Taxonomy of Nets

Michael O'Keeffe

Enumeration and classificaion of crystal nets

Taxonomy of nets and tilings: Classification by transitivity

Tiling a surface

1. Tiling of sphere (polyhedra, 0-periodic)
2. Tiling of cylinder (1-periodic nets)
3. Tiling of plane (2-periodic nets)

transitivity: 111 regular
112 quasiregular
21*r* other edge transitive

Tiling of space (3-periodic nets)

transitivity: 1111 regular
1112 quasiregular
11*rs* semiregular
21*rs* other edge transitive

Reminder

2-D tilings: transitivity = *pqr*

p kinds of vertex

q kinds of edge

r kinds of face (2-D tile)

3-D tilings: transitivity = *pqrs*

p kinds of vertex

q kinds of edge

r kinds of face

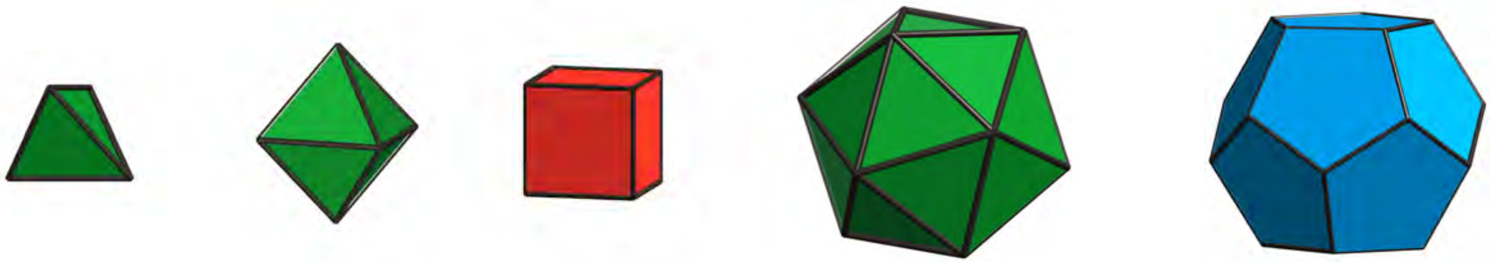
s kinds of tile

There are infinitely many polyhedra and nets
with one kind of vertex. But...

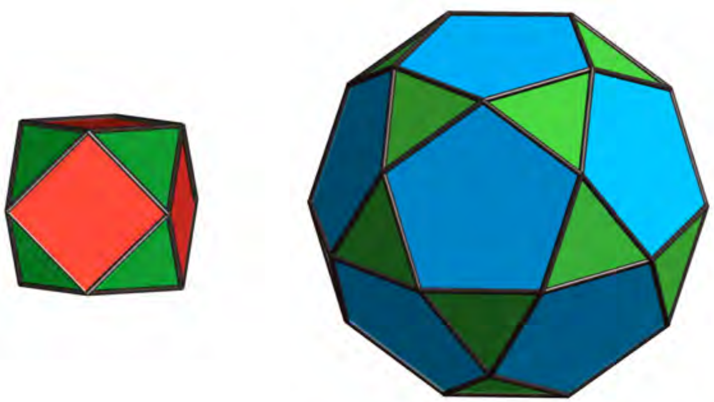
The are only a small number with one kind of edge

This has important implications for chemistry

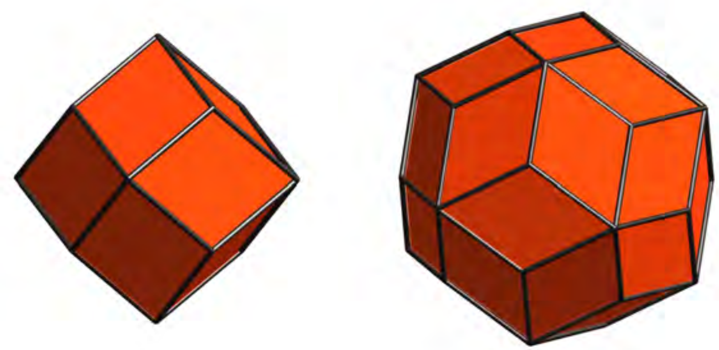
All edge-transitive polyhedra – tilings of $\mathbf{S}^2$



regular: transitivity 111

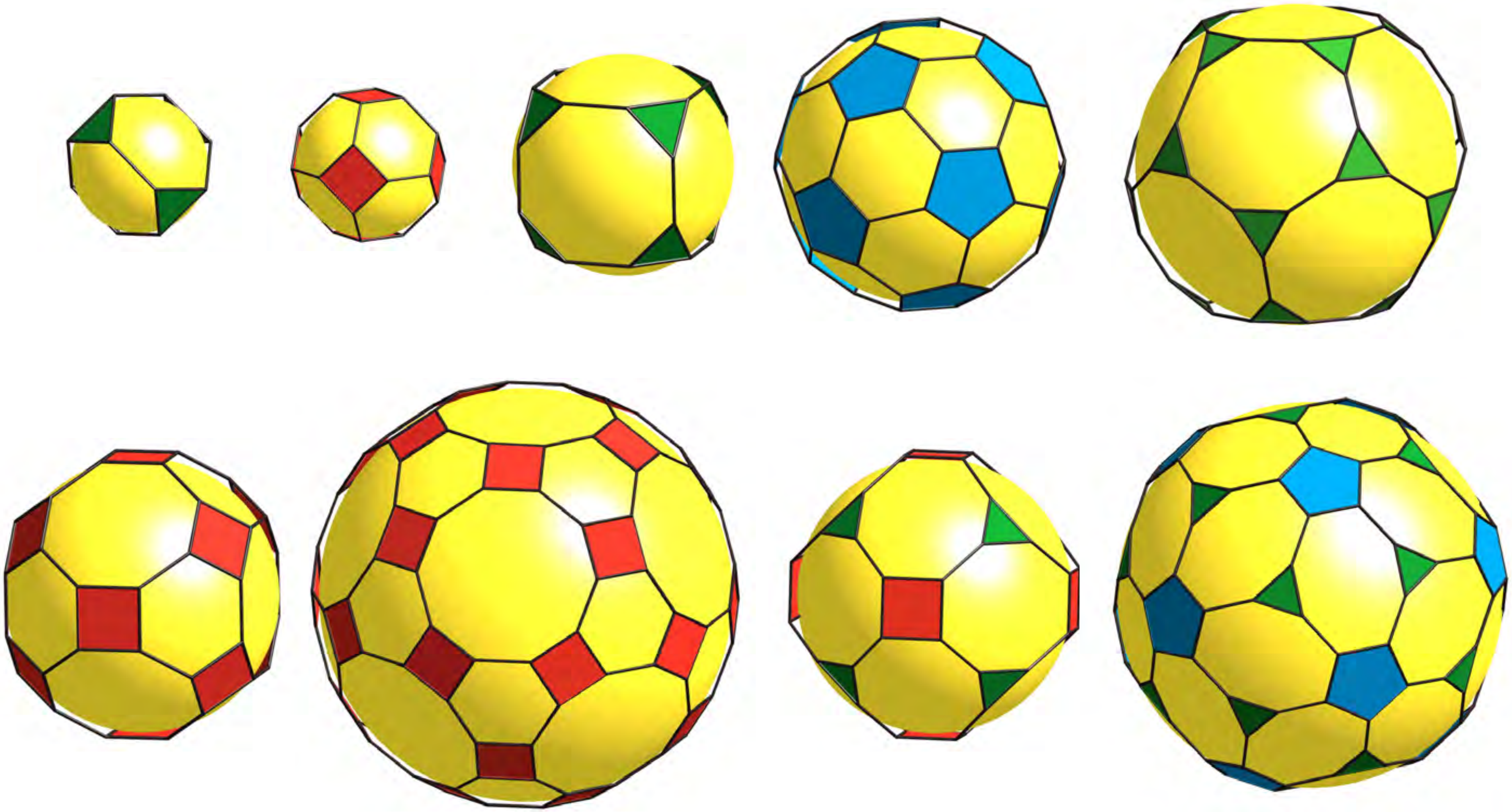


quasi-regular: transitivity 112



duals of quasi-regular:
transitivity 211

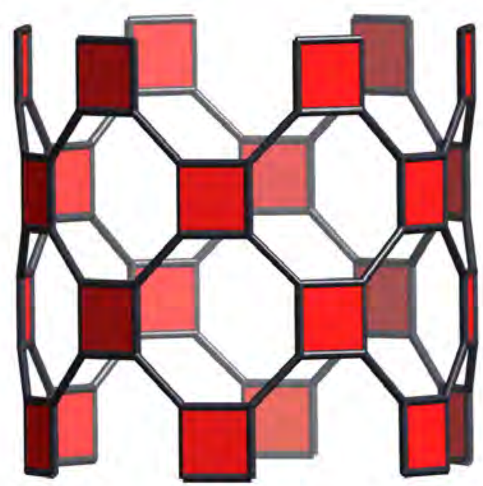
All possible ways of linking polygons with one kind of link to form 0-periodic structures



Augmented (truncated) edge-transitive polyhedra

The only family of edge-transitive tilings of cylinder

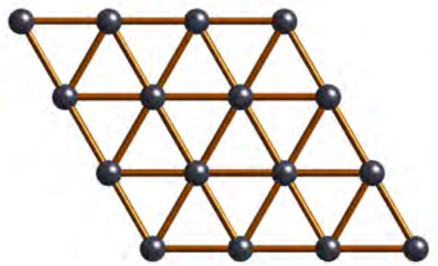
special case



regular cylinder tiling:
transitivity 111

The augmented structure: The only 1-periodic structure of polygons joined by equal links

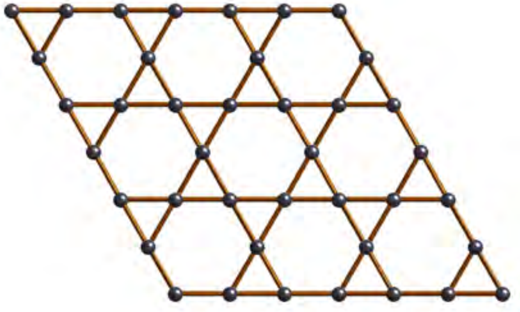
all edge-transitive 2-periodic nets



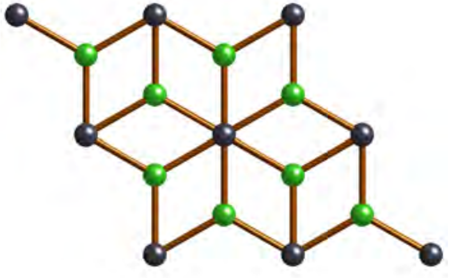
hexagonal lattice 111

square lattice 111

honeycomb 111

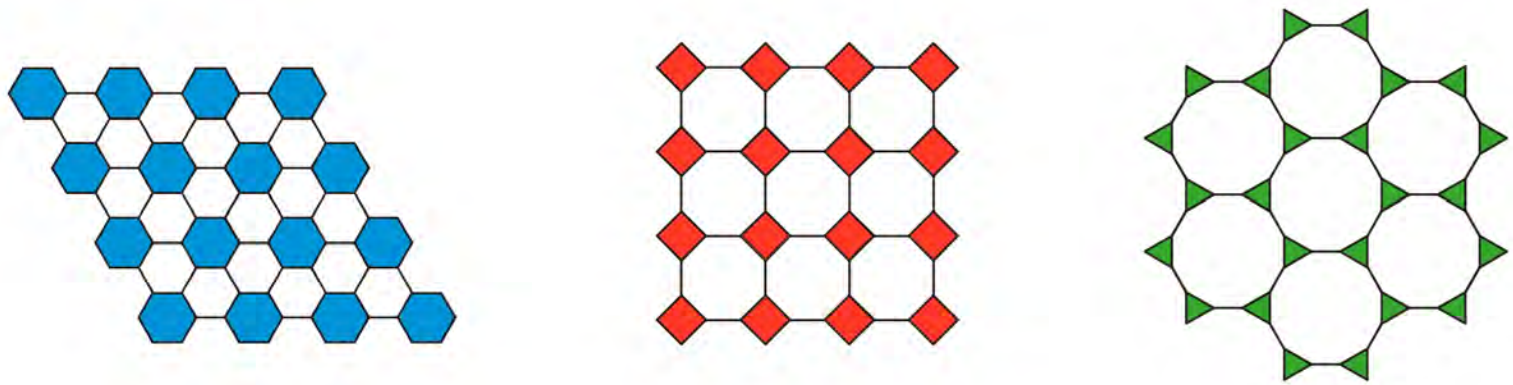


kagome 112 (quasiregular)

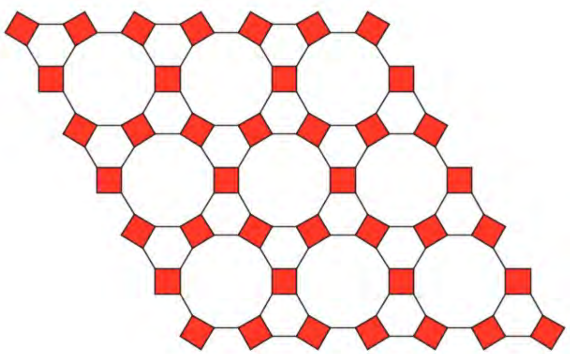


kagome dual 211

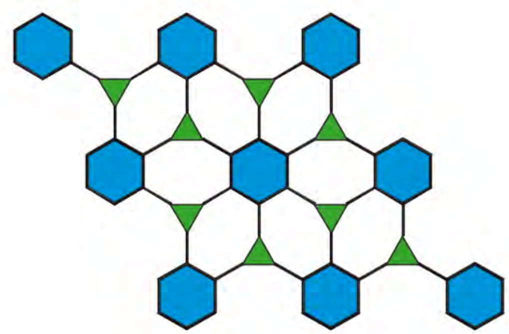
All possible ways of linking polygons with one kind of link to form 2-periodic structures



augmented regular nets



augmented quasiregular



augmented dual of quasiregular

Summary of tiling 2-surfaces. All edge-transitive structures

Sphere -> 111 = 5 regular polyhedra 112 = 2 quasiregular polyhedra 211 = 2 duals of above	9	15
Plane -> 111 = 3 regular nets 112 = 1 quasiregular net 211 = 1 dual of above	5	
cylinder->111 one family	1	

So there aren't too many
(but if we include hyperbolic surfaces the number becomes infinite – S. T. Hyde).

Regular 3-periodic nets

Vertex (coordination) figure is a regular polygon or polyhedron

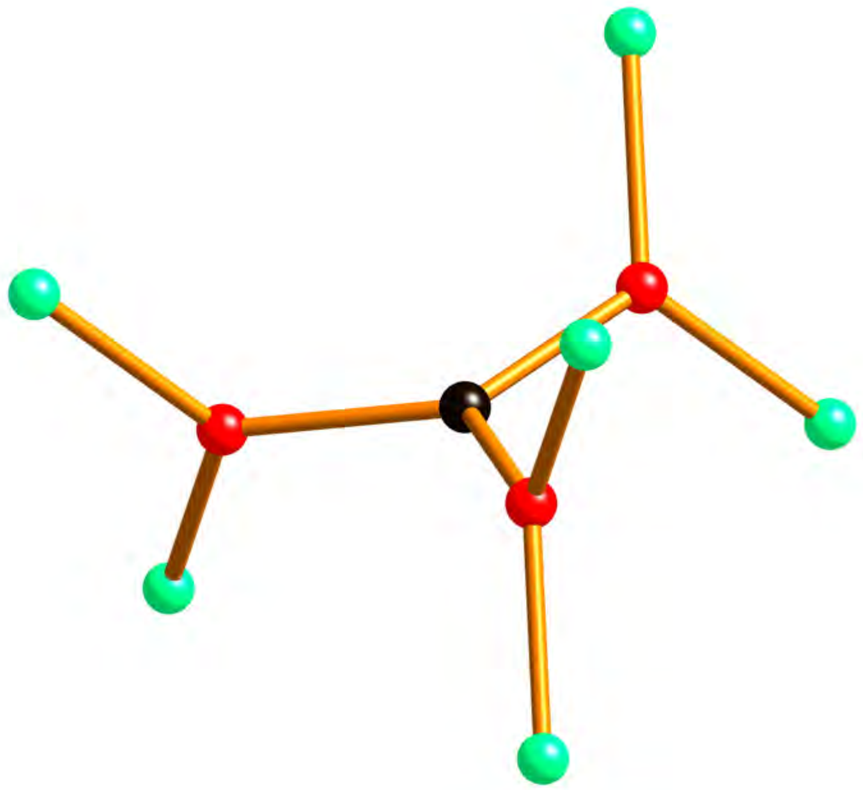
As the net is periodic, the vertex figure can only have crystallographic symmetry (1-, 2-, 3-, 4- or 6-fold rotations)
So possibilities are

