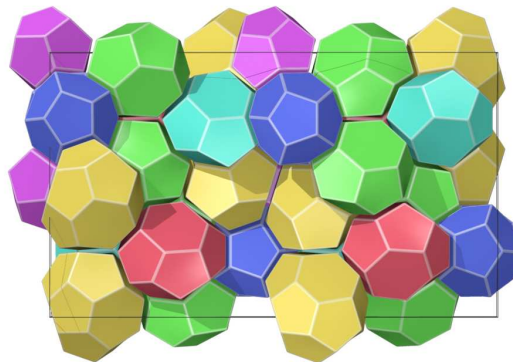
Nr. 40 (6, 6, 4, 0)



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

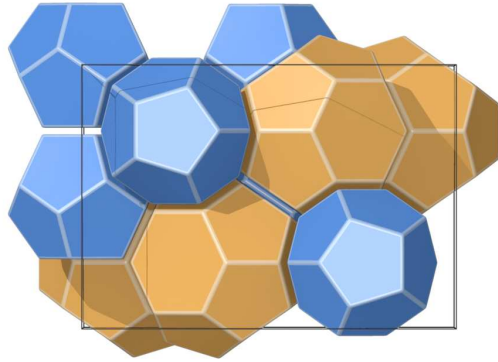


Nr. 1 (7, 4, 2, 2)

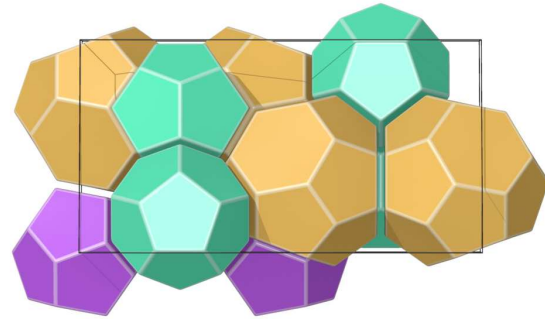


Nr. 63 (6, 8, 4, 0)

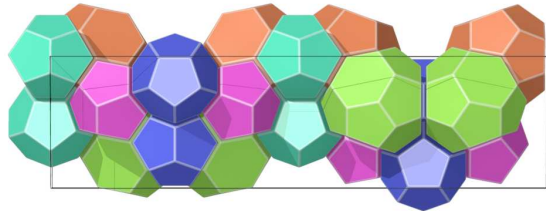
All found with known fraction (2,0,0,1)



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



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



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



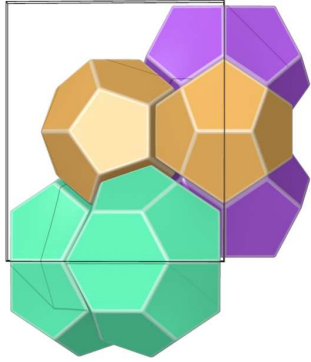
$MgNi_2$ -55 mol% $MgCu_2$
(6-layer stacking)



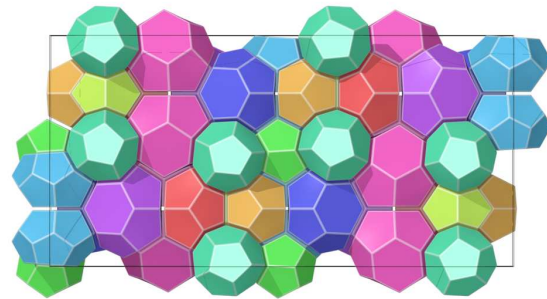
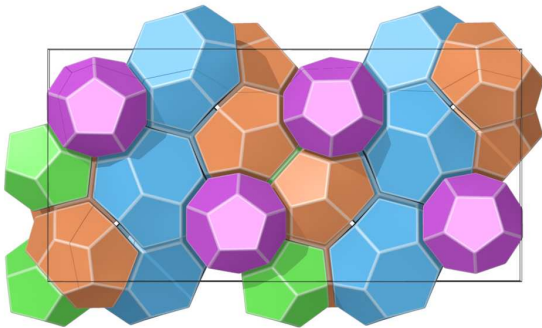
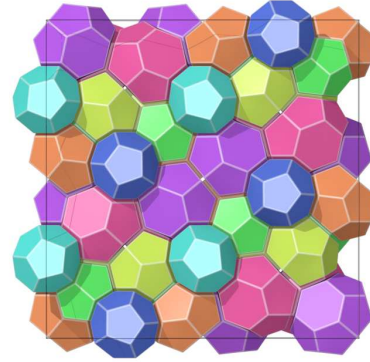
$MgZn_2+0.07MgAg_2$ (9-layer stacking)

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

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

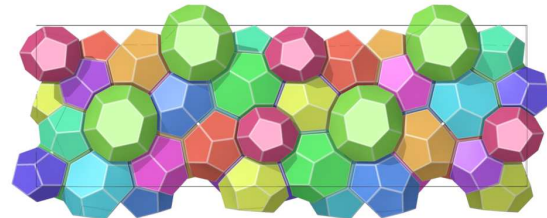
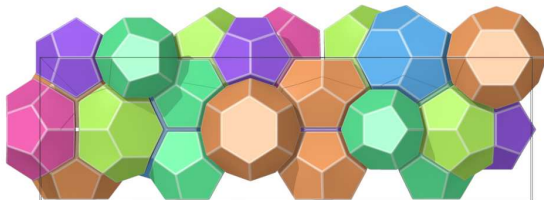
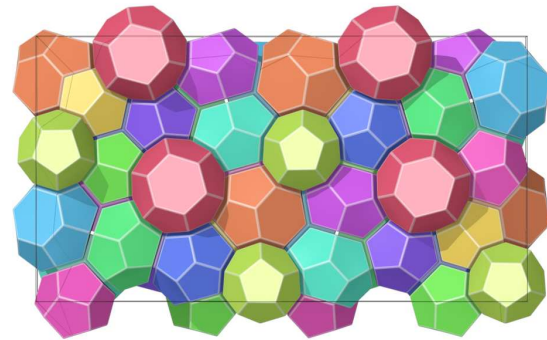
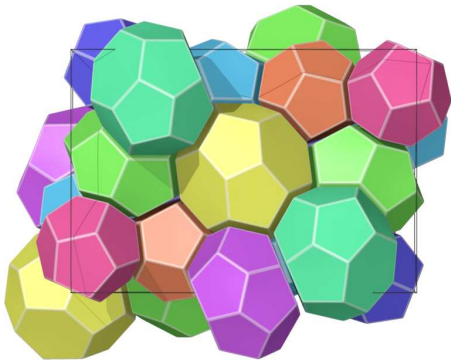
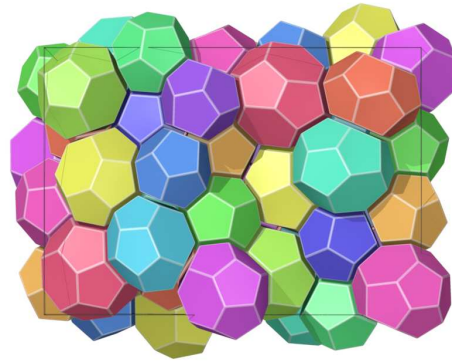


Z



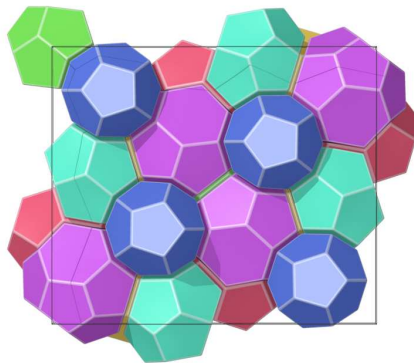
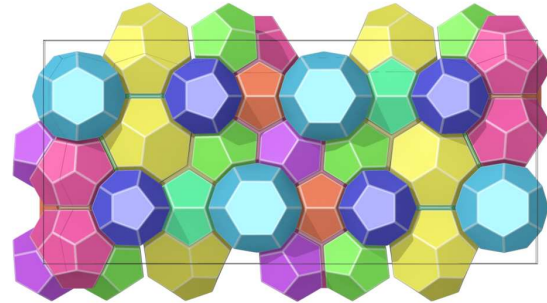
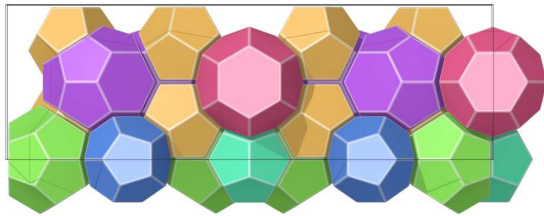
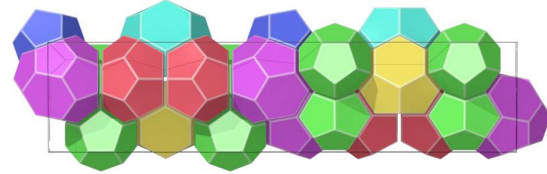
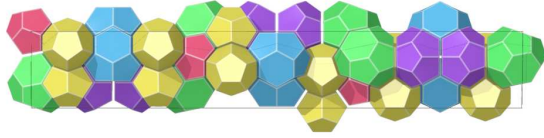
One structure, *Z*, is known.

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



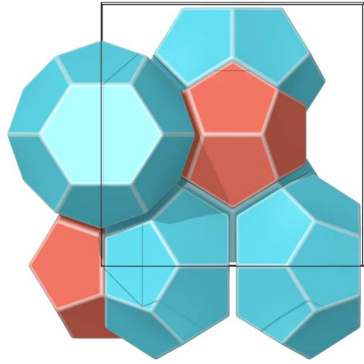
1st structure is δ : the only known other one, P , is not here.