1. triangle
2. square
3. tetrahedron
4. octahedron
5. cube

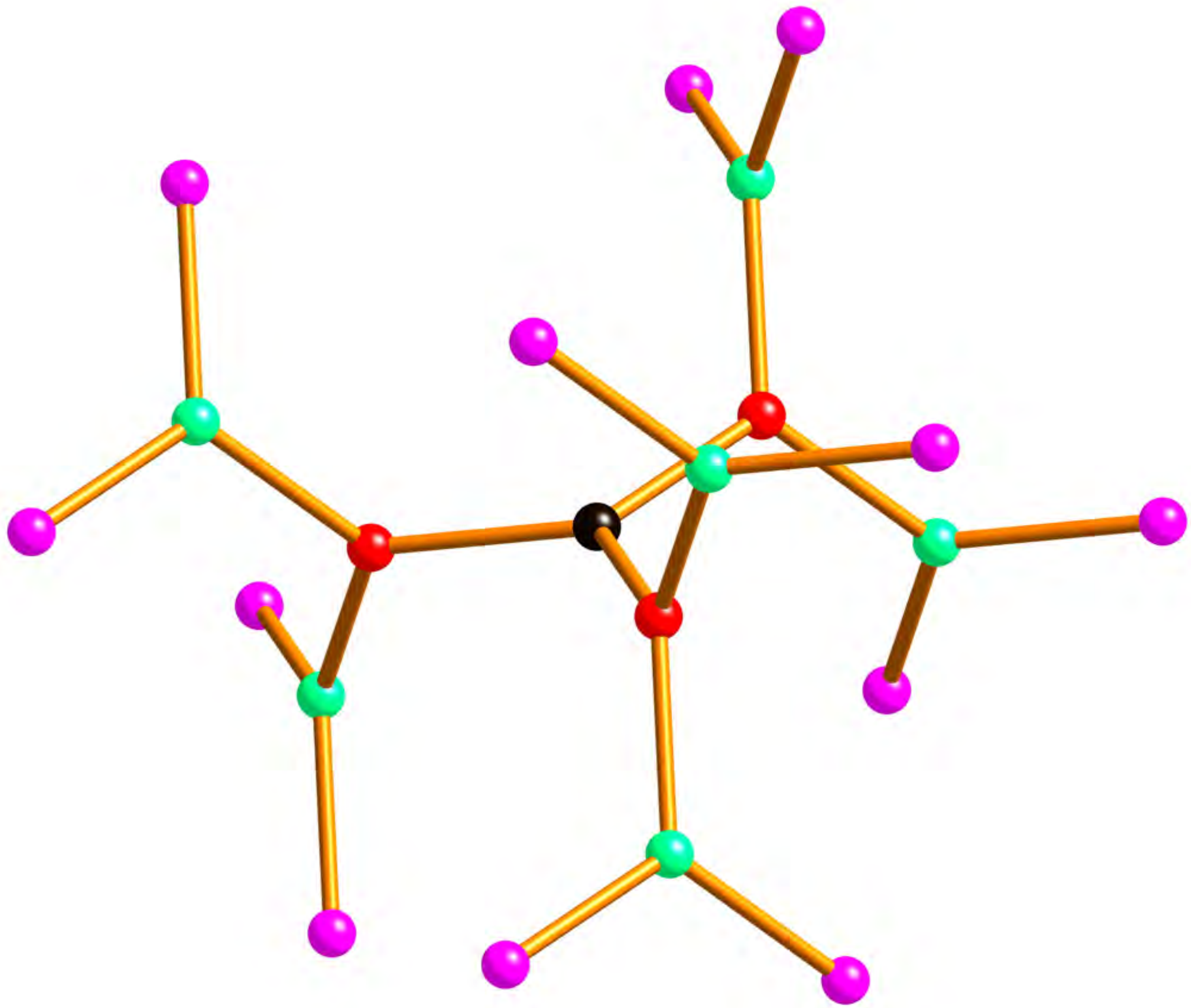
(hexagon cannot lead to a 3-D structure as all 6-fold axes must be parallel)

There is only one possibility in each case → 5 regular nets

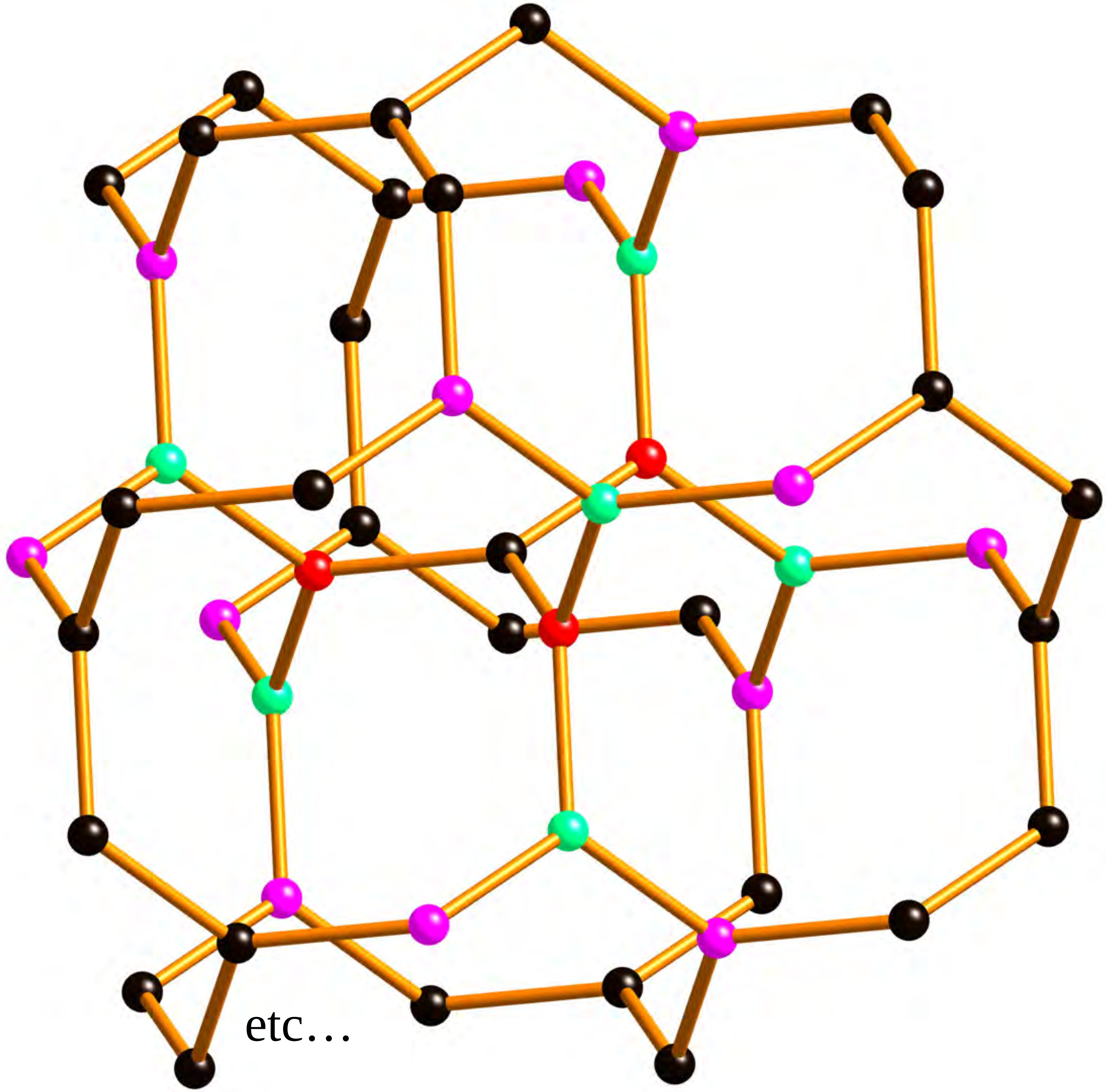
Start with one node linked to three others



add next neighbors



and next


etc…

It turns out that:

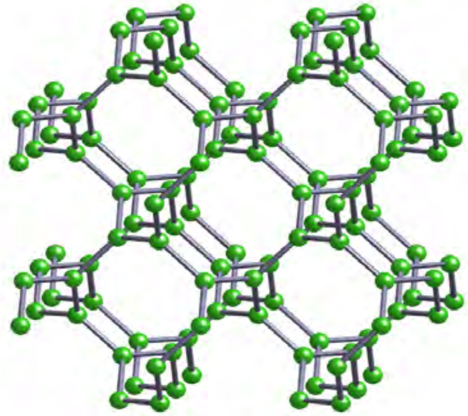
regular nets have transitivity 1111

For *natural* tilings there are no more with

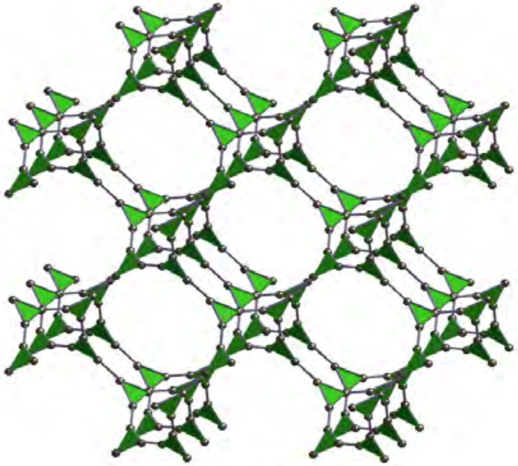
transitivity 1111

(this is rather nice)

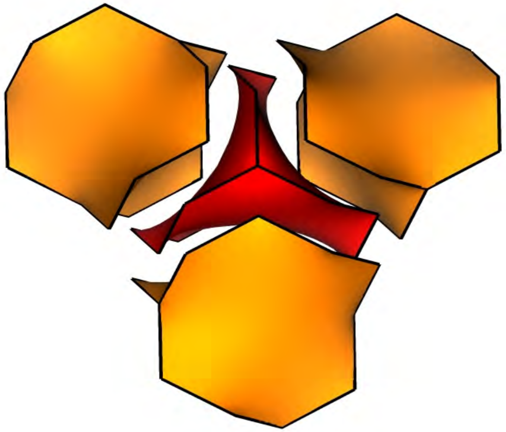
vertex figure: triangle



srs (the $SrSi_2$ net)



the augmented net **srs-a**



natural tiling $[10^3]$

skeleton of tile with dual (self)

BULLETIN (NEW SERIES) OF THE AMERICAN MATHEMATICAL SOCIETY

A Crystal that Nature May Have Missed

K_4 crystal. Created by Hisashi Naito.

January 3, 2008
Providence, RI: For centuries, human beings have been entranced by the captivating glimmer of the diamond. What accounts for the stunning beauty of this most precious gem? As mathematician Toshikazu Sunada explains in an article appearing today in the Notices of the American Mathematical Society, some secrets of the diamond's beauty can be uncovered by a mathematical analysis of its microscopic crystal structure. It turns out that this structure has some very special, and especially symmetric, properties. In fact, as Sunada discovered, out of an infinite universe of mathematical crystals, only one other shares these properties with the diamond, a crystal that he calls the "K4 crystal". It is not known whether the K4 crystal exists in nature or could be synthesized.

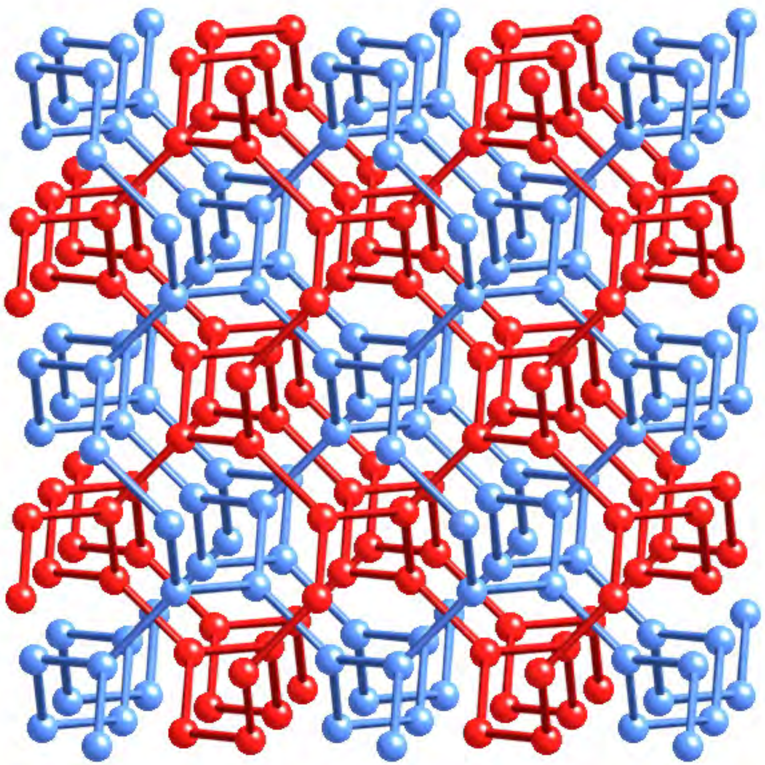
"K4" = srs which is ubiquitous in nature from the structure of high-pressure nitrogen to butterfly wings

A light read on **srs**

Hyde, S. T.; Proserpio, D. M.; O’Keeffe, M.

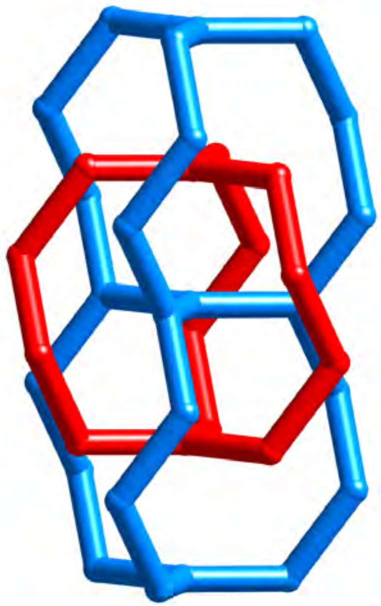
A short history of an elusive, yet ubiquitous structure in chemistry, materials, and mathematics.

Angew. Chem. Int. Ed. **2008**, *47*, *7996*.

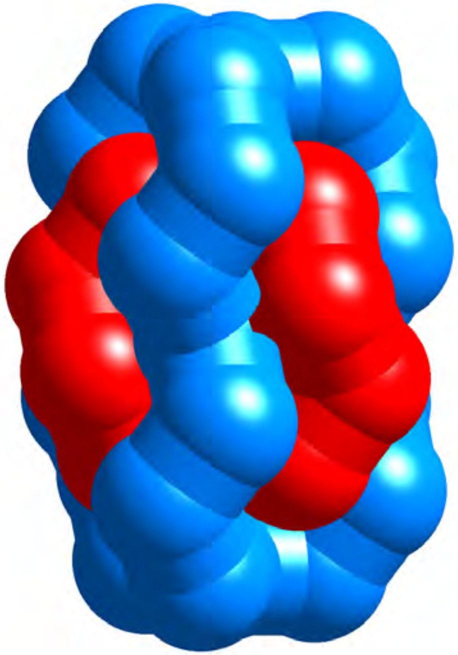


The **srs** net is chiral (symmetry $I4_132$).
The dual is the enantiomorph. Here two **srs** nets of opposite hand are intergrown to form a centrosymmetric structure (symmetry *Ia*-3*d*). The surface separating the two nets is the *G* minimal surface (*gyroid*)

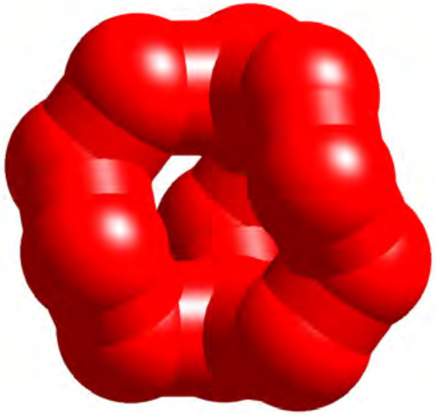
Alan Schoen's gyroid – periodic minimal surface *G*



Fragments of
two **srs nets**



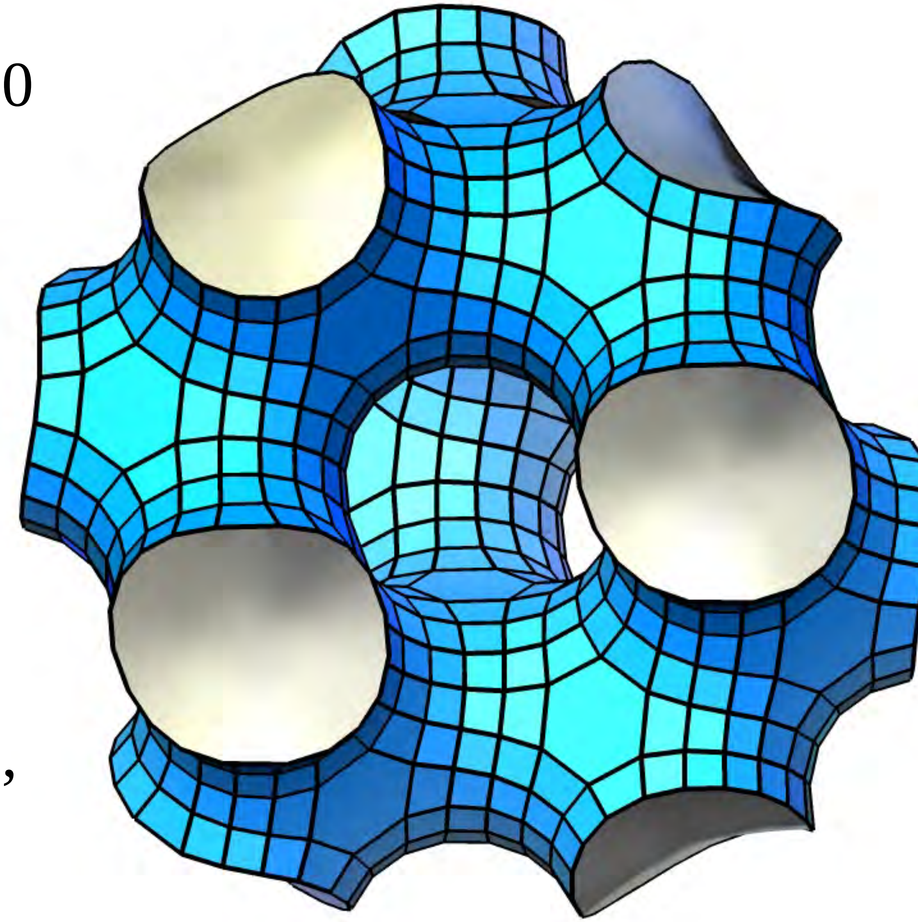
The same
"blown up"