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

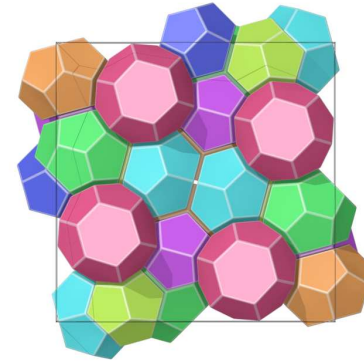


1st, 2nd, 5th are μ , $-^* = (K_7Cs_6)$, $p\delta$; remaining M is out.

Others found with known fractions



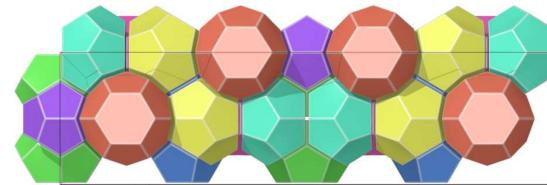
$(1,3,0,0)$ A_{15}



$(5,8,2,0)$ σ

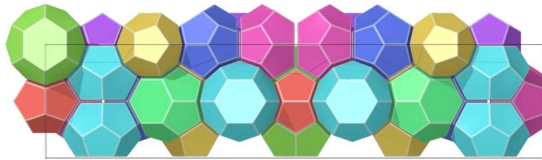


$(4,5,2,0)$ **not** J

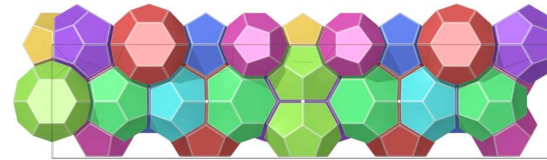


$(5,8,2,0)$ H -complex

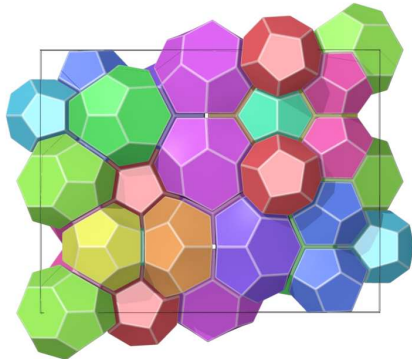
Unique found with their new fraction



(7, 8, 2, 1)



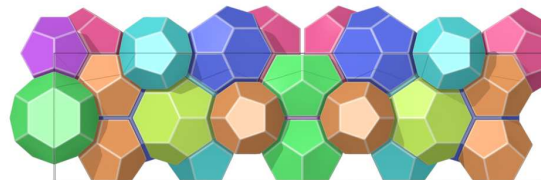
(7, 7, 4, 0)



(11, 1, 4, 3)



(6, 11, 2, 0)

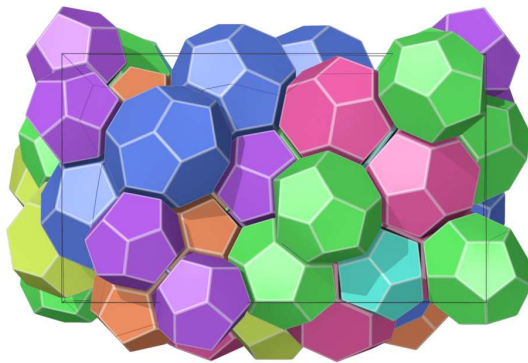


(9, 2, 2, 3)

All found with 2 other new fractions

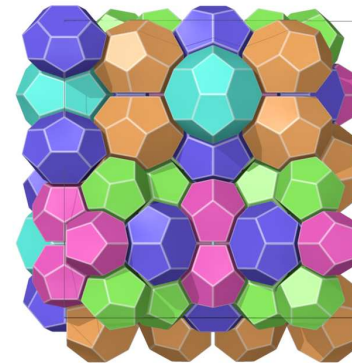


$(8,5,2,2)$



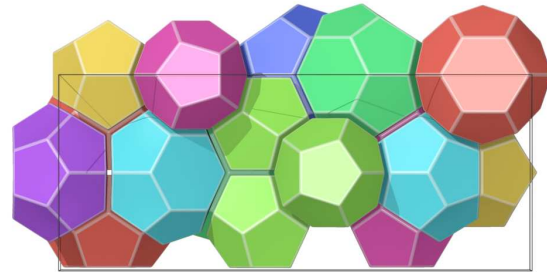
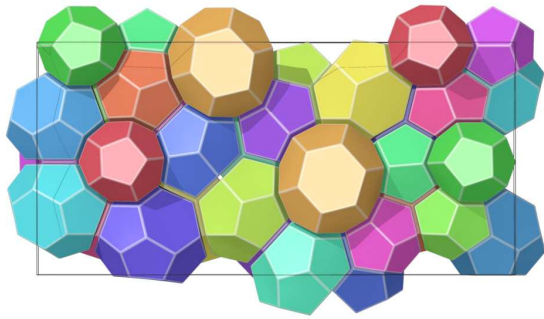
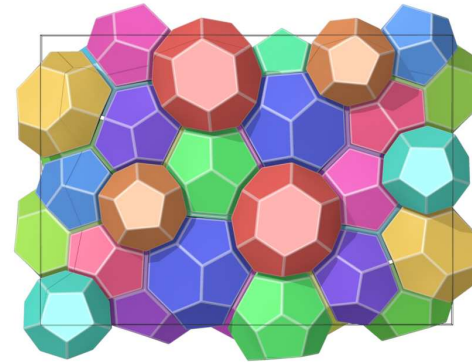
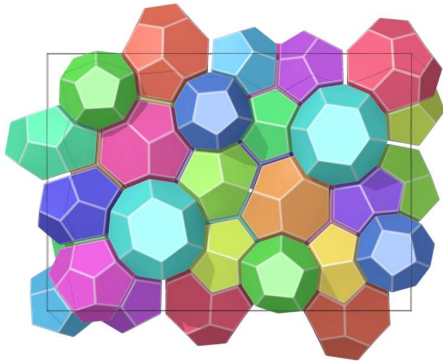
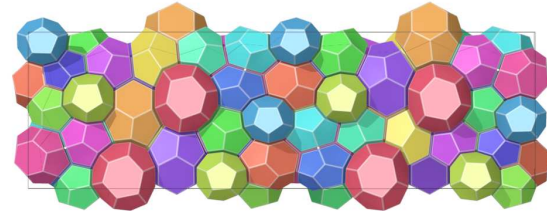
$(8,5,2,2)$

$(8,4,4,1)$



$(8,4,4,1)$

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 $F_{n_0} \subset F_{n_1} \subset \dots \subset F_{n_r}$ 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)?
Pasini, 2001: 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 $\mathbb{H}^3$.

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 $G = \text{Aut}(\mathcal{C})$, we speak simply of **Delaney symbol** of $\mathcal{C}$.
- **Dress, 1987**: any simply connected manifold $\mathcal{C}$ (incl. $\mathbb{E}^3$) is entirely described by its Delaney symbol.

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 $x \rightarrow xA + b$ 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 representatives 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 isometric equivalence, there are (Wolf, 1967) 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 $u \rightarrow v + A(u)$ for given translation t_v and 3×3 matrix A with respect to the basis a, b, c .
- 9 manifolds are 5 torus $T^2 \times [0, 1]/(x, y, 0) \sim (\phi(x, y), 1)$ and 4 Klein bottle $K^2 \times [0, 1]/(x, y, 0) \sim (\phi(x, y), 1)$ bundles over $\mathbb{S}^1$, for some homeomorphisms $\phi(x, y) : T^2 \rightarrow T^2$ or $K^2 \rightarrow K^2$. 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:

$$\begin{aligned} &\{C_1\} \\ &\{C_1, C_2\} \\ &\{C_1, C_2, C_3\} \\ &\vdots \\ &\{C_1, C_2, \dots, C_N\} \end{aligned}$$

- 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

Major skeleton

- The **major skeleton** $Maj(\mathcal{F})$ of a space fullerene $\mathcal{F}$ is the graph with the vertices being the cells of $\mathcal{F}$ and an edge whenever corresponding cells share a 6-gon.
- For example, A_{15} has an infinity of infinite paths going in three different directions, while structure Z has an infinity of layers $\{63\}$ stacked with an infinity of infinite paths passing through the hexagons.
- A priori, it is possible to have $\mathcal{F}$ and $\mathcal{F}'$ non-isomorphic and $Maj(\mathcal{F})$ isomorphic to $Maj(\mathcal{F}')$ but we did not find a single example of such pairs in the list of known before and obtained space fullerenes.