A "tile" of
the *G* surface

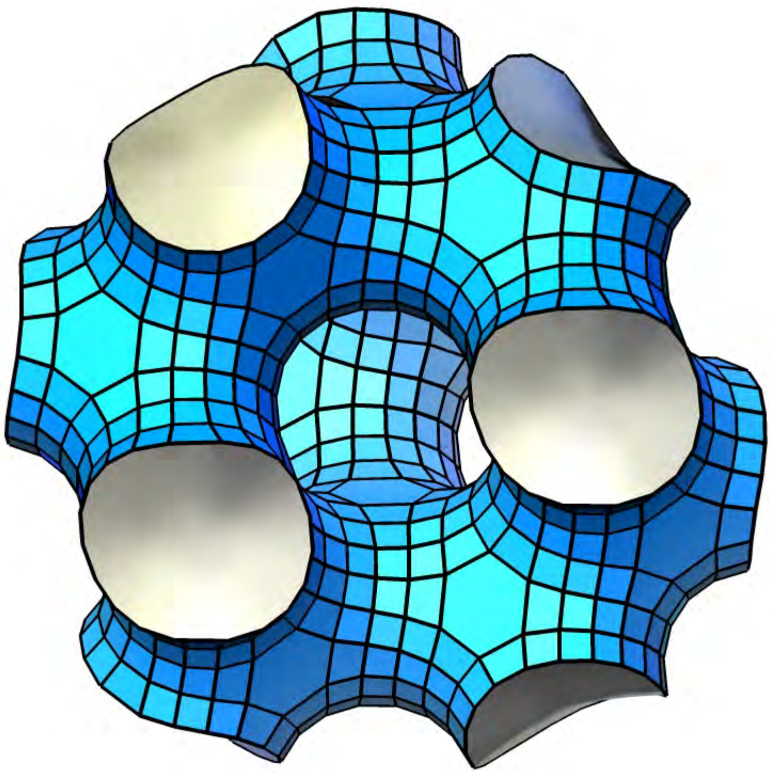
G surface of Alan Schoen in 1970

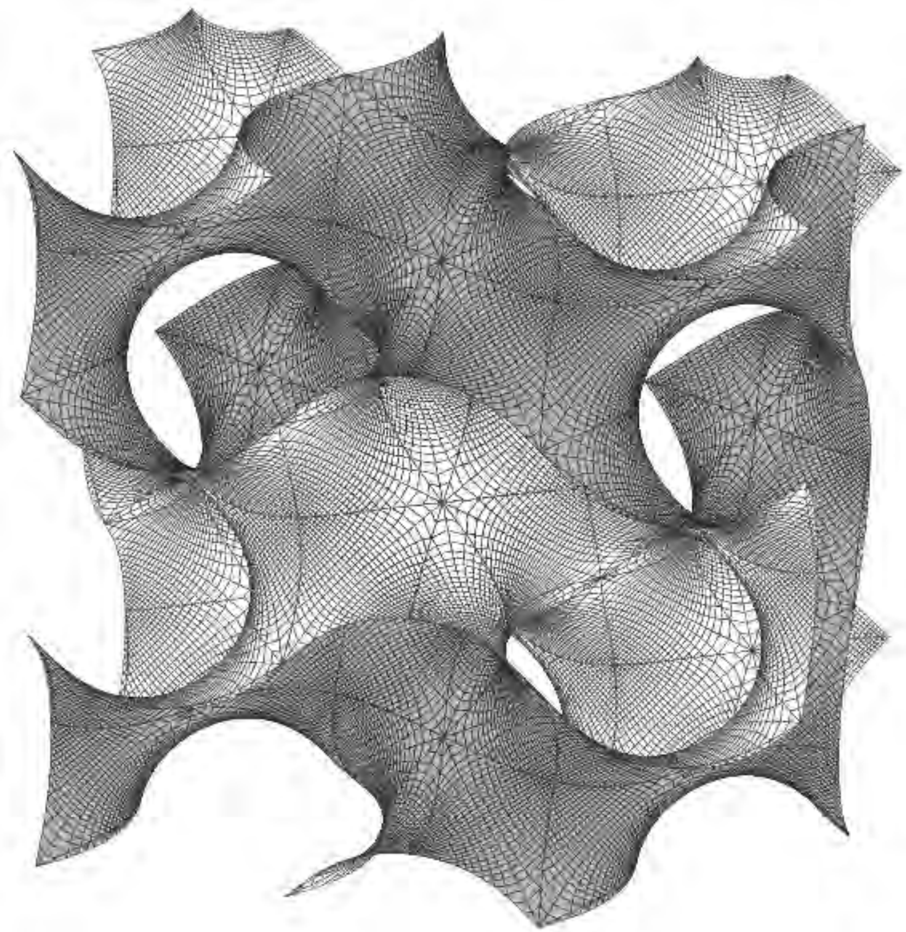
bicontinuous surfactant/water phases =>
mesoporous silicates, etc



A minimal surface has positive and negative principal curvatures, k_1 and k_2. For minimal surface:

Mean curvature = $(k_1 + k_2)/2 = 0$
Gaussian curvature $k_1 k_2 < 0$

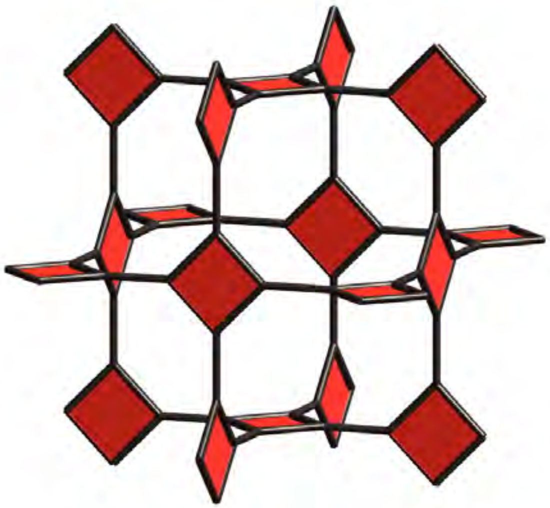




the gyroid is a surface !

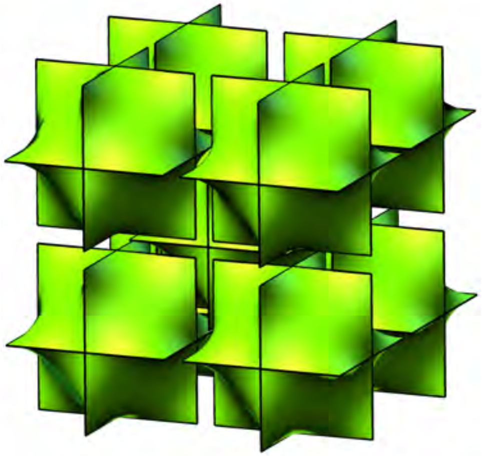
vertex figure: square

The **nbo** net



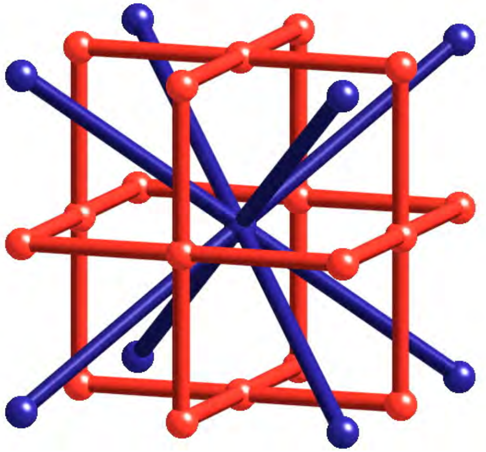
augmented net

nbo-a



natural tiling

$[6^8]$

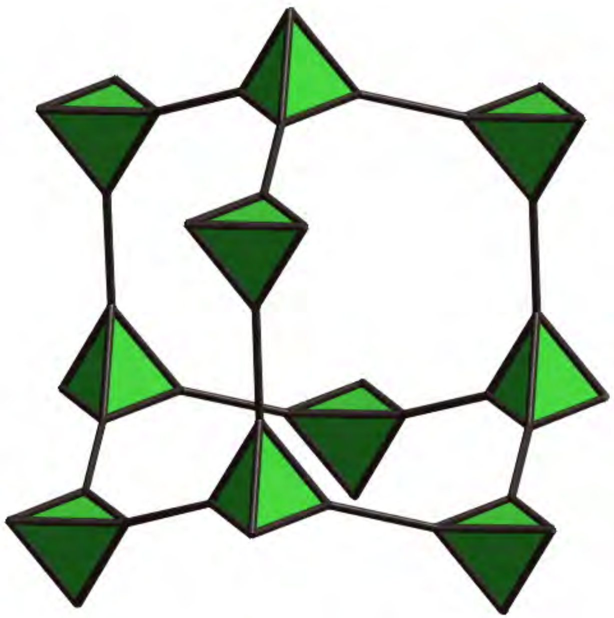


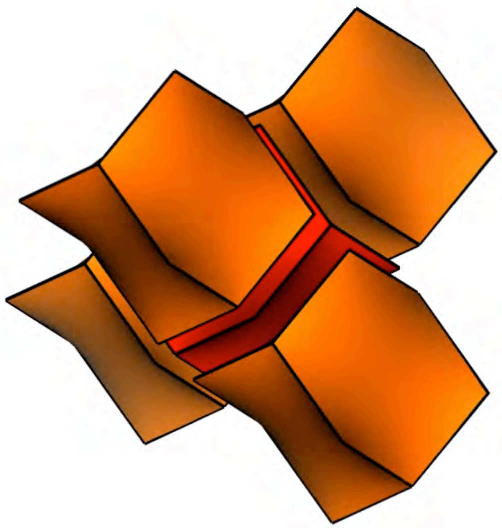
dual is 8-coordinated

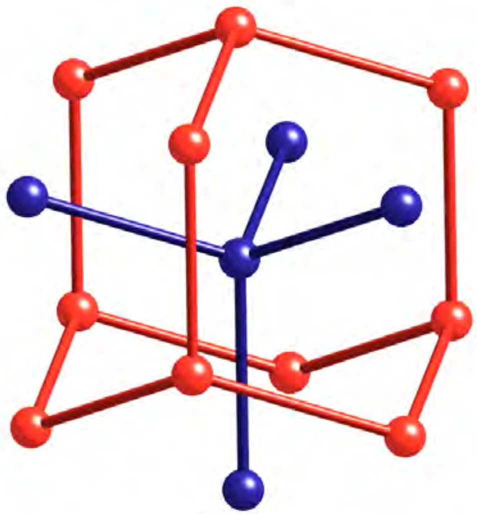
bcu net (bcc, blue)

vertex figure: tetrahedron

dia (diamond) net





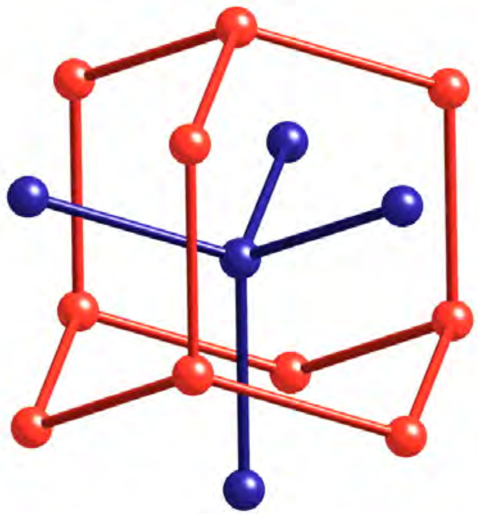


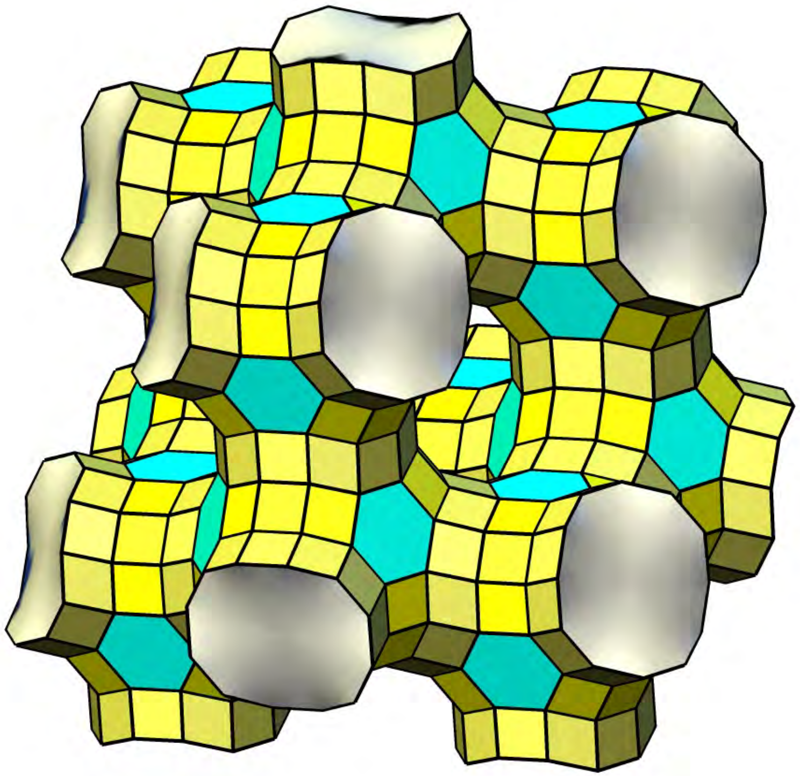
augmented net
dia-a

tiling
[6^4]

tile with dual
(self dual)

D minimal surface separates two **dia** nets

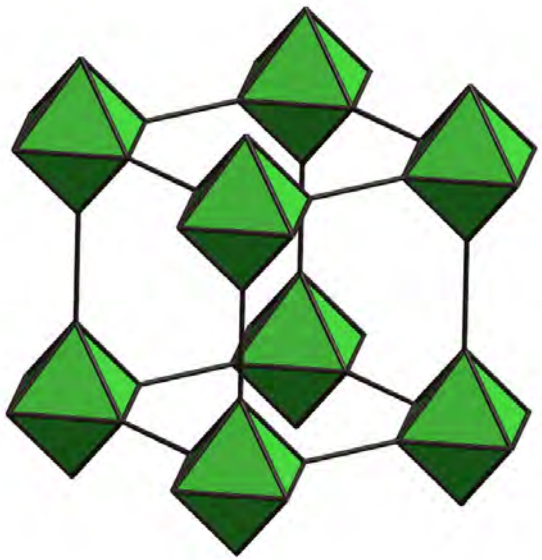




Red is skeleton of tile of **dia**

approximation to the D surface (should be smooth) *vertex figure: octahedron*

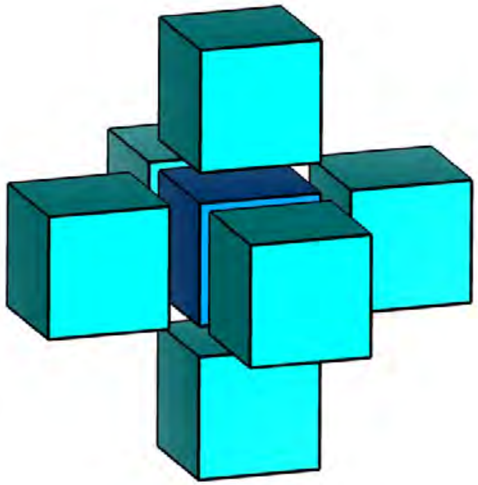
pcu (primitive cubic) net



augmented net

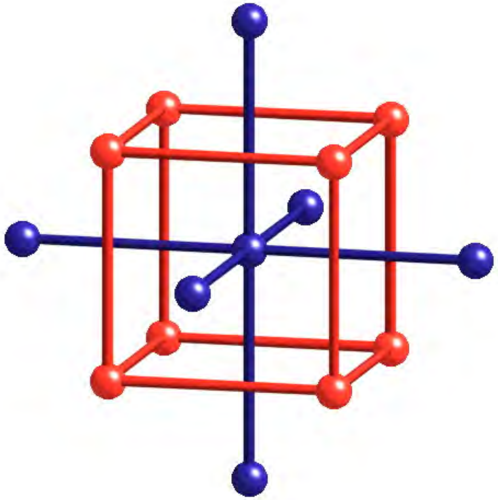
pcu-a = cab

(B in CaB_6)