Sadoc-Mosseri inflation

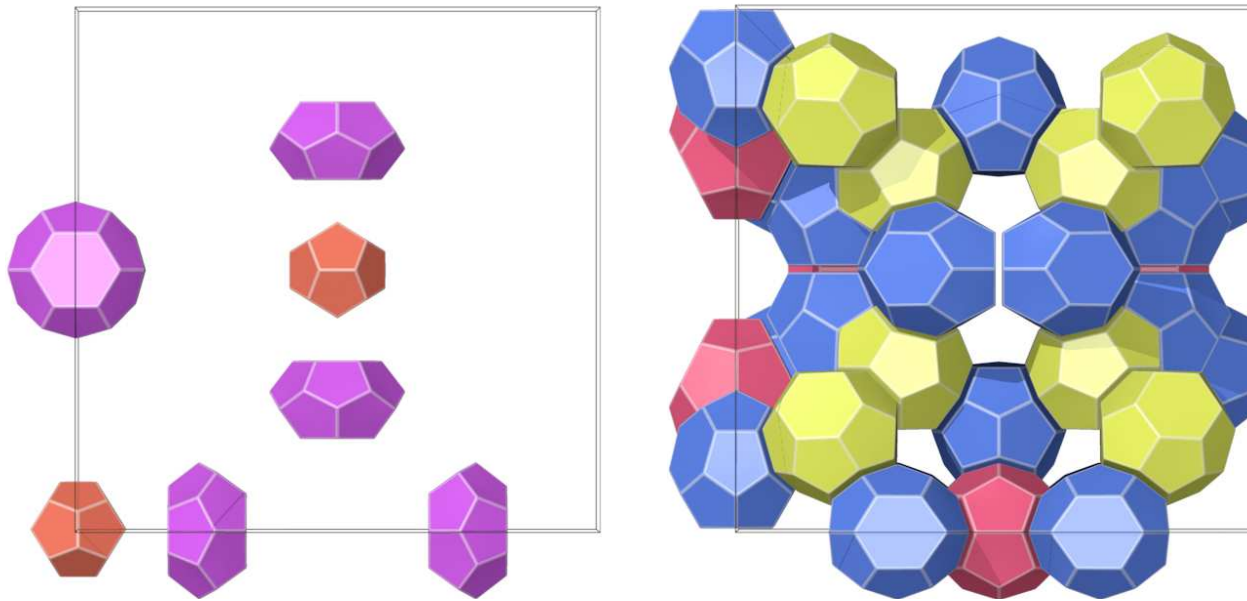
- Given a space fullerene $\mathcal{F}$ by its cells P , define the *inflation* $IFM(\mathcal{F})$ to be the simple tiling such that
 - Every cell P has a shrunk copy P' of P in interior.
 - On every vertex of P a F_{28} has been put.
 - On every m -gonal face of P' , a F_{20} or F_{26} is put (if $m = 5$ or 6 , respectively) which is contained in P .
- Thus, if $\mathcal{F}$ is a space fullerene with fraction $(x_{20}, x_{24}, x_{26}, x_{28})$, then its inflation $IFM(\mathcal{F})$ is a space fullerene with fraction $(x'_{20}, x'_{24}, x'_{26}, x'_{28})$, where

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

Sadoc-Mosseri inflation

$Maj(IFM(\mathcal{F}))$ is formed by the skeleton of $\mathcal{F}$ and $Maj(\mathcal{F})$ with all edges being tripled by insertion of two F_{24} in them.

- Inflation of A_{15} : its shrunken cells and generated F_{28} .



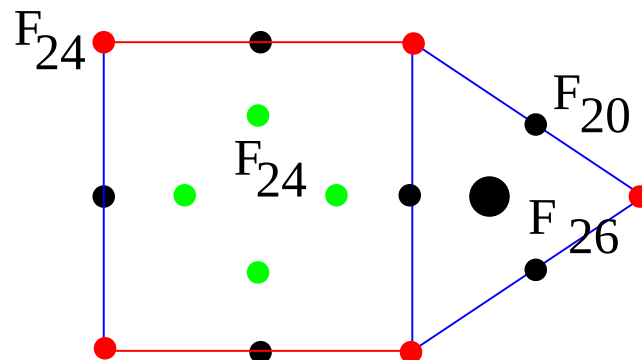
- Resulting space fullerene SM has fraction $(49, 9, 0, 23)$; cf. physical space fullerene T with fraction $(49, 6, 6, 20)$ and equal number 162 of cells in fundamental domain.

DS construction

- **Snub $Prism_m$** is a 3-valent plane graph with two m -gonal faces separated by two m -rings of 5-gons. **$BSPrism_m$** is obtained from Snub $Prism_m$ by inserting m -ring of 6-gons between those two rings.
- Take a **plane fullerene** G (3-valent plane partition with only 5- and 6-gonal faces). There is at most six 5-gonal faces as discussed in [Deza-Shtogrin, 2009](#) and the number of possibilities is countable.
- DS construction $DS(G)$ is a tessellation of the Euclidean space by snub $Prism_m$, $BSPrism_m$ and F_{20} . On every 6-gon put $BSPrism_6$ and on each of its two 6-gonal faces put a snub $Prism_6$. This structure is stacked in infinite lines. The residual space is then filled with F_{20} 's.
- Resulting space fullerene is 3-periodic only if $G = \{63\}$; it is MDS, 1st found 3-periodic **not FK** space fullerene.

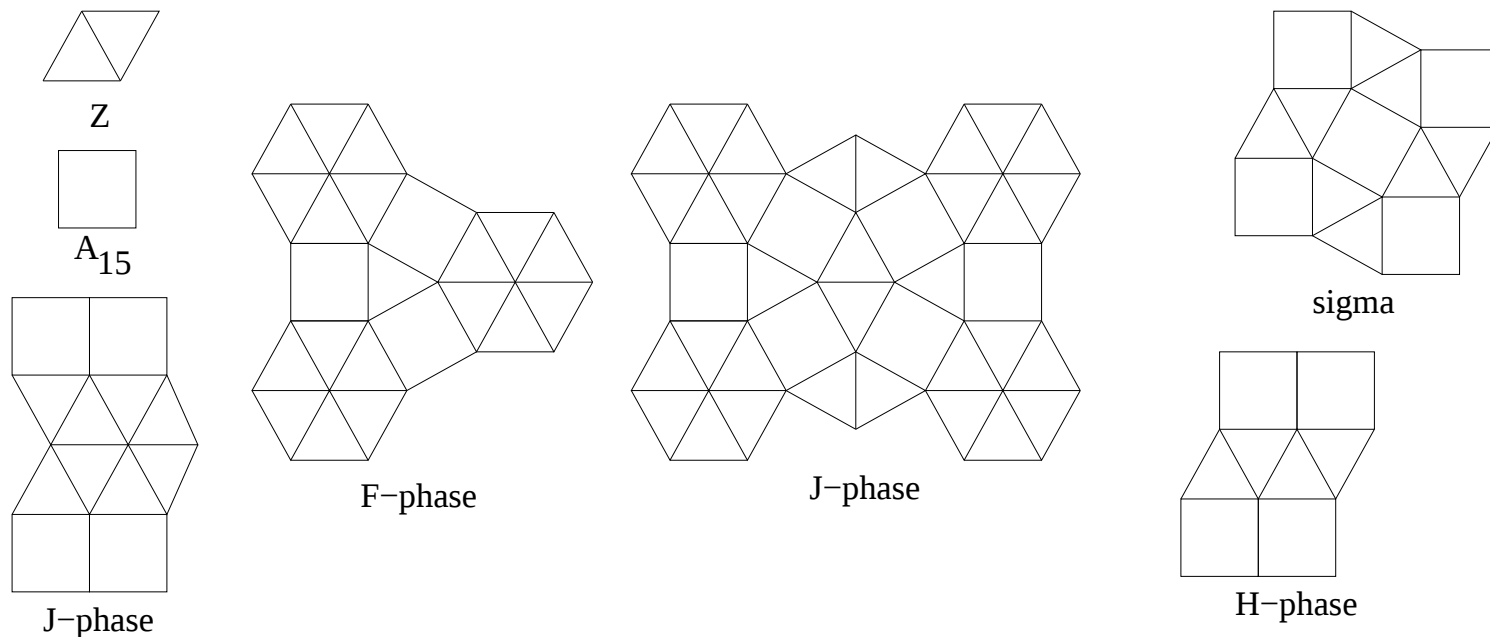
Frank-Kasper-Sullivan construction

- This construction is first described in [Frank & Kasper, 1959](#) but a better reference is [Sullivan, 2000](#):
New tetrahedrally closed-packed structures.
- Input: a plane tiling T by regular 3- and 4-gons.
Output: 1-periodic space fullerene with $x_{28}=0$ satisfying Y-K rule. It is 3-periodic if and only if T is 2-periodic.
- 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 all 7 physically realized structures with $x_{28} = 0$:



- Another name for the construction in [Kuo et al., 1986](#) is **hexagonal t.c.p. phases**.