tiling

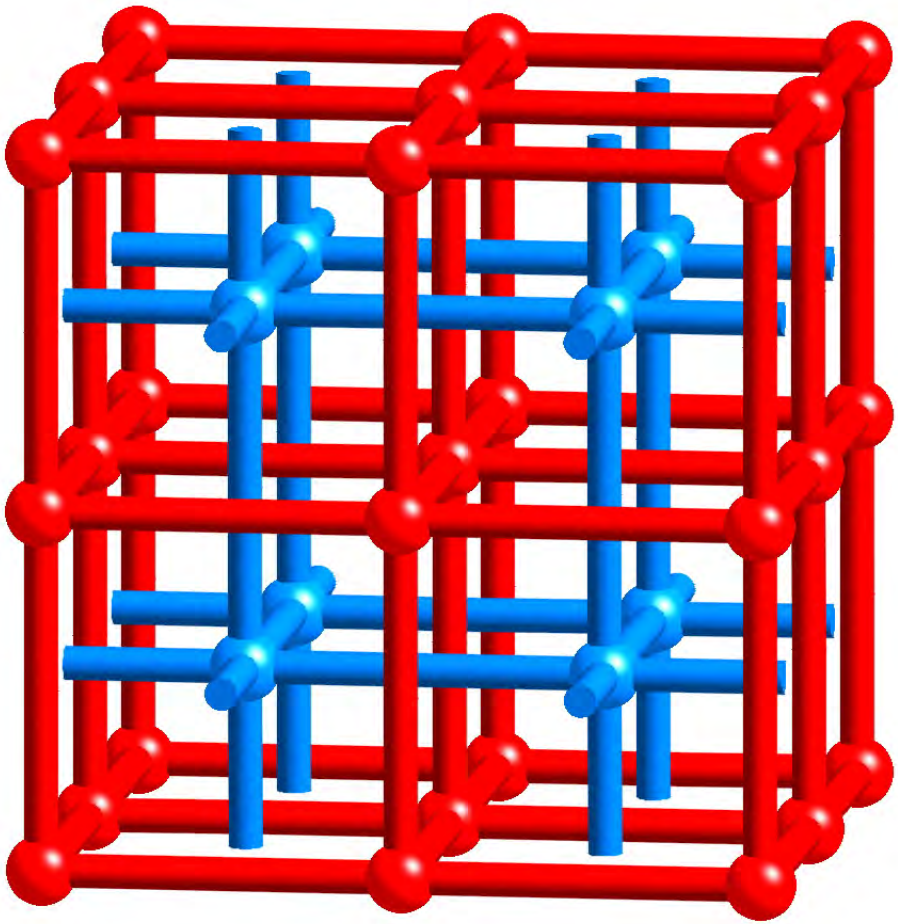
$[4^6]$



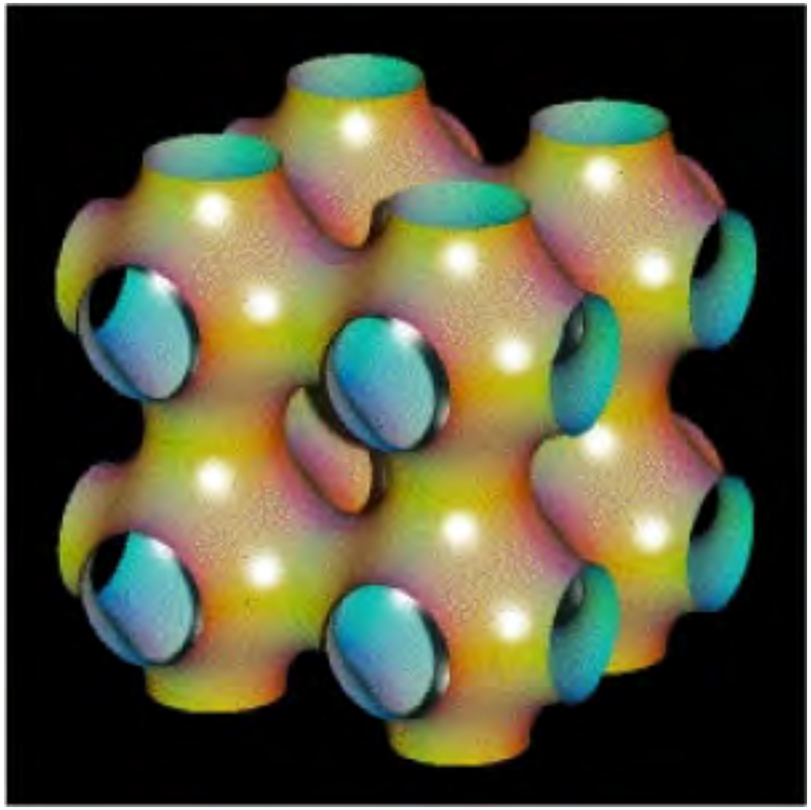
tile with dual

(self dual)

P minimal surface separates two **pcu** nets

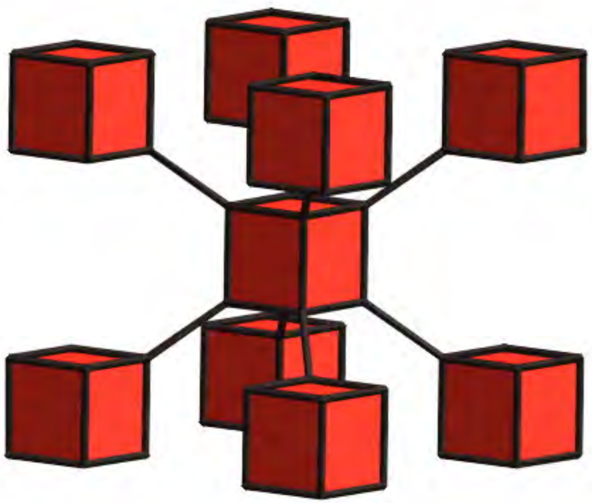


Two interpenetrating **pcu** nets
(notice that the nets are self-dual)

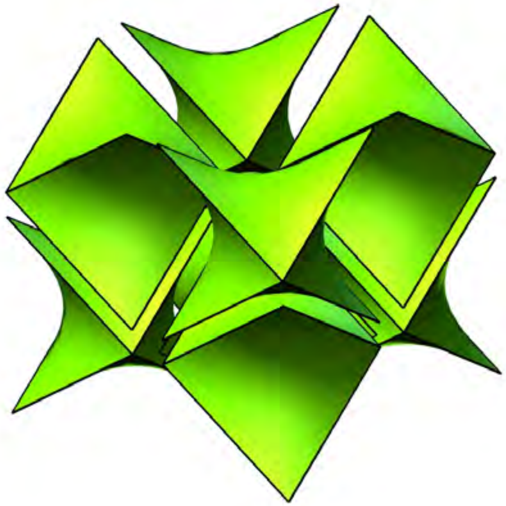


The *P* minimal surface
separates the two nets.
Average curvature zero
Gaussian curvature neg.

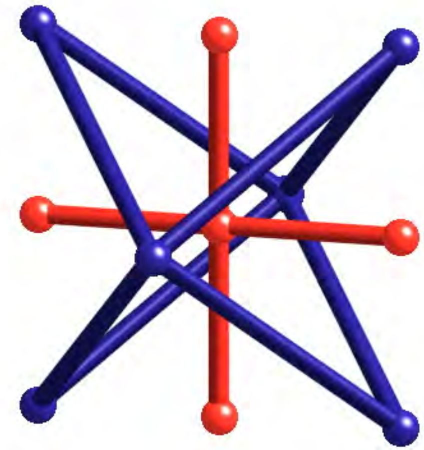
vertex figure: cube
bcu (body-centered cubic) net



augmented net
bcu-a = **pcb**
(polycubane)



tiling
[4^4]

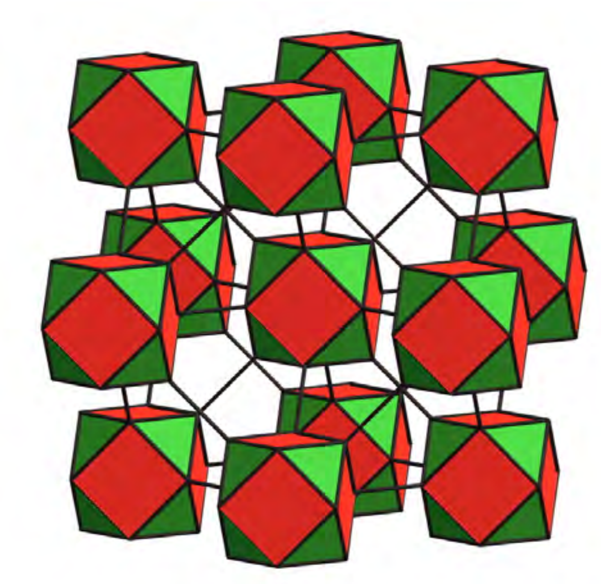


tile with dual
(dual is **nbo**)

Quasiregular net: *vertex figure cuboctahedron*

fcu (face-centered cubic) net

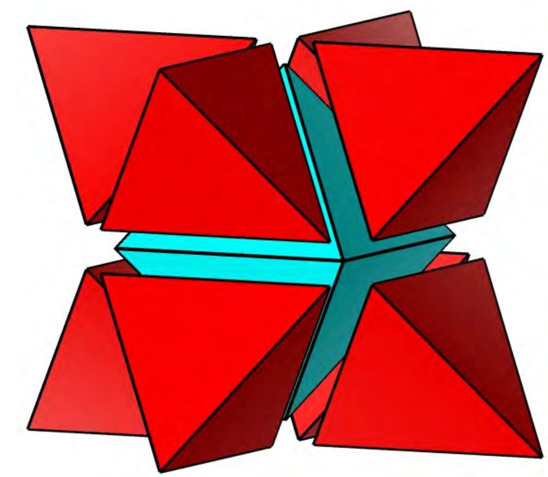
transitivity 1112



augmented net

fcu-a = **ubt**

(B in UB_{12})

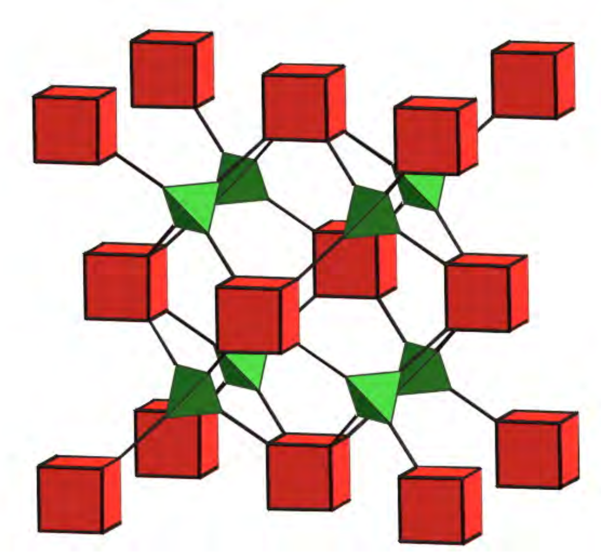


tiling

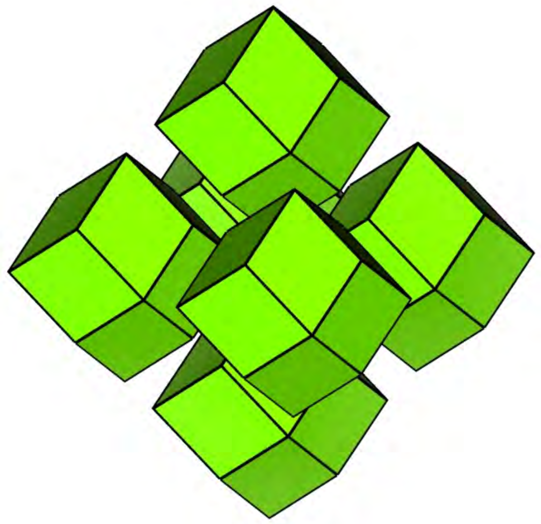
(note dual has two vertices)

$2[3^4] + [3^8]$

Normal dual of the **fcu** net. **flu** (fluorite)
transitivity 2111



augmented net
flu-a



tiling
$[4^{12}]$

3-periodic nets. The story so far:

The Regular Nets. Transitivity 1111

1. **srs,** triangle, $I4_132$, Si net of $SrSi_2$ (self-dual)
2. **nbo,** square, *Im*-3*m*, all atoms of NbO (dual = **bcu**)
3. **dia,** tetrahedron, *Fd*-3*m*, diamond net (self-dual)
4. **pcu,** octahedron, *Pm*-3*m*, primitive cubic (self dual)
5. **bcu,** cube, *Im*-3*m*, body-centered cubic (dual = **nbo**)

Quasiregular. Transitivity 1112

6. **fcu,** cuboctahedron, face-centered cubic dual is …

7. **flu,** cube and tetrahedron, net of fluorite (CaF_2)
(transitivity 2111)

there are 14 more vertex and edge transitive nets 11*rs*:

What 11*rs* structures are there?

1111 5 regular

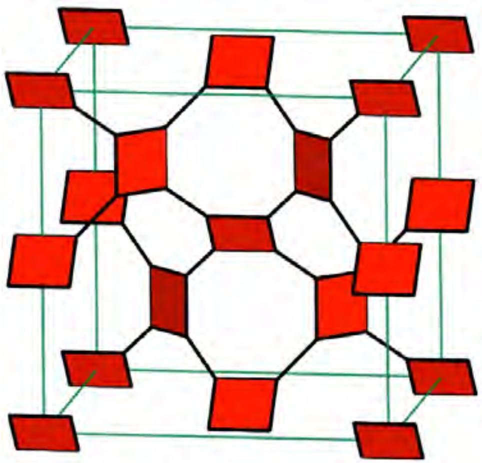
1112 1 quasiregular

11*rs* 14 semiregular

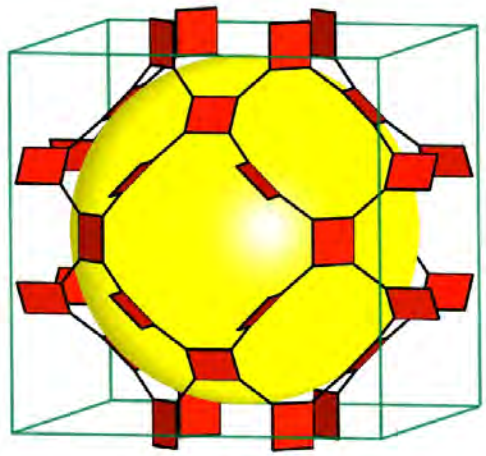
(these have embeddings in which there is no inter-vertex distance shorter than edges)

The augmented regular, quasiregular, and semiregular nets are ways of linking polygons or polyhedra with one kind of link.

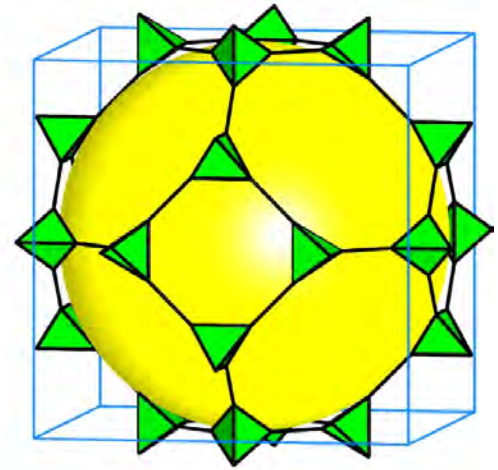
augmented semiregular nets -1



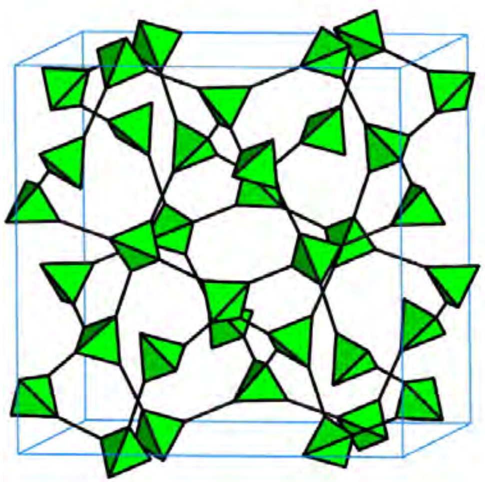
lvt-a



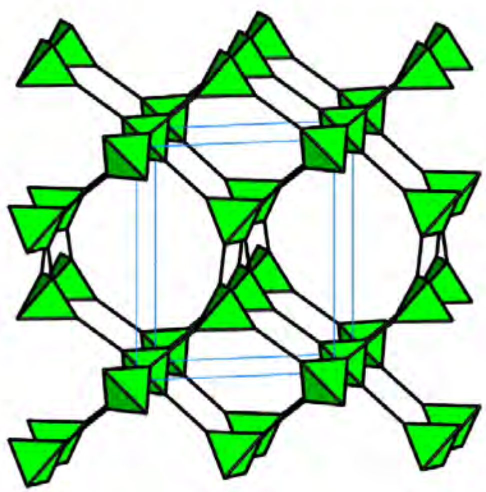
rhr-a



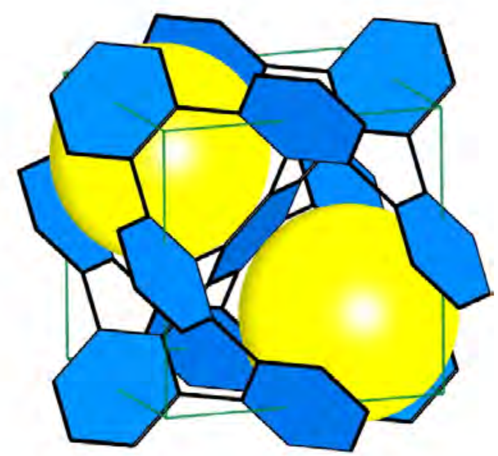
sod-a



lcs-a

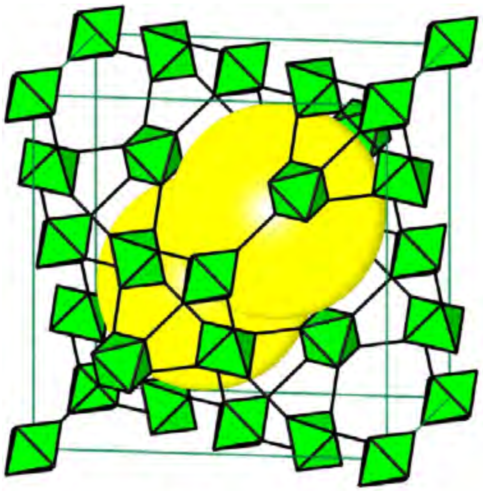


qtz-a

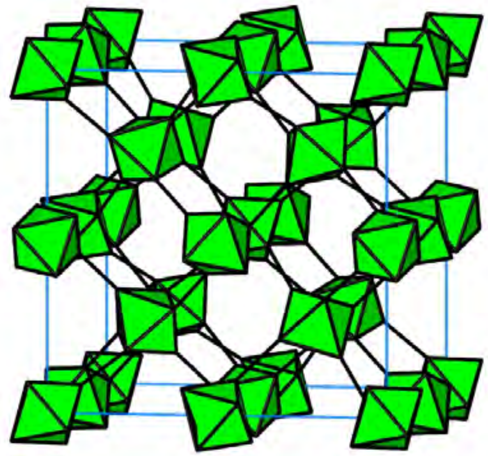


hxg-a = pbz

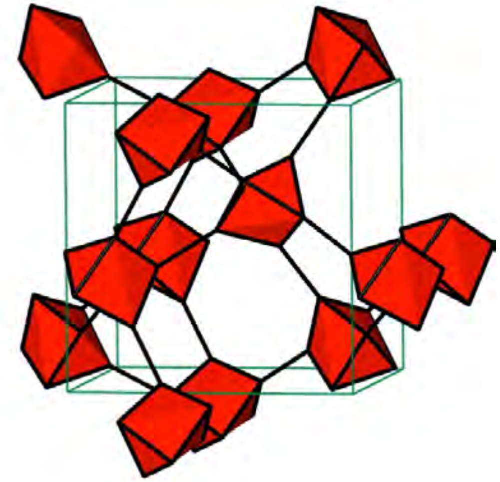
augmented semiregular nets -2



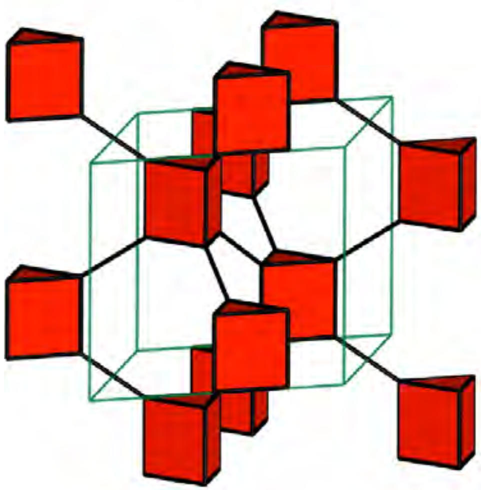
crs-a



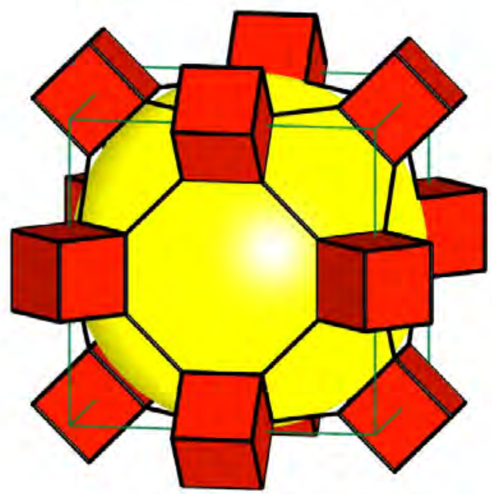
bcs-a



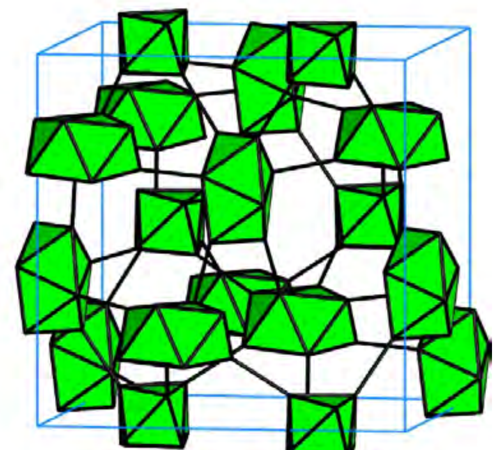
lcy-a



acs-a

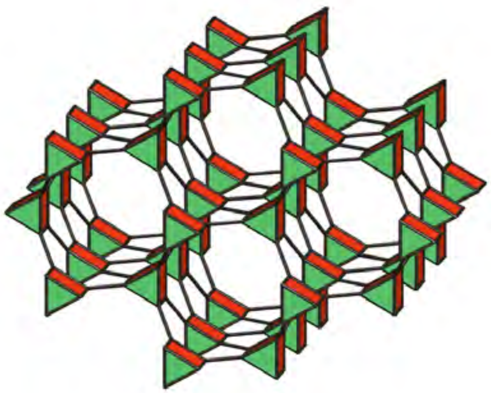


reo-a = lta

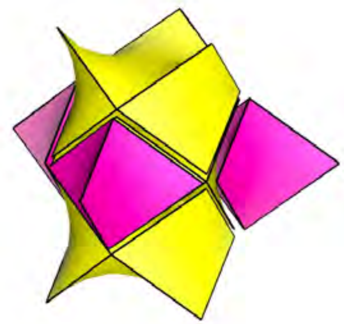


thp-a

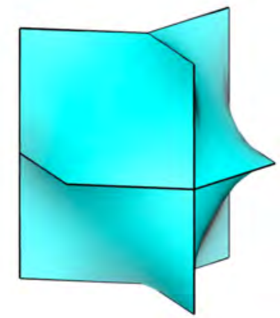
Default structure for linking trigonal prisms: **acs** trans 1122



augmented net **acs-a**

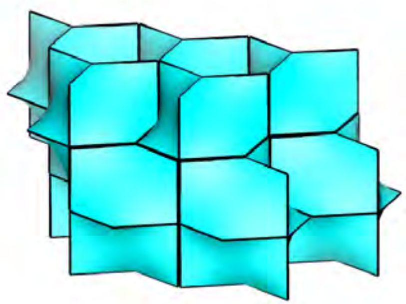


tiling
$2[4^3] + [4^3.6^2]$

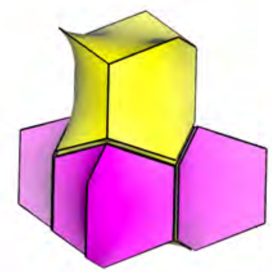


dual $[6^6]$
(not natural)

Half this tile
is the natural
tile for graphite.
Dual of this is
a 4-coordinated
structure:



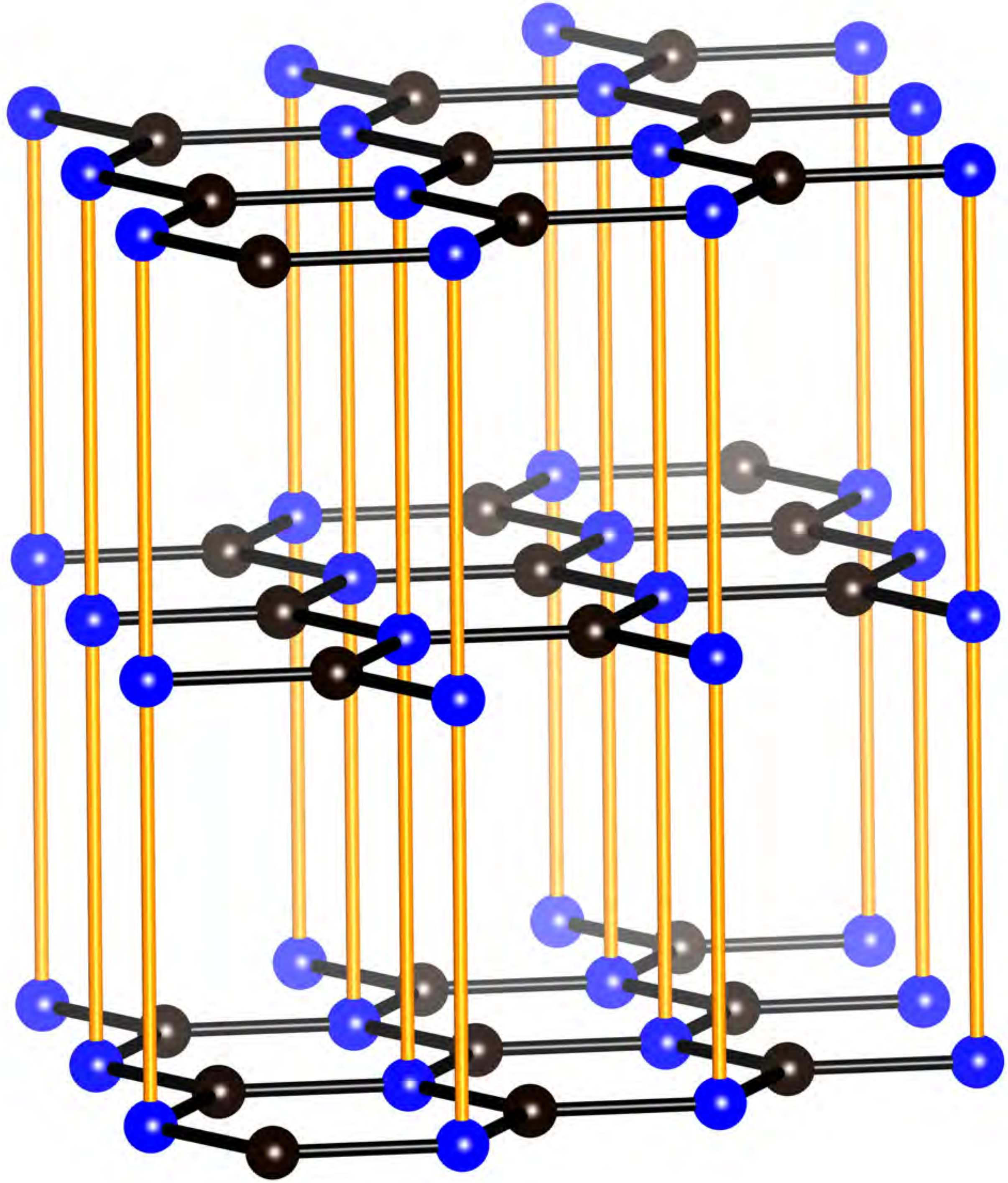
more of the dual tiling
the net is **gra** (graphite)



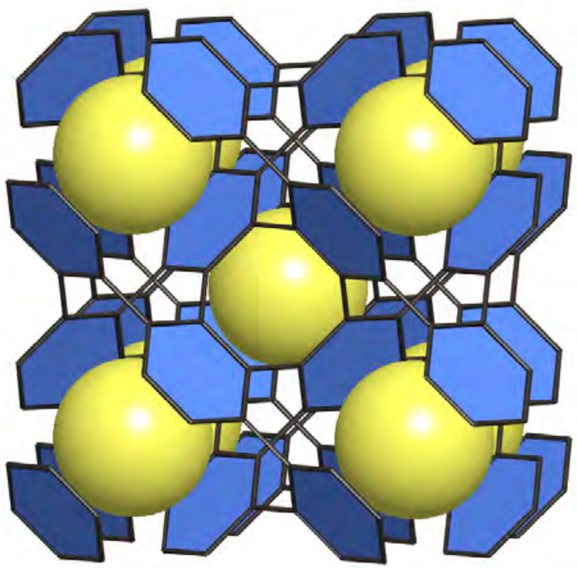
lns (lonsdaleite)
dual of **gra** (graphite)
using natural $[6^4]$ tiles

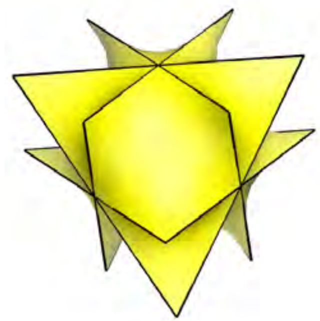
graphite
yellow “bonds’ are shortest distances between layers

The net **gra** is (3,5)-c

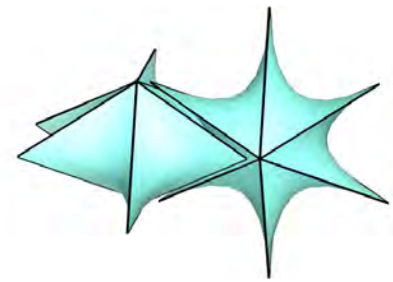


Default structure for linking hexagons **hxg**
Symmetry *Pn*-3*m*. Transitivity 1121.





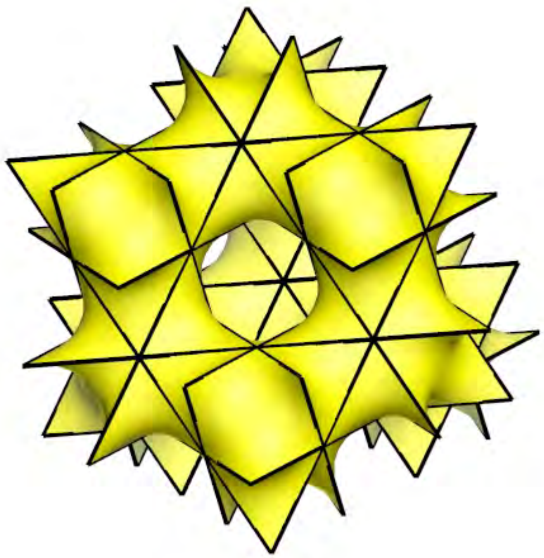
natural tile [$4^6.6^4$]



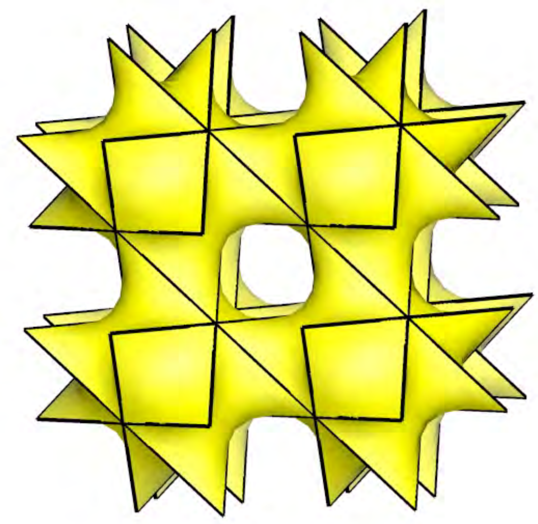
dual [4^6]

the augmented net
hxg-a = **pbz**
(polybenzene)

Digression: we can use the **hxg** tiles to build models of minimal surfaces. In each of the two models below, the filled and empty spaces are the same and the surface separating the two surfaces are the *D* and *P* minimal surfaces



D surface. The lines are edges of an **hxg** net

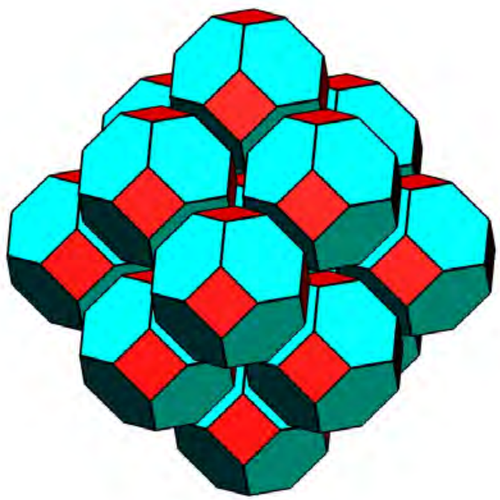


P surface

the net **sod**, symmetry *Im*-3m with transitivity 1121

atomic positions
1/2, 1/4, 0 etc

"imvariant lattice complex" *W**



tiling has transitivity 1121
simple tiling

Cubic invariant lattice complexes. O'K&H p. 281

International Tables for Crystallography, Vol. A

RCSR symbol	lattice complex	space group		coordination
fcu	*F*	*Fm*-3*m*	4 *a*	12
bcu	*I*	*Im*-3*m*	2 *a*	8
reo	*J*	*Pm*-3*m*	3 *c*	8
lcs	*S*	*I*-43*d*	12 *a* or 12 *b*	8
crs	*T*	*Fd*-3*m*	16 *c* or 16 *d*	6
lcy	^{+}Y	$P4_332$	4 *a*	6
lcy	^{-}Y	$P4_132$	4 *a*	6
dia	*D*	*Fd*-3*m*	*8 a* or 8 *b*	4
lcv	^{+}V	$I4_132$	12 *d*	4
lcv	^{-}V	$I4_332$	12 *d*	4
nbo	*J**	*Im*-3*m*	6 *b*	4
sod	*W**	*Im*-3*m*	12 *d*	4
lcs	*S**	*Ia*-3*d*	24 *c*	4
srs	$^{+}Y*$	$I4_132$	8 *a*	3
srs	$^{-}Y*$	$I4_132$	8 *b*	3
srs-c	*Y***	*Ia*-3*d*	16 *b*	3
lcw	*W*	*Im*-3*m*	6 *c* or 6 *d*	2

Structures based on edge-transitive nets with two kinds of vertex (transitivity 21*rs*)

These are of two kinds

1. Structures based on coloring of nets with one kind of vertex (e.g. the NaCl structure is derived from **pcu** (primitive cubic) by alternating Na and Cl at the vertices.

2. Structures in which the vertices have different vertex figures (e.g. tetrahedron + square or triangle + octahedron)

Edge-transitive binodal nets

These form the basis for structures formed by joining two shapes by one kind of link.