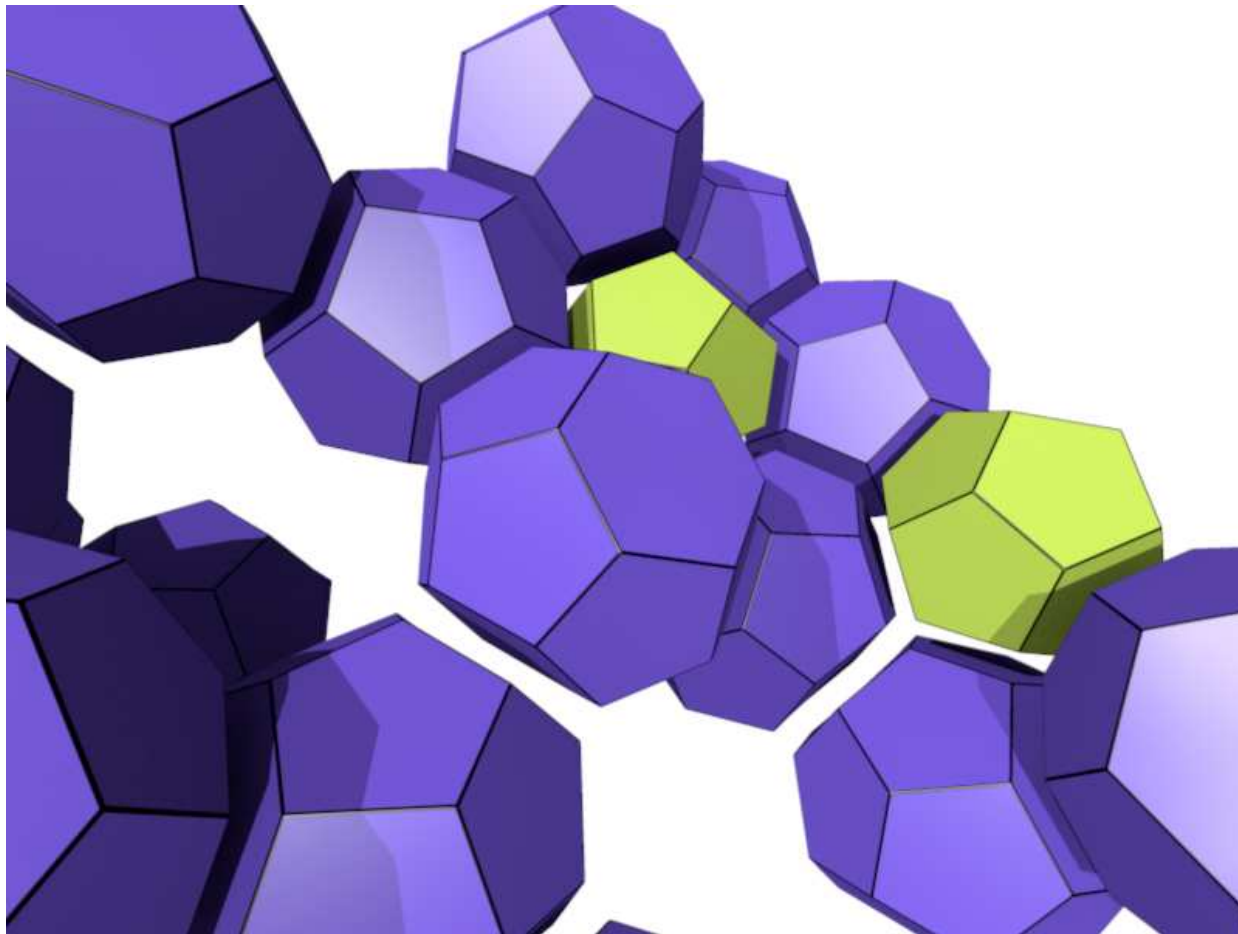
Shoemaker-Shoemaker construction

- **Pentagonal t.c.p.** by Shoemaker-Shoemaker, 1972 generalizing Section 2.1 of Frank-Kasper, 1959.
- Input: a plane tiling by 3- and 4-gons with vertex types (3^6) , $(3^5, 4)$, (3^5) , $(3^4, 4)$, $(3^3, 4^2)$, $(3^2, 4, 3, 4)$ and (4^4) .
- Then some edges are doubled and the non-doubled edges are colored in red and blue so that:
4-gons have =2 doubled edges on opposite sides,
3-gons have =1 double edge, non-doubled edges of any face have the same color and two faces sharing a black edge have same color iff their sizes are different.
- Once non-doubled edges are chosen, their coloring is unique. Obtained FK space fullerene has $x_{24} = x_{26}$.
- It gives 15 of 27 known space fullerenes and all 10 of 71 new found by us but belonging to known infinite series.

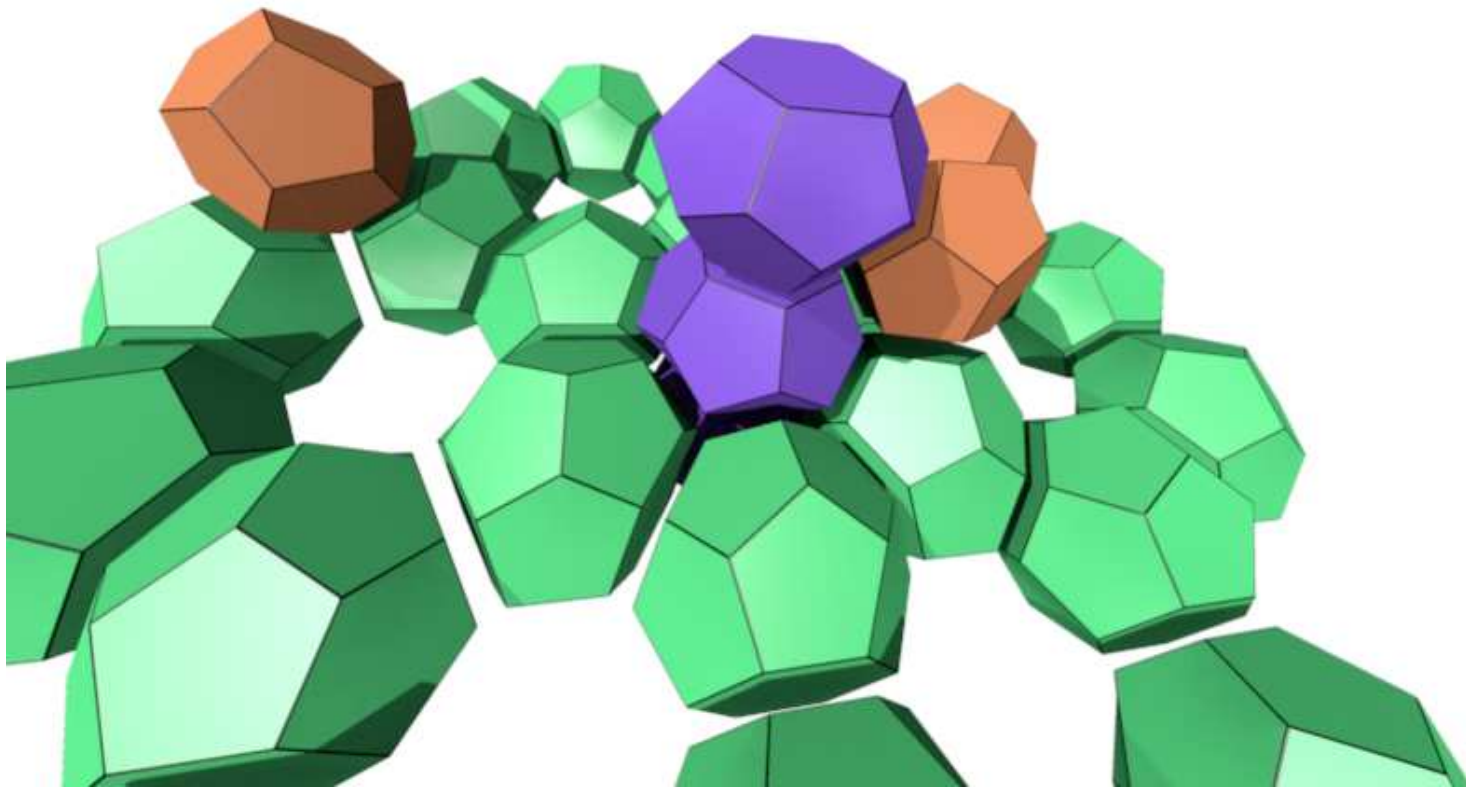
VII. Closer look on obtained structures

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

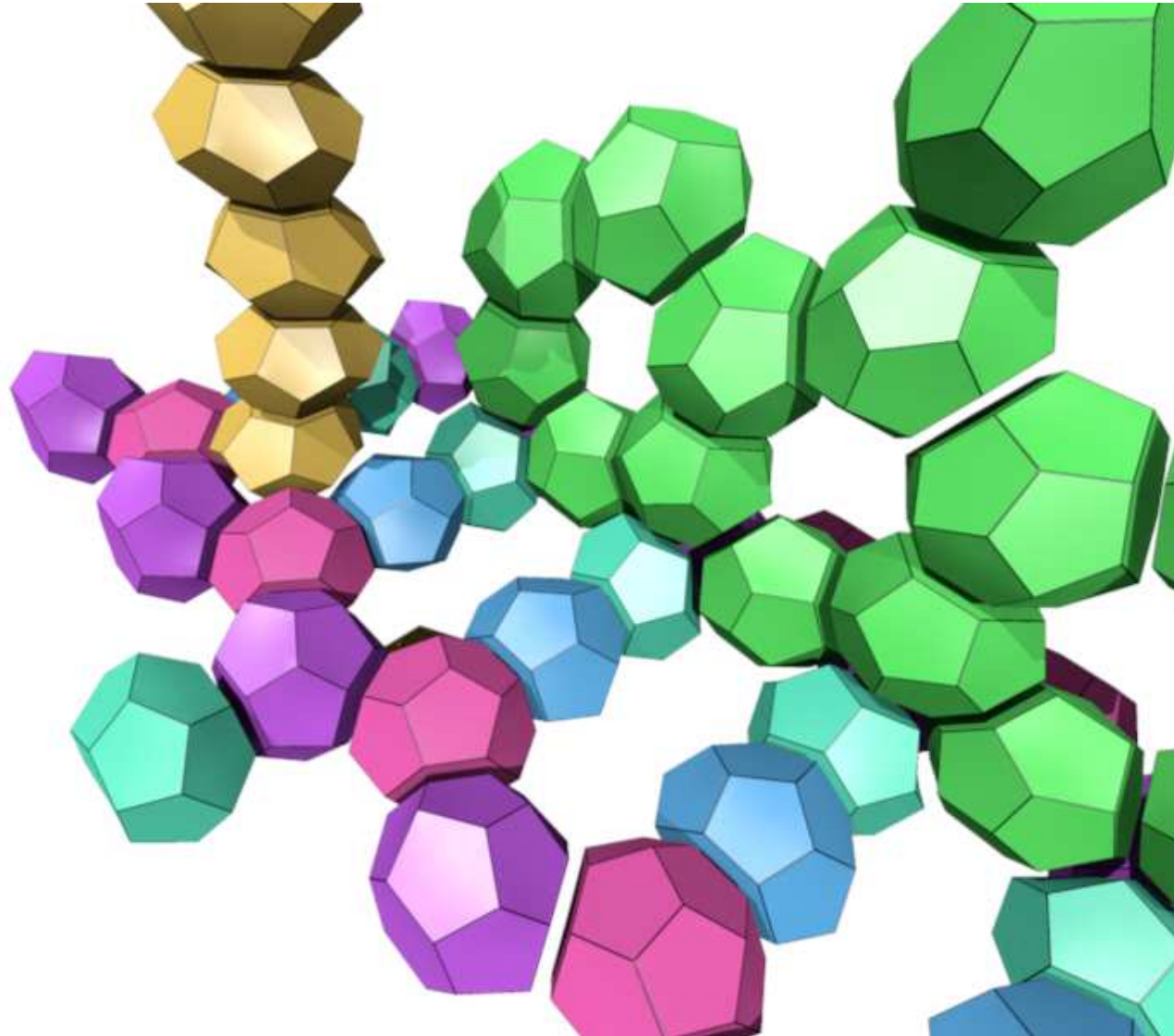
Cubic C_{15} : gravicenters of cells F_{28} (larger atoms A in AB_2) form diamond network (centered fcc). In hexagonal C_{14} they form "hexagonal diamond" (**lonsdaleite** found in meteorites). There is a continuum of $(2, 0, 0, 1)$ -structures.



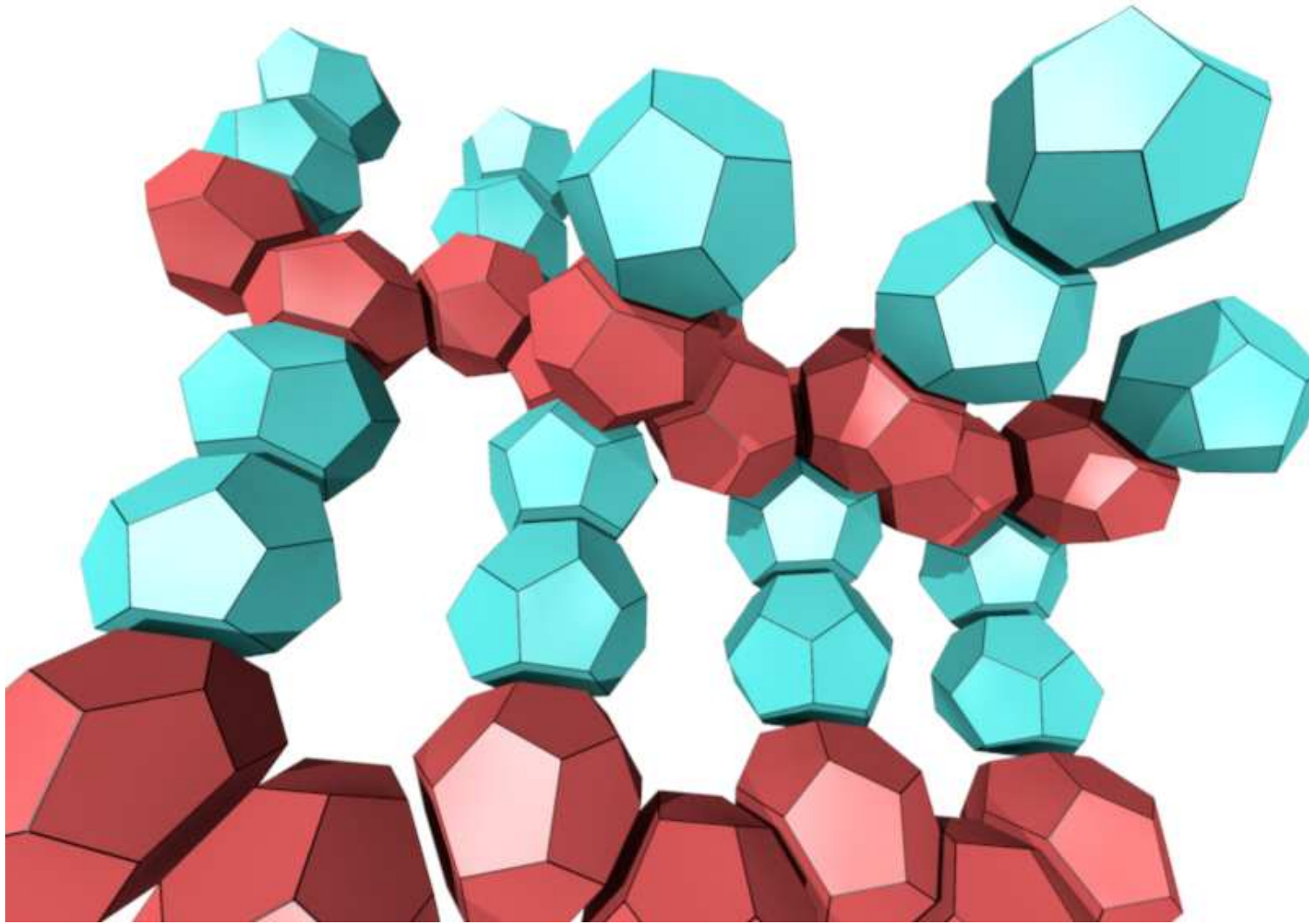
Z , one of 4 found with $(3, 2, 2, 0)$



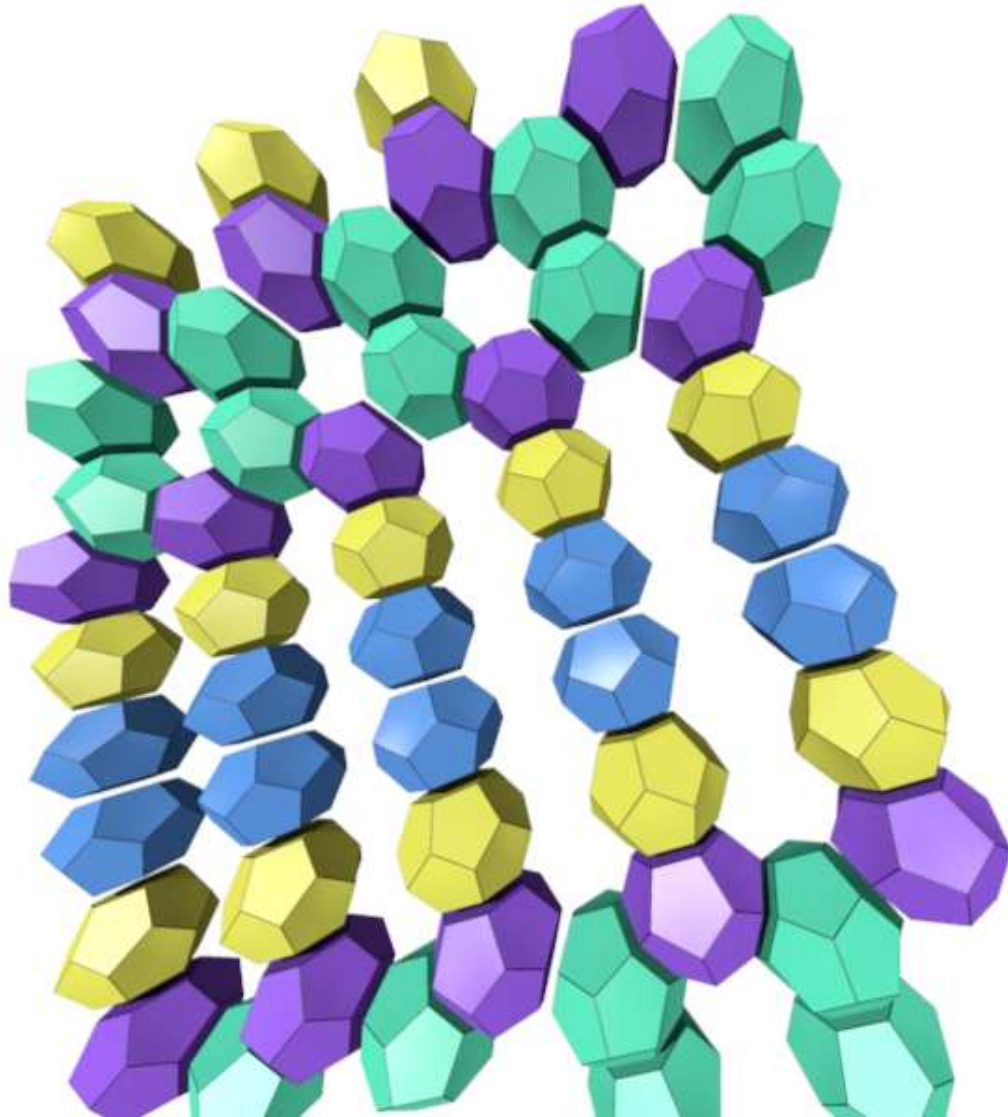
2nd found structure $(3, 2, 2, 0)$



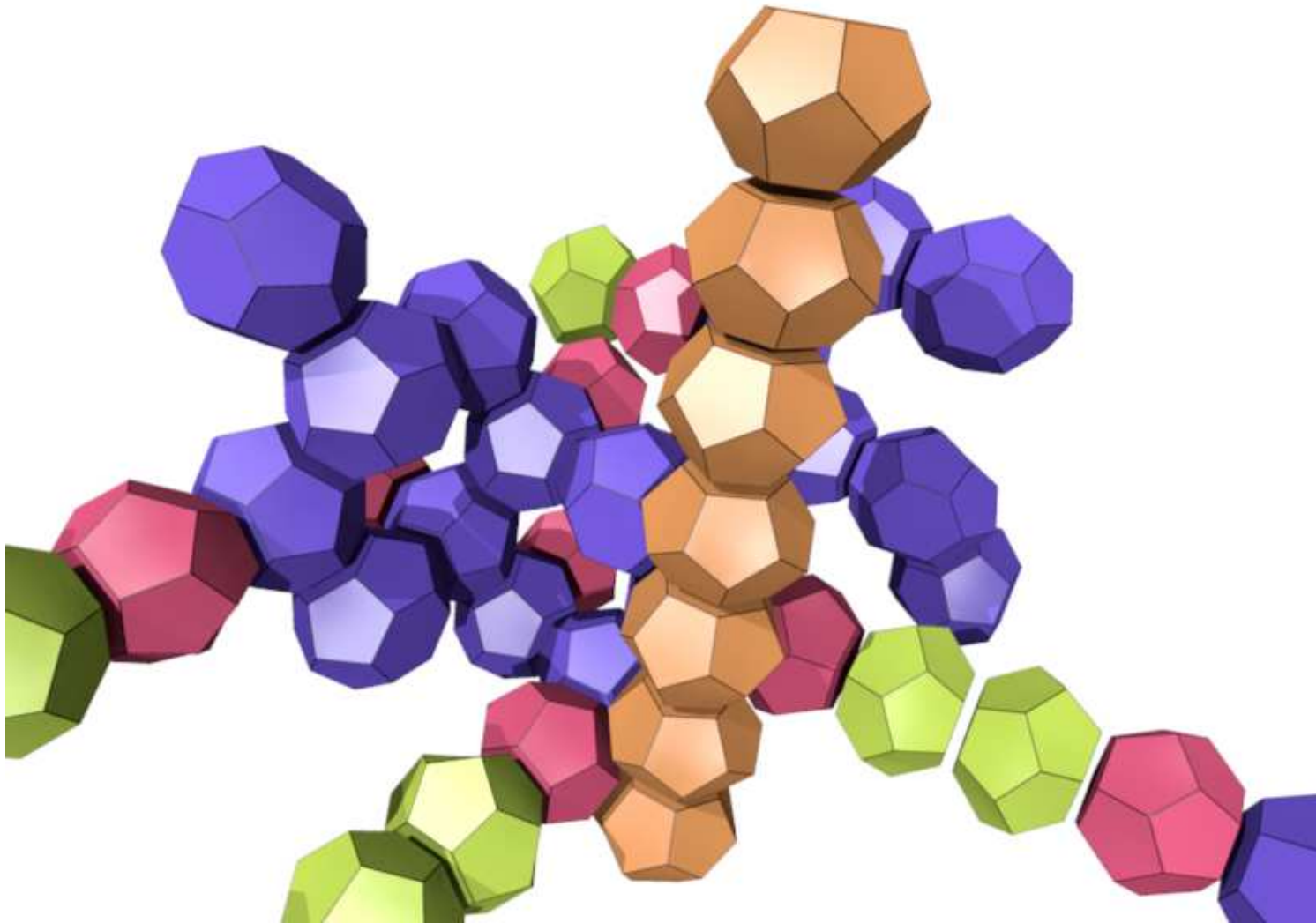