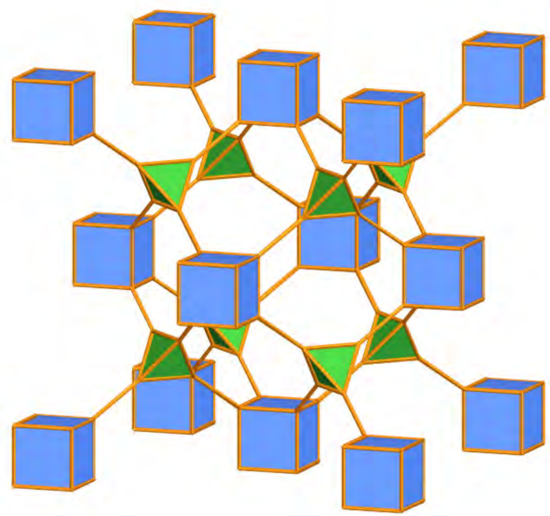
O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Cryst.* ***A*62**, 350-355 (2006)

Edge-transitive 3-periodic nets

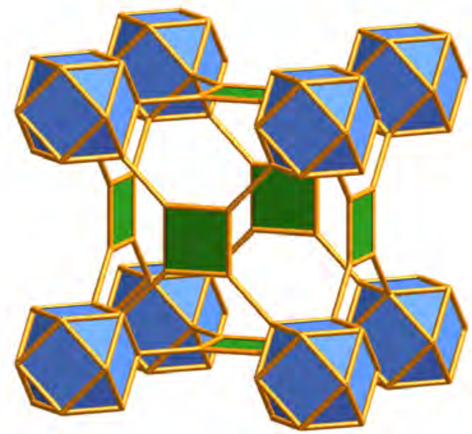
11*rs* 20
21*rs* 13 binary versions of above
>34 others

Note:
These are nets that have embeddings with edge lengths equal to the shortest distance between vertices.
Without this restriction there are infinitely many

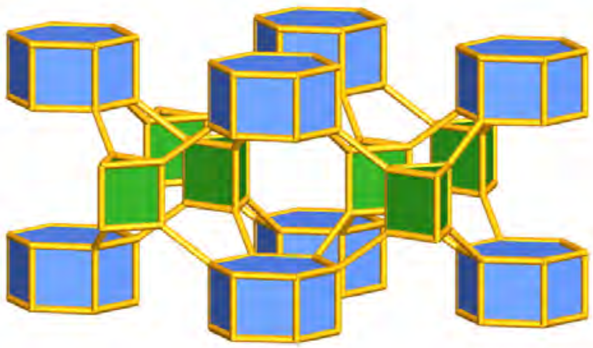
Edge-transitive binodal nets



flu-a *o*/*z* = 6



ftw-a *o*/*z* = 4



alb-a *o*/*z* = 2

Possible ways of linking polyhedra with full symmetry

Order of a symmetry group =
number of symmetry operations

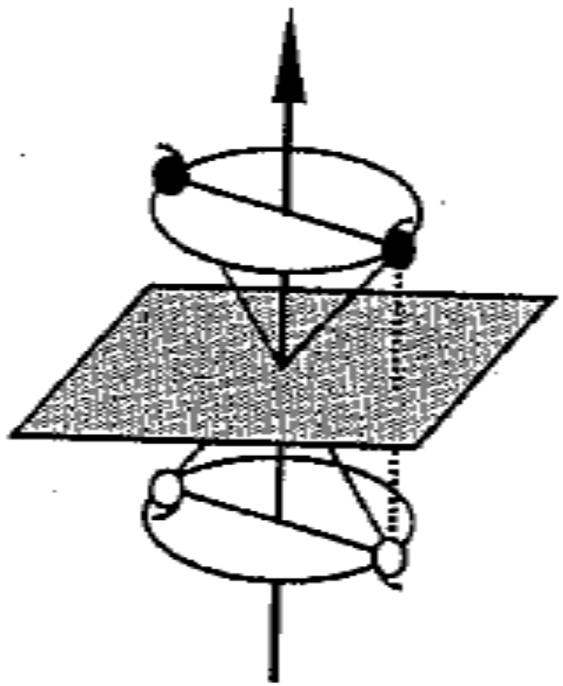
group 4 order is 4

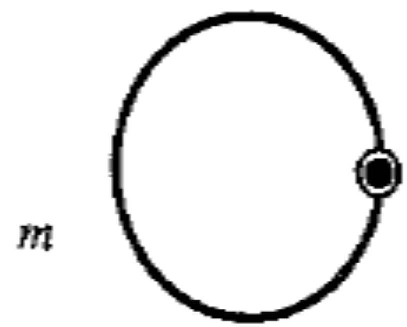
¼ turn
½ turn
¾ turn
full turn (identity)

Group 2/*m*

order 4

½ turn
reflection
inversion
identity





group 23

four 3-fold rotation axes (symmetry elements)
eight three fold rotations (symmetry operations)

three 2-fold rotations
three 3-fold rotations

identity

Total operations = 12 = order of group

In a periodic structure

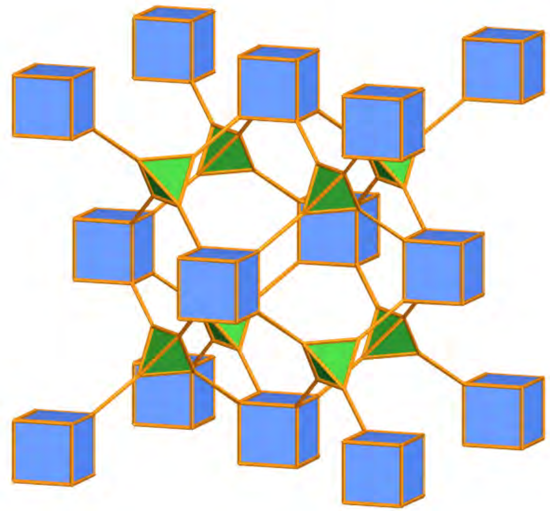
number of points (atoms) pf a given kind in primitive cell multiplied by the order pf symmetry at that site

= order of the point group (class) of the apace group

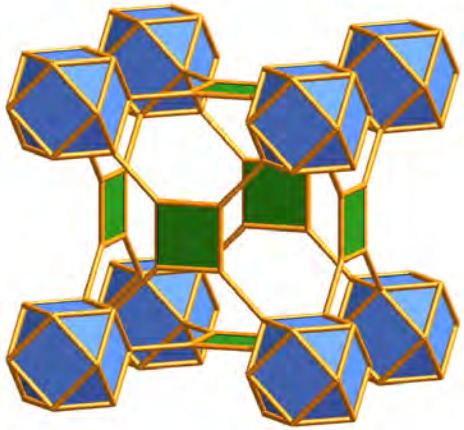
In a bipartite structure A_nB_m

number of atoms x coordination number = constant

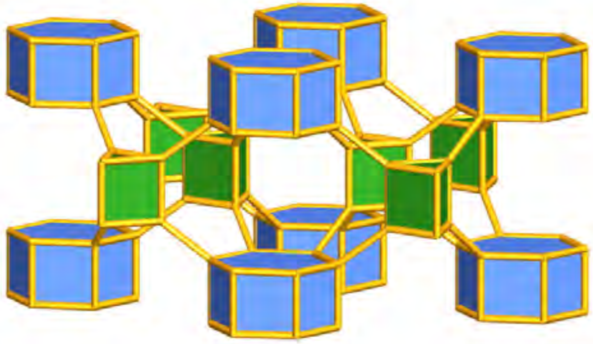
Edge-transitive binodal nets



flu-a *o*/*z* = 6



ftw-a *o*/*z* = 4



alb-a *o*/*z* = 2

Possible ways of linking polyhedra with full symmetry

Why not
square (symmetry 4/*mm* order 16) and
eqilateral triangle (symmetry -6*m*2, order 12)?

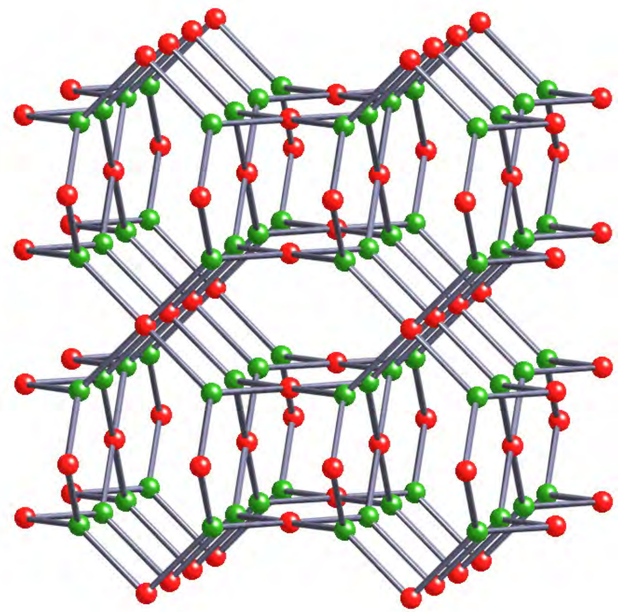
Answer -6 only compatible with hexagonal
4/*mmm* only cubic or tetragonal.

Highest possible symmetry for triangular coordination in cubic system is 3*m* or 32 (order 6).
So:
Triangle – square combination maximum symmetry order is 6-8

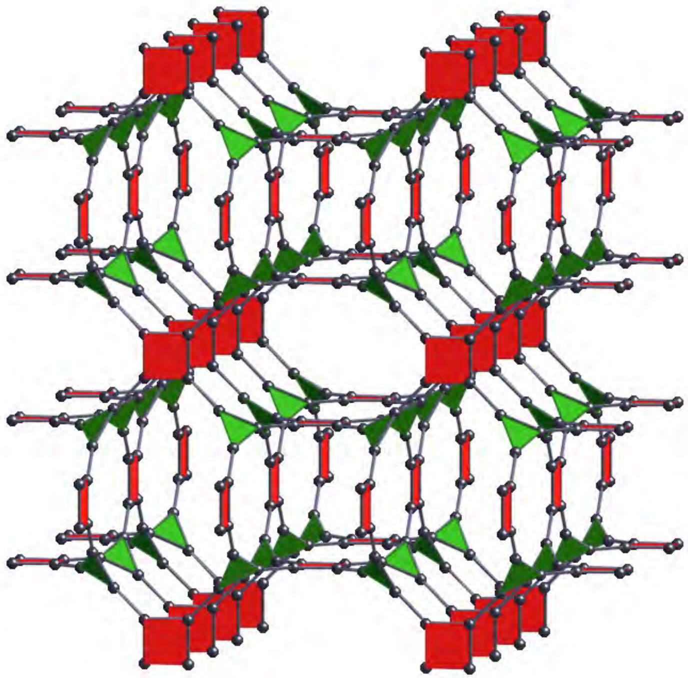
Edge-transitive binodal nets

triangle - square; order 6 - 8

this is the order of the point symmetry of the vertices



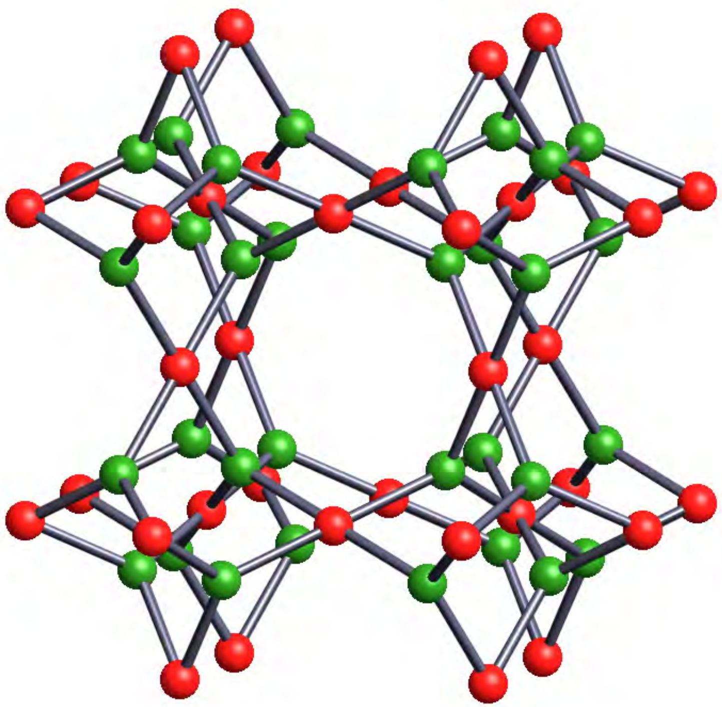
the Pt_3O_4 net,
pto



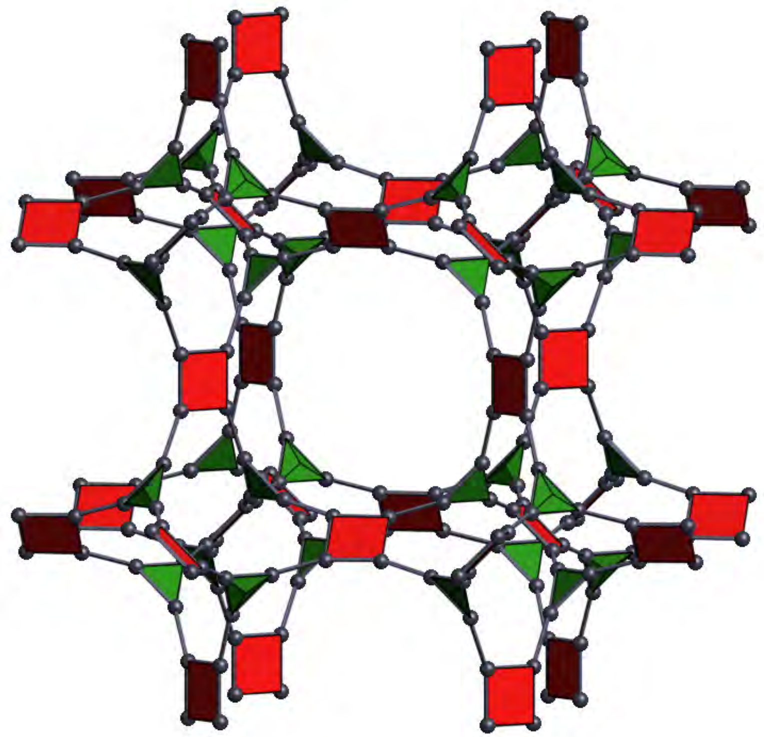
the augmented structure
pto-a

Edge-transitive binodal nets

triangle - square: order 6 - 8



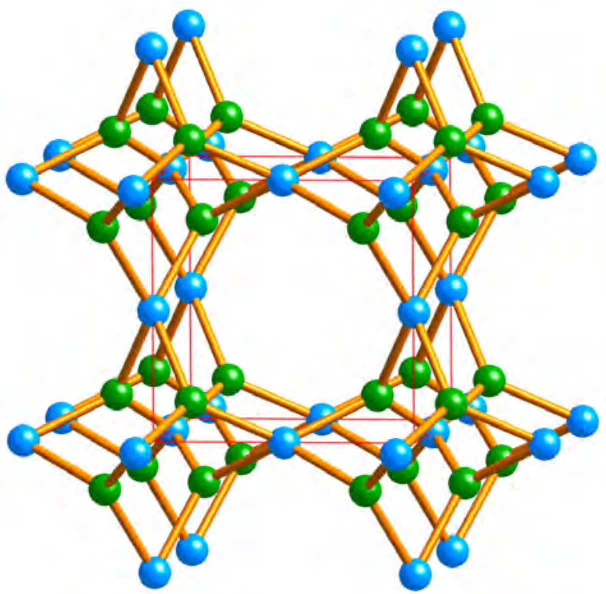
the "twisted boracite" net
tbo *Fm*-3*m*



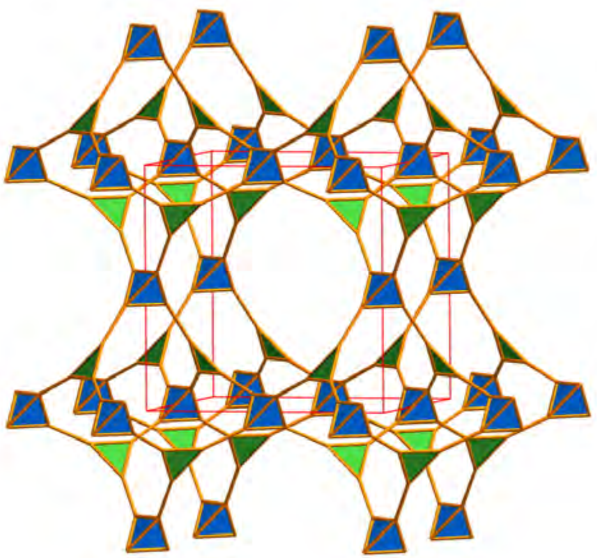
the augmented structure
tbo-a

Edge-transitive binodal nets

triangle - tetrahedron: order 6 - 8



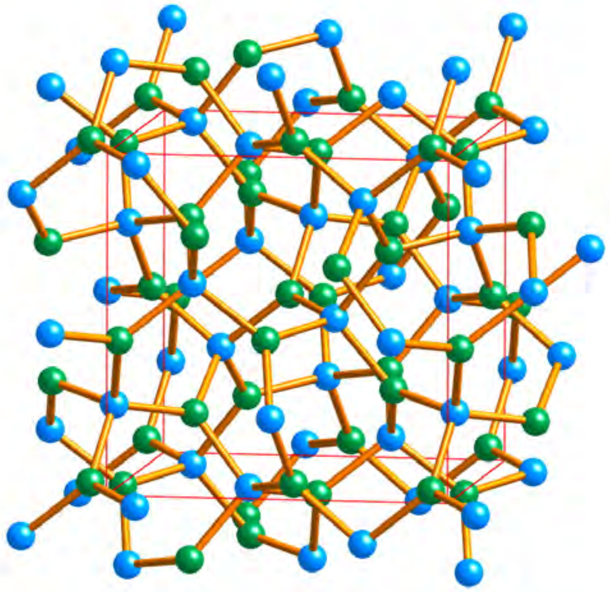
the boracite net
bor, *P*-43*m*



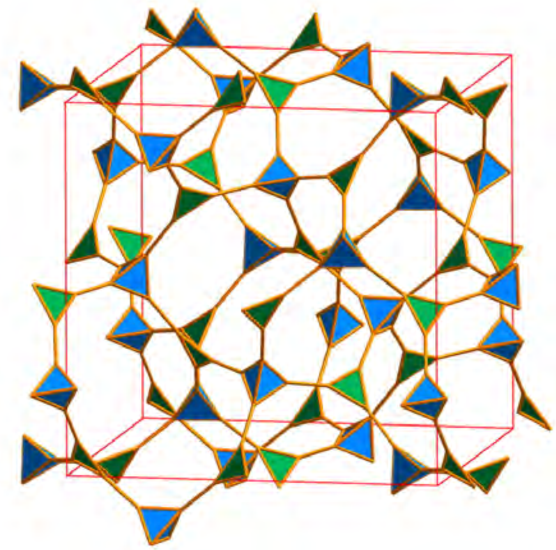
the augmented structure
bor-a

Edge-transitive binodal nets

triangle - tetrahedron: order 3 - 4



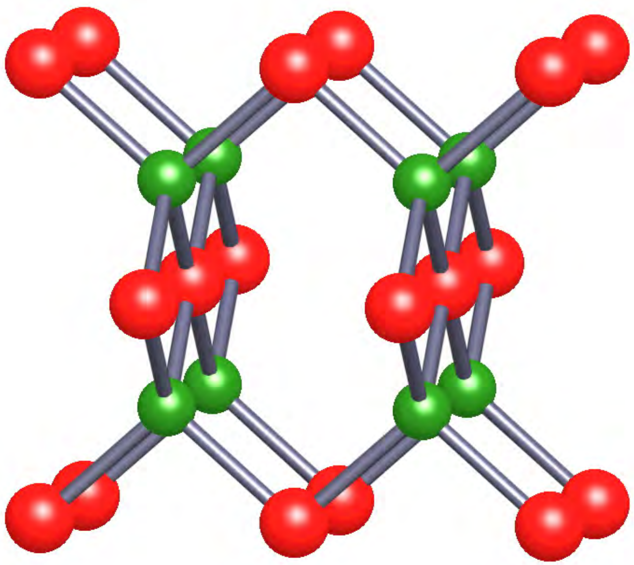
The "C_3N_4" net
ctn, *I*-43*d*



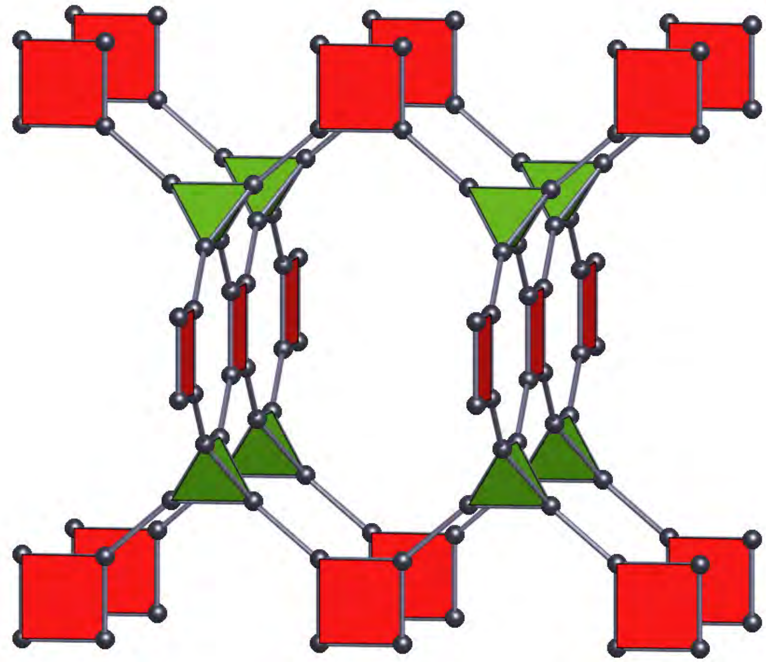
the augmented structure
ctn-a

Edge-transitive binodal nets

square - tetrahedron: order 8 - 8



the PtS net
pts $P4_2/mmc$



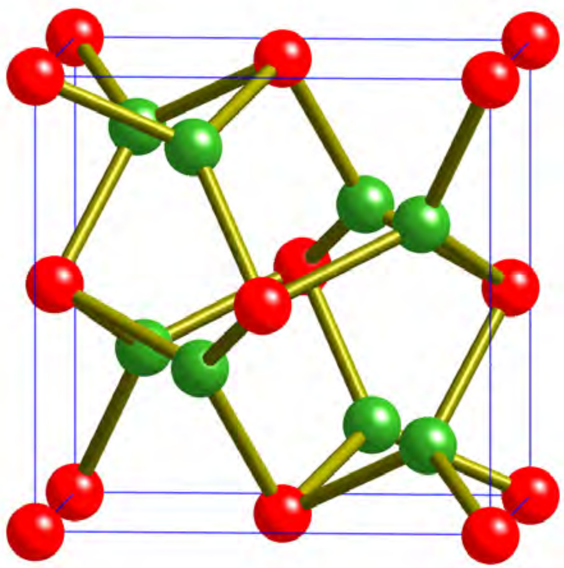
the augmented structure
pts-a

Although the full symmetry of a tetrahedron, -43*m* and that of a square 4/*mmm* are both compatible with cubic symmetry, there is no space group with both sites of both symmetries.

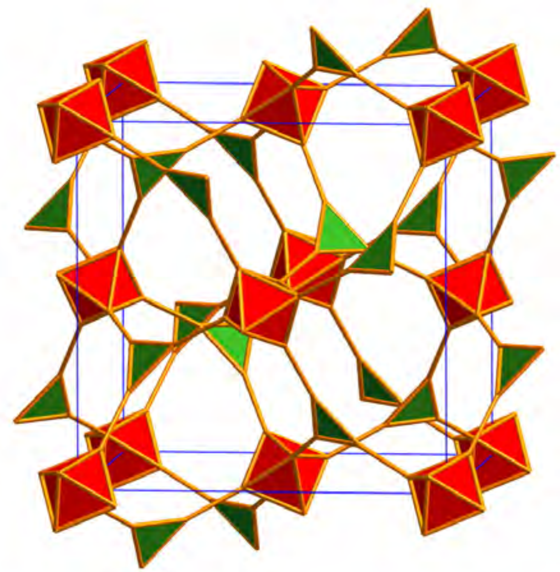
It is probably not possible, even in lower symmetry, to have square and regular tetrahedral coordination in any 4-c net.

Edge-transitive binodal nets

triangle - octahedron: order 3 - 6



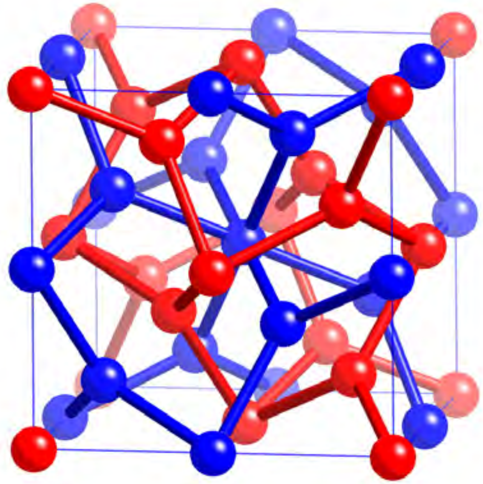
the pyrite (FeS_2) net
pyr *Pa*-3



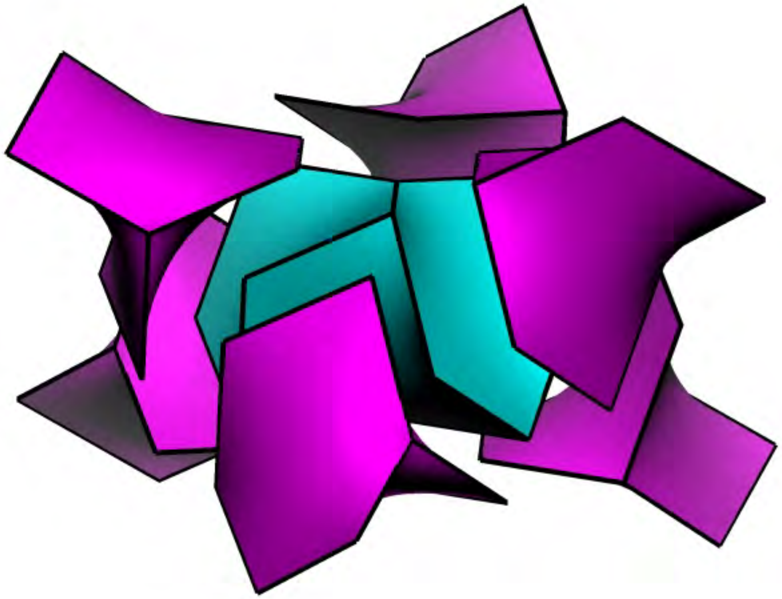
the augmented structure
pyr-a

Edge-transitive binodal nets

The **pyr** structure is naturally self dual
transitivity 2112. Tiles $2[6^3] + [6^6]$



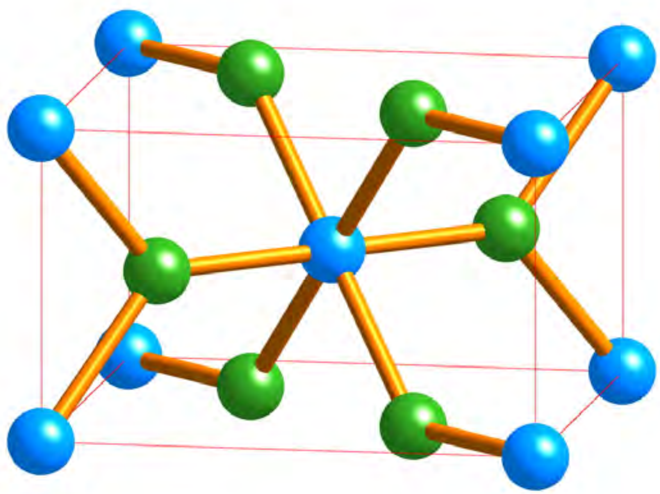
two fully catenated **pyr** nets



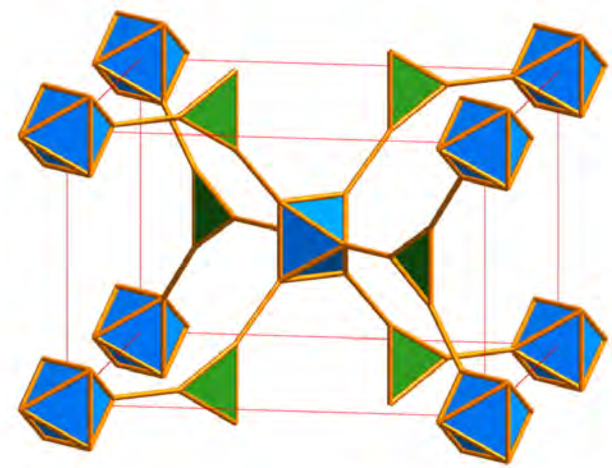
tiling

triangle - octahedron: order 4 - 8

the rutile structure symmetry $P4_2/mnm$



rtl



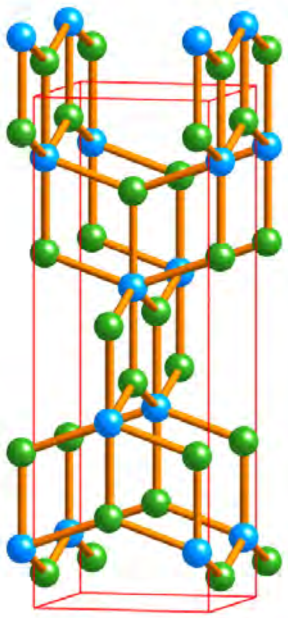
rtl-a

although the vertices here have higher site symmetry than in **pyr**,

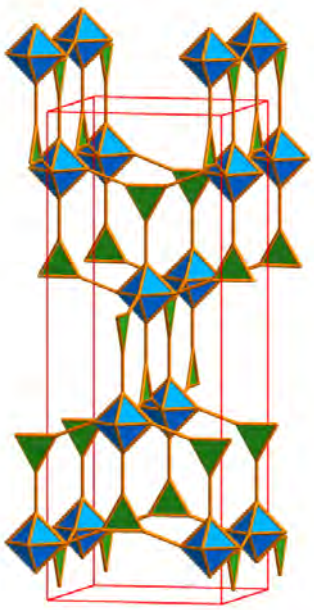
this is *not* an edge-transitive structure triangle - octahedron: order 4 - 8

the anatase structure symmetry $I4_1/amd$

ant



ant-a

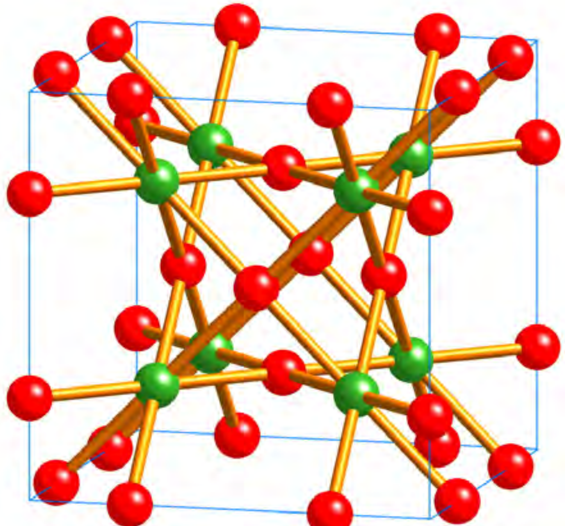


although the vertices here have higher site symmetry than in **pyr**,

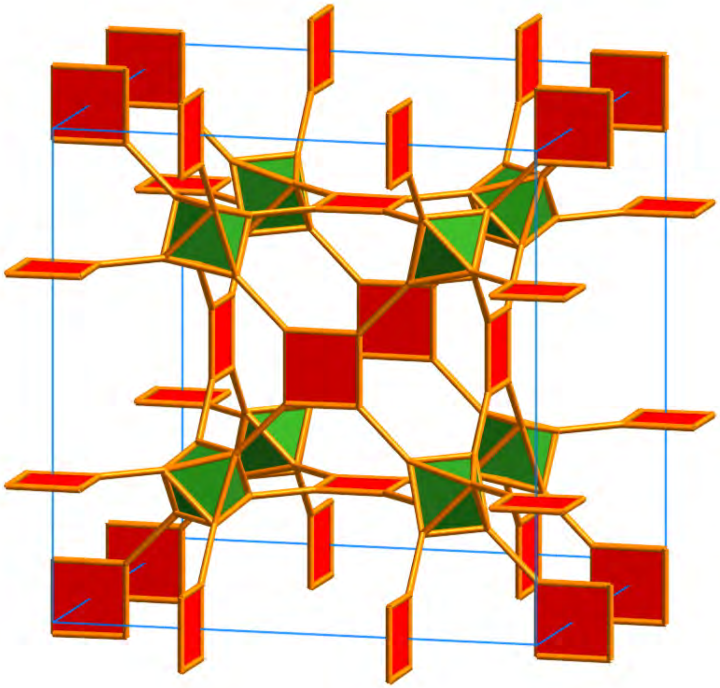
this is *not* an edge-transitive structure

Edge-transitive binodal nets

square - octahedron: order 8 - 12



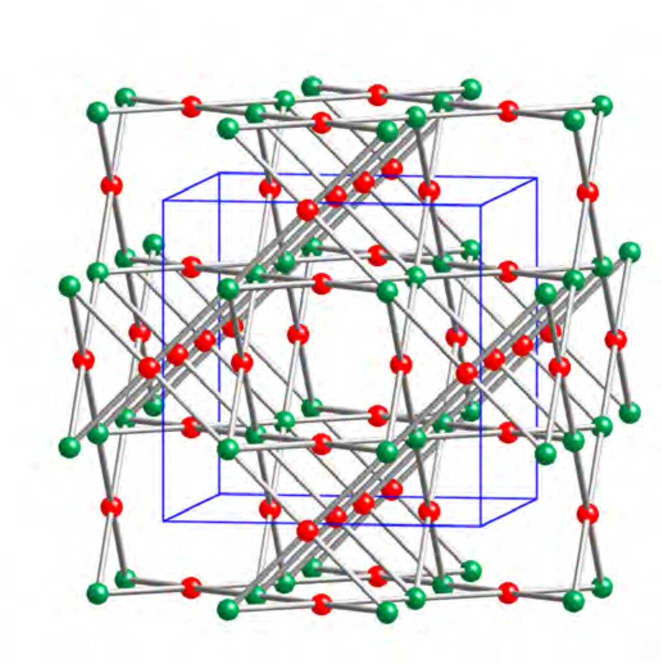
soc *Im*-3*m*



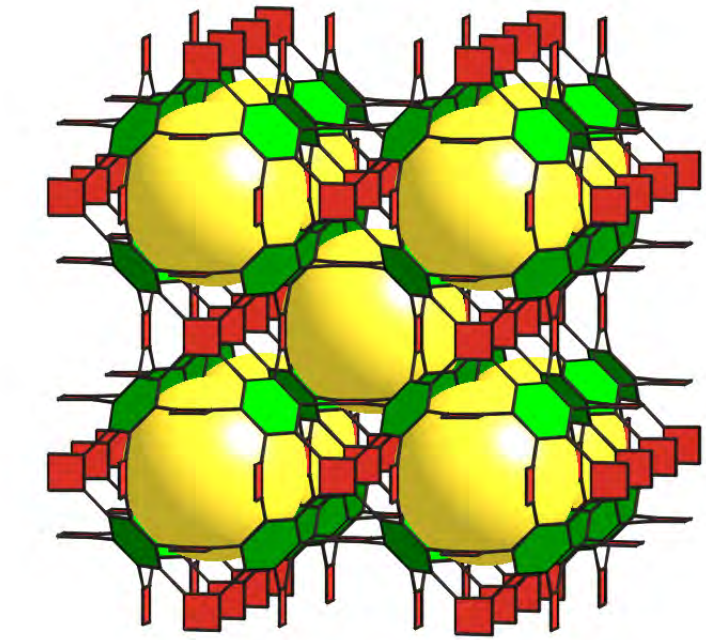
soc-a

Edge-transitive binodal nets

square - hexagon: order 8 - 12



she



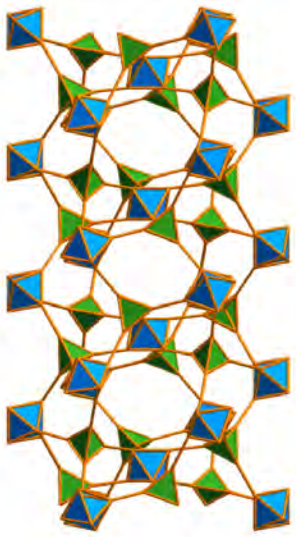
the augmented structure
she-a

Edge-transitive binodal nets

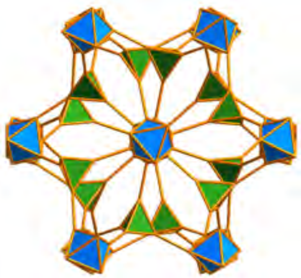
tetrahedron - octahedron: order 4-6

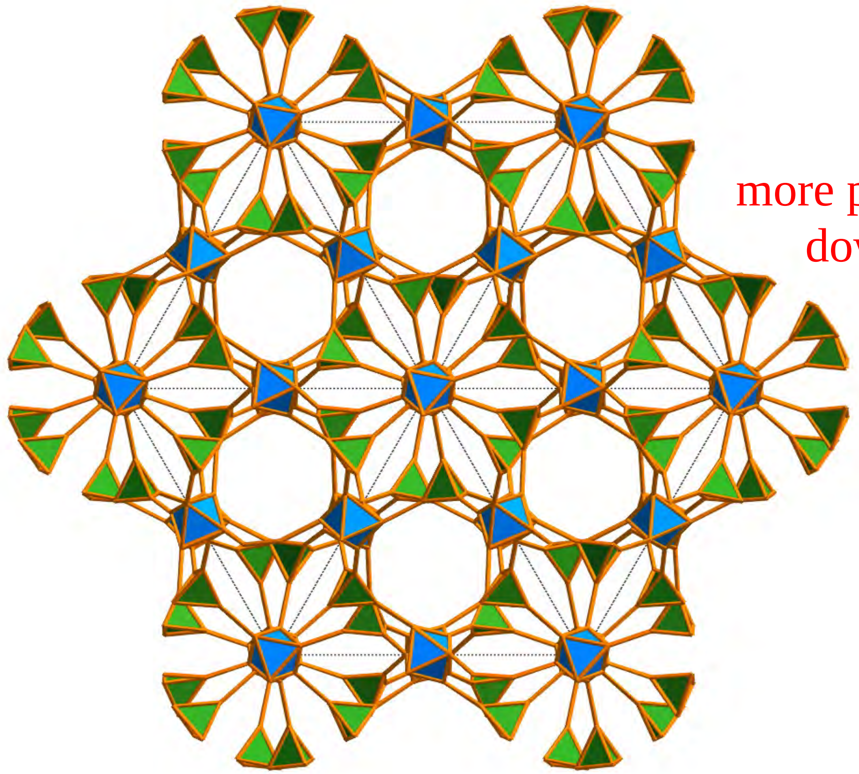
augmented garnet net: **gar-a**. symmetry *Ia*-3*d*

a fragment normal to [111]



the same fragment down [111]





more projected down [111]