3rd found structure $(3, 2, 2, 0)$



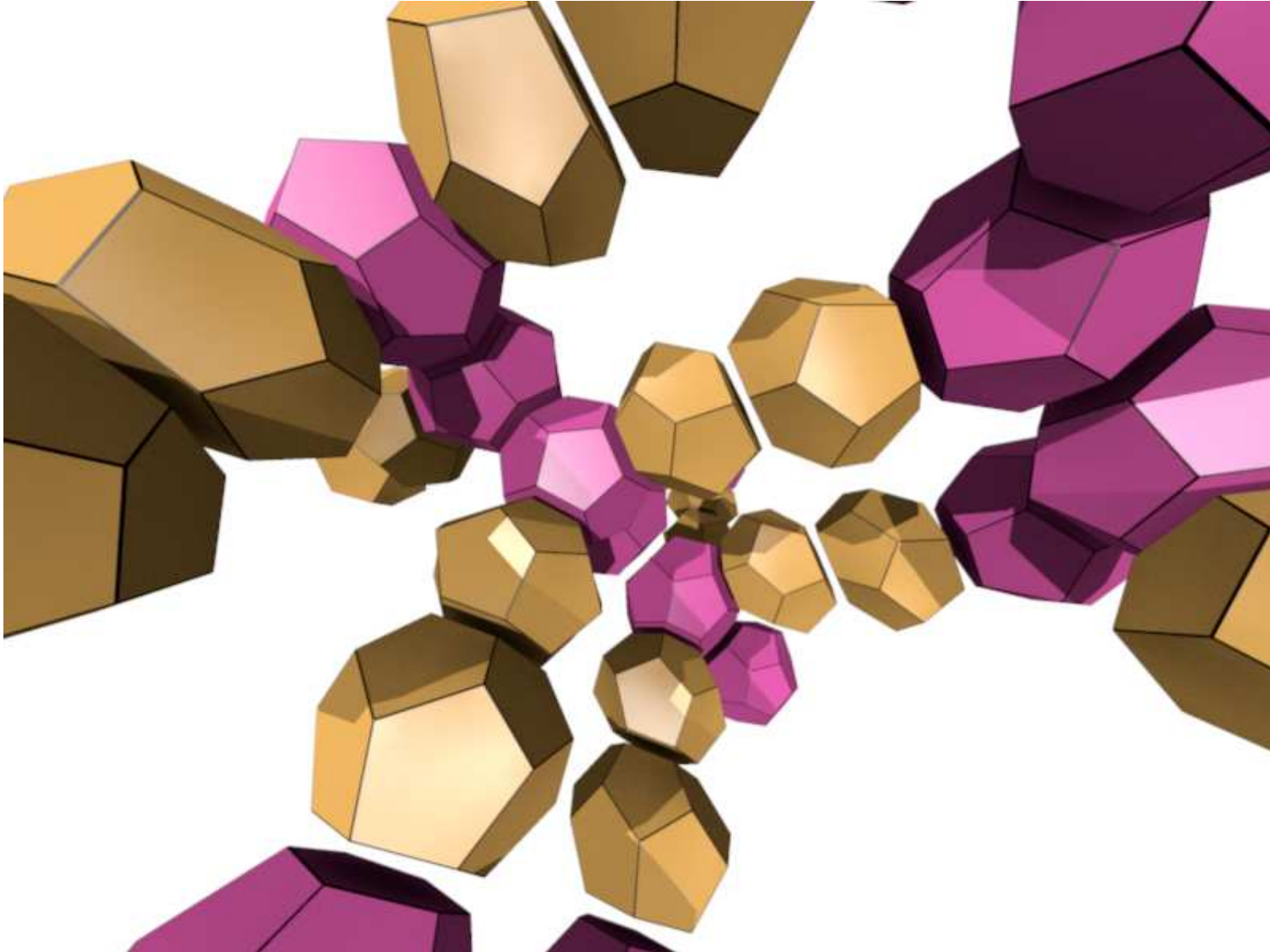
4th found structure $(3, 2, 2, 0)$



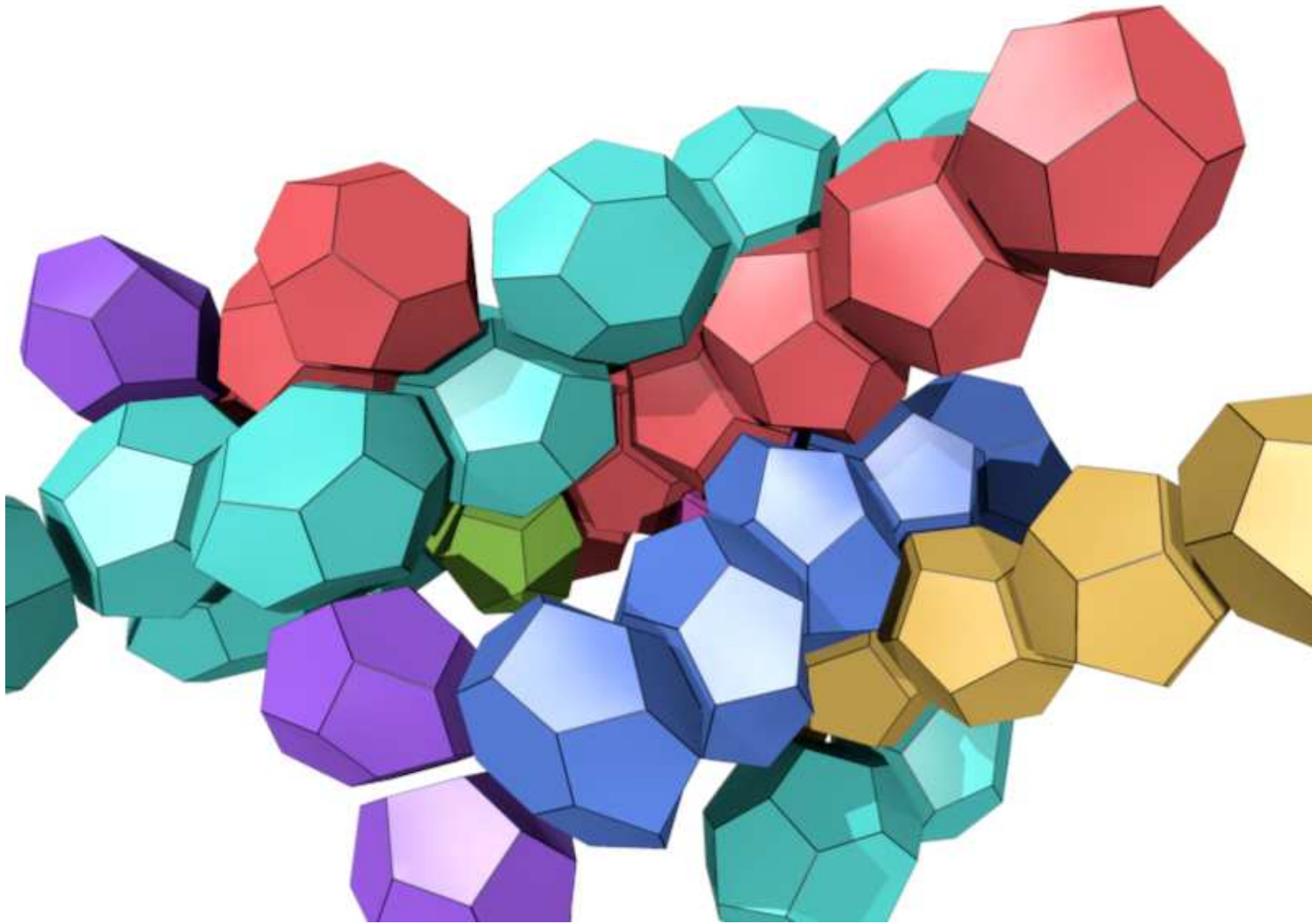
One of 3 found structures $(3, 3, 0, 1)$



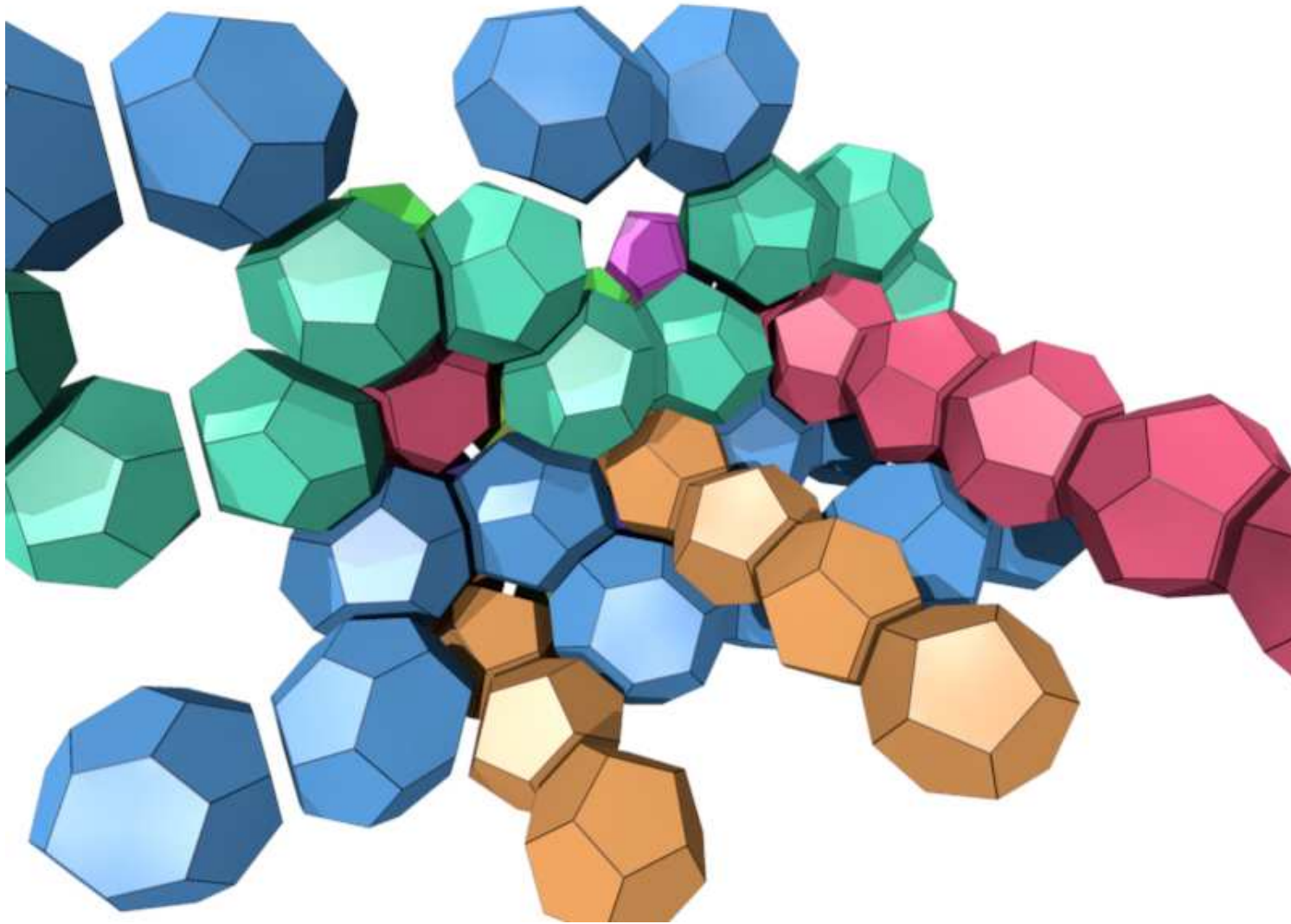
2nd found structure with $(3, 3, 0, 1)$



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

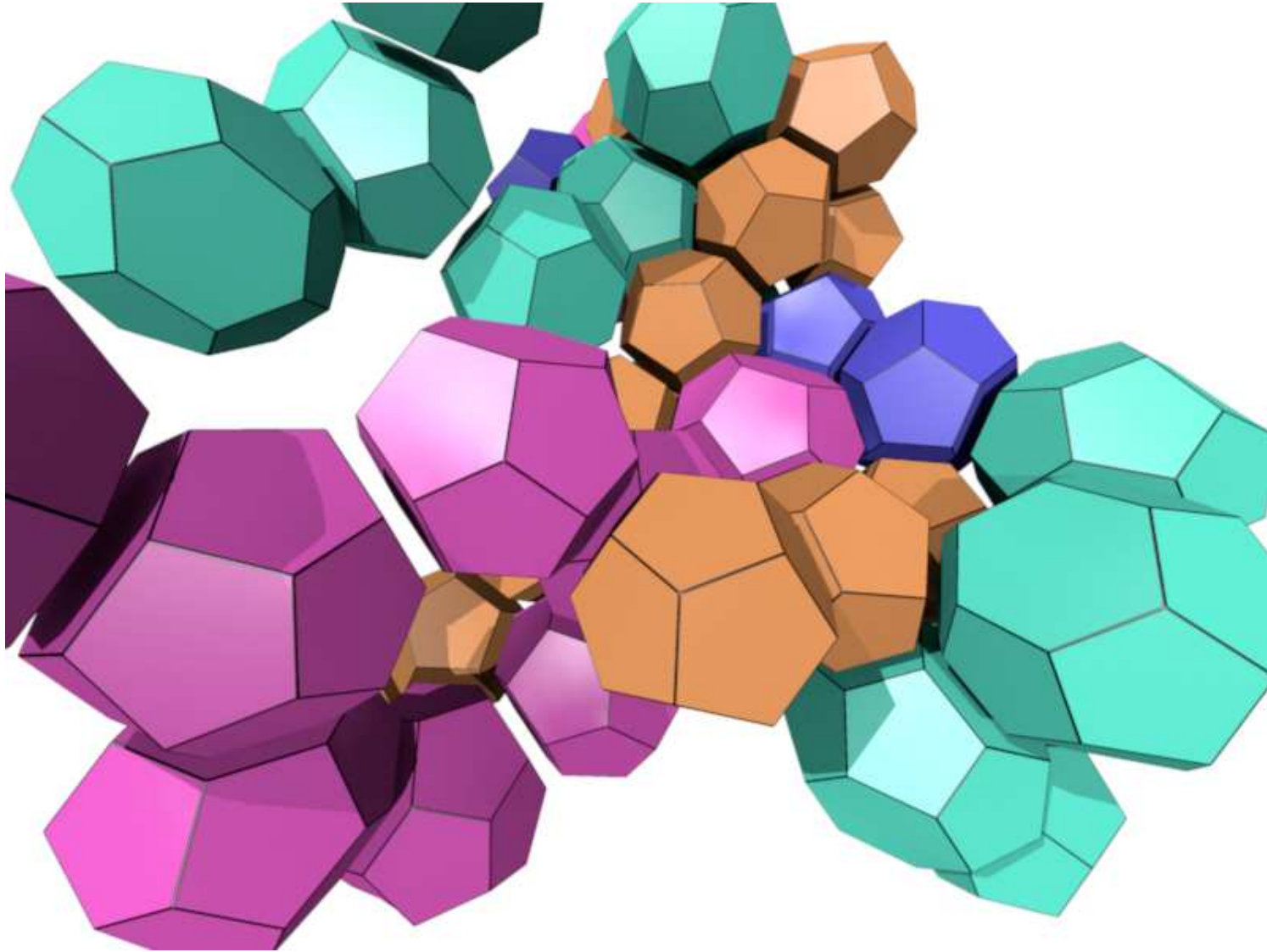


One of 5 found structures $(7, 2, 2, 2)$



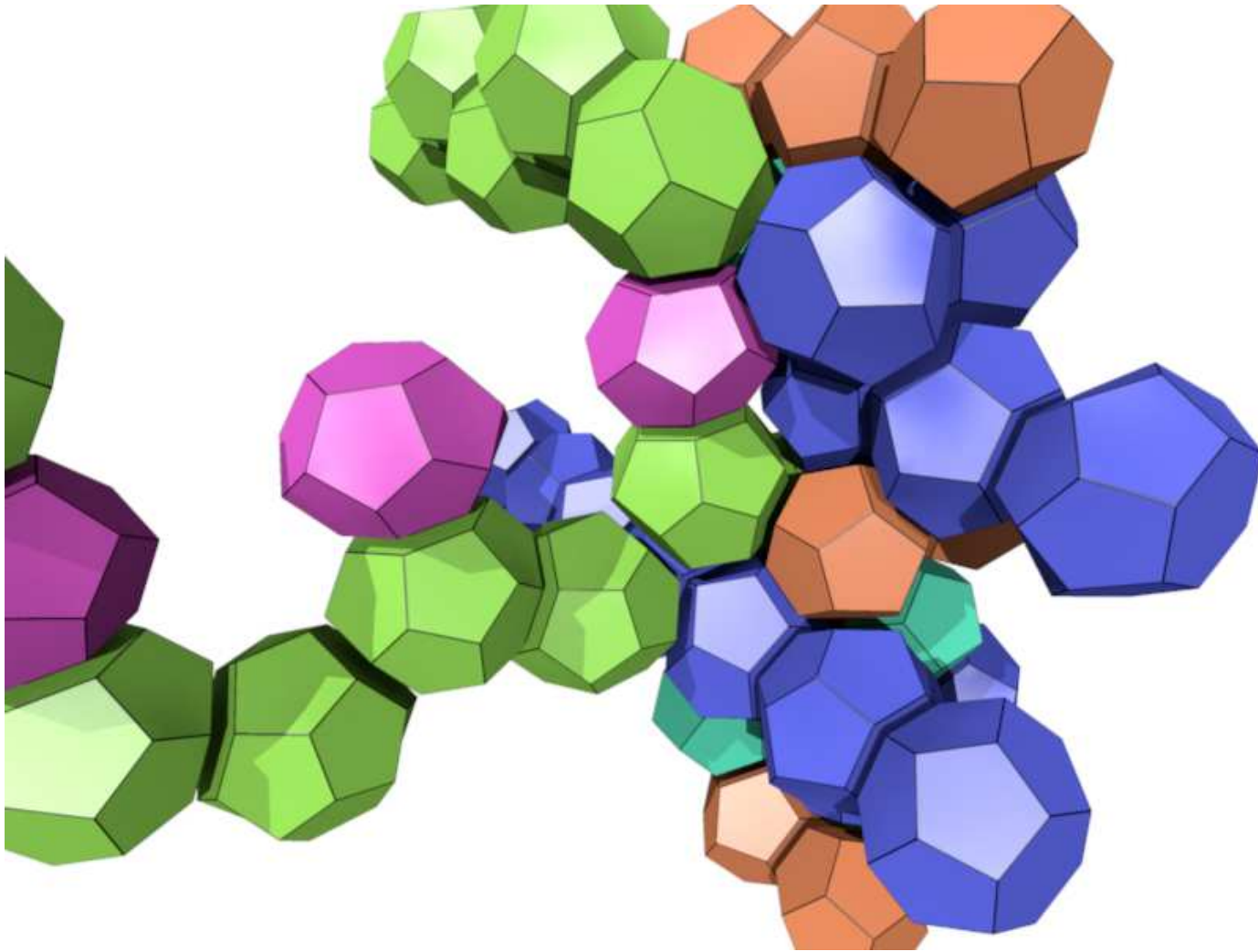
It is a mix of C_{15} and A_{15} in layers.

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



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

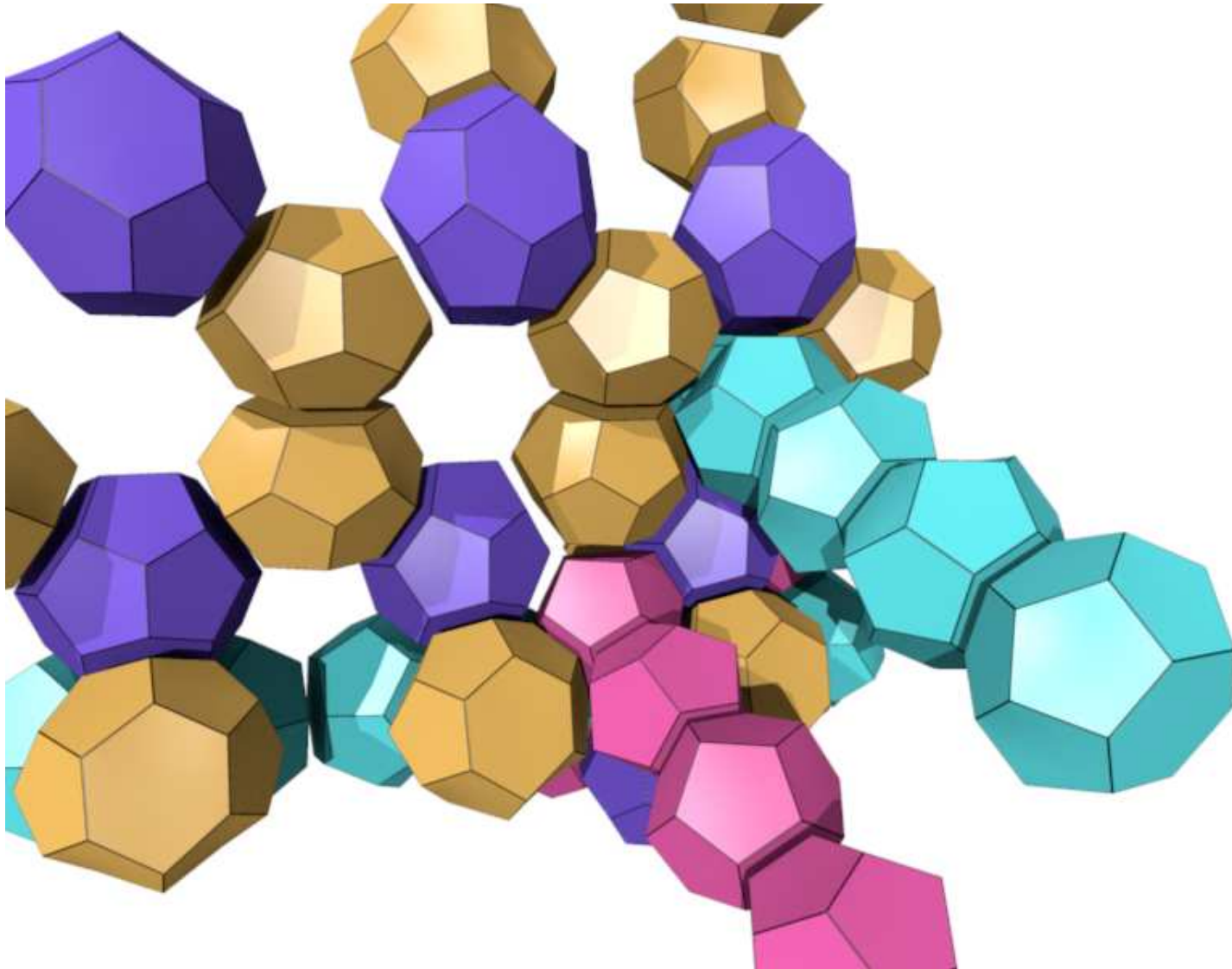
Unique found structure $(4, 5, 2, 0)$



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, preventing 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.

Some of next directions

- Our list of possible combinatorial candidates can be used to match (via stability simulations) some new physical structures or used as starting point to find better affine variants for some variational optimization procedures, say, **weak Kelvin problem** (partition $\mathbb{E}^3$ into equal volume cells D with maximal $IQ(D) = \frac{36\pi V^2}{A^3}$) or for **Hamiltonian energy** minimization.
- To try another enumeration process: to build first the major skeleton or its component and then consider the addition of F_{20} in all possible ways.
- To check whether or not obtained FK space fullerenes have faces that are contained in affine planes.
- To find more infinite series constructions.

New frontier: generalized perovskites

- 4-regular fullerene analogs: **octahedrites**, i.e. 4-regular polyhedra with only 3- and 4-gonal faces; so, $p_3 = 8$.
- All octahedrites without adjacent 4-gons: $APrism_3$ (Octahedron), $APrism_4$, $APrism_3^2$ and Cuboctahedron.
- **Space octahedrite**: 6-regular (octahedral, instead of tetrahedral, star) 3-periodic $\mathbb{E}^3$ -tiling by them.
- Such tiling by Octahedron and Cuboctahedron, in proportion 1:1, is the Delaunay tiling of J -complex: mineral **perovskite** structure ABX_3 , where anion X bonds to cations A, B . $MgSiO_3$ is most abundant solid phase in the Earth, making $\approx 80\%$ of the lower mantle. It is one of 28 **uniform** $\mathbb{E}^3$ -tilings (vertex-transitive tilings by regular or semi-regular polyhedra) also.