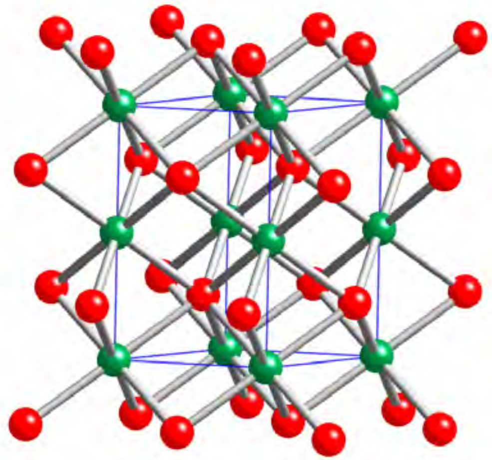
the garnet structure is notoriously difficult to illustrate!

Edge-transitive binodal nets

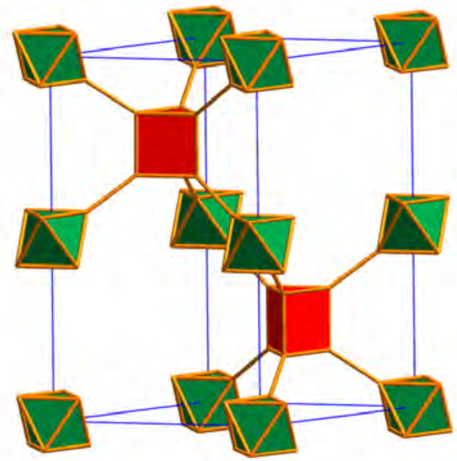
trigonal prism - octahedron: order 12-12

NiAs **nia**, symmetry $P6_3/mmc$

nia



nia-a

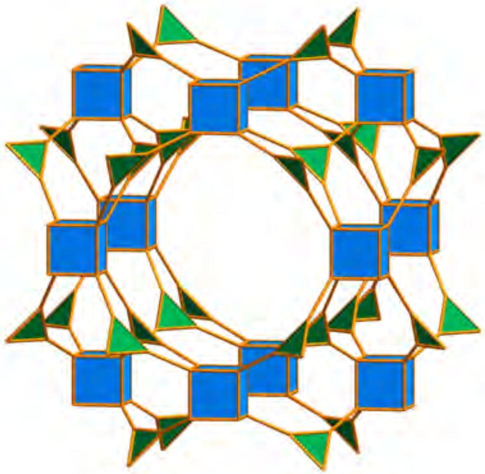


The green balls ("Ni") are in trigonal prismatic coordination and at the points of a hexagonal lattice. The red balls ("As") are in octahedral coordination and arrangeds as in hexagonal closest packing.

Edge-transitive binodal nets

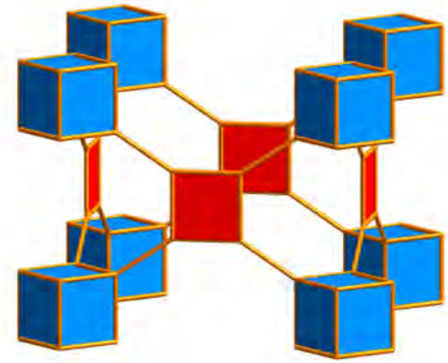
triangle - cube 6 - 16

the-a
Pm-3*m*



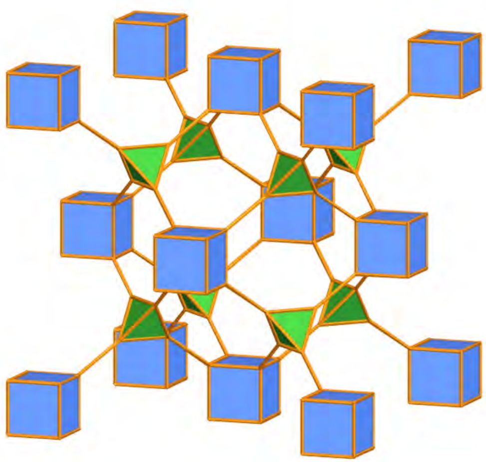
square - cube 8 - 16

scu-a
*P*4/*mmm*



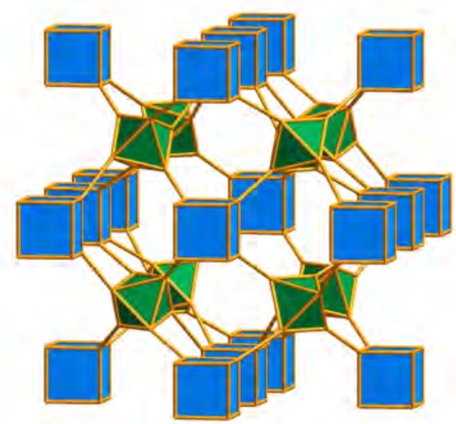
tetrahedron - cube 24 - 48

flu-a
Fm-3*m*

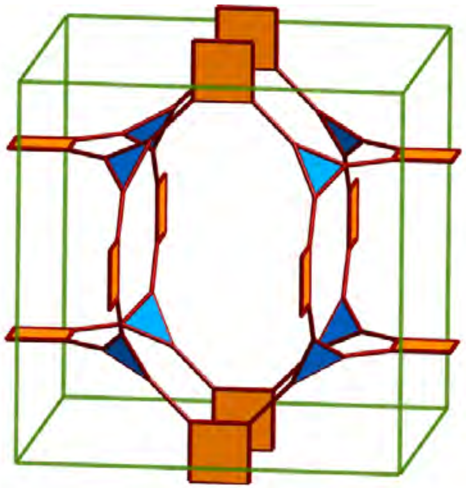


octahedron - cube 12 - 16

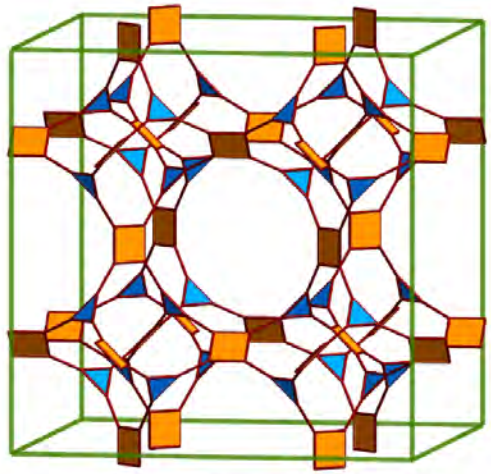
ocu-a
Im-3*m*



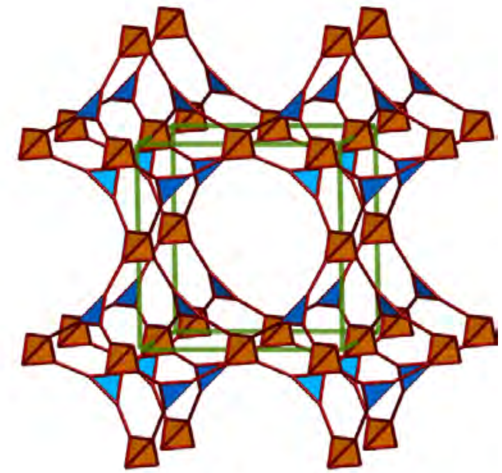
Edge-transitive binodal nets - summary 1



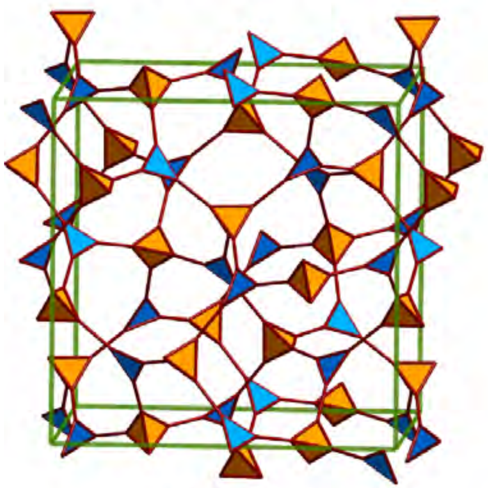
pto-a



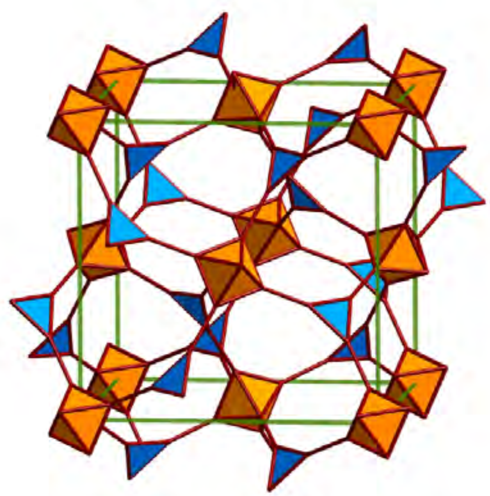
tbo-a



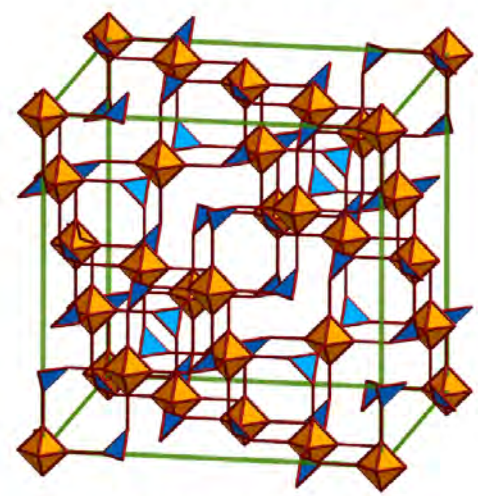
bor-a



ctn-a

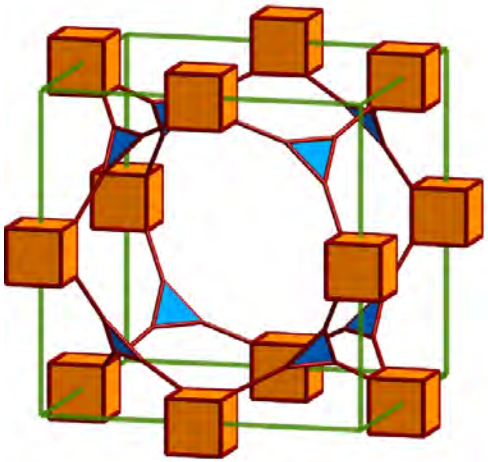


pyr-a

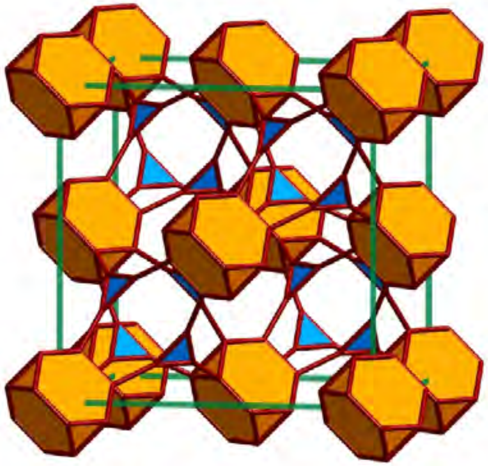


spn-a

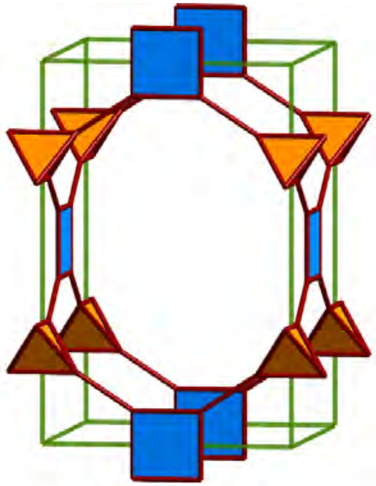
Edge-transitive binodal nets - summary 2



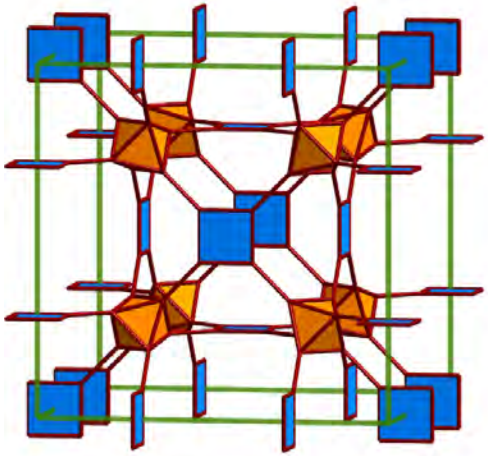
the-a



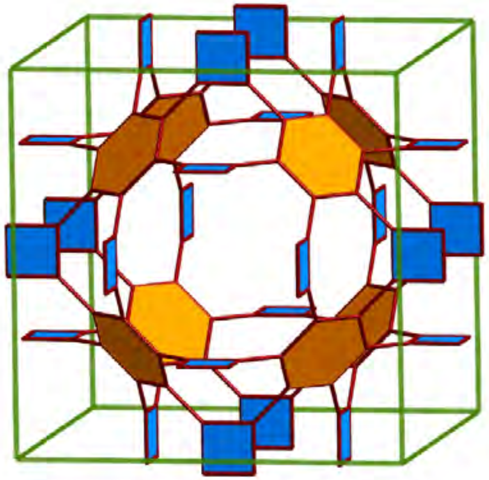
ttt-a



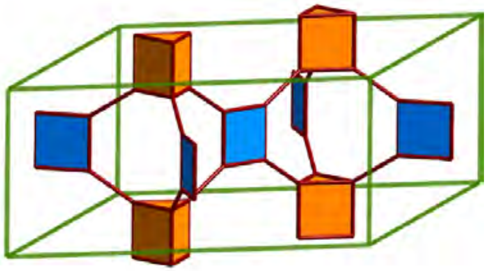
pts-a



soc-a

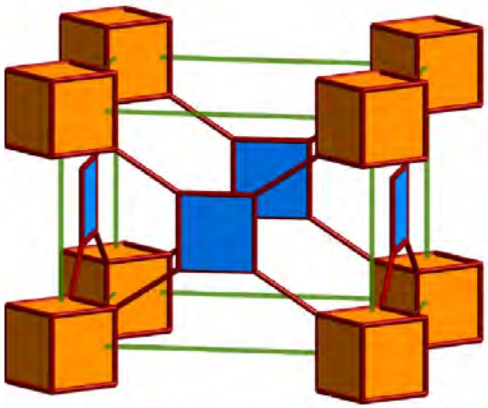


she-a

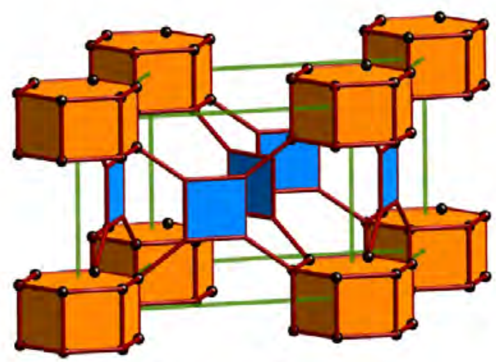


stp=a

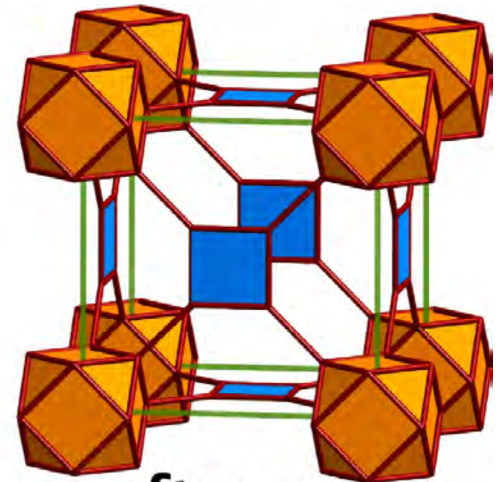
Edge-transitive binodal nets - summary 3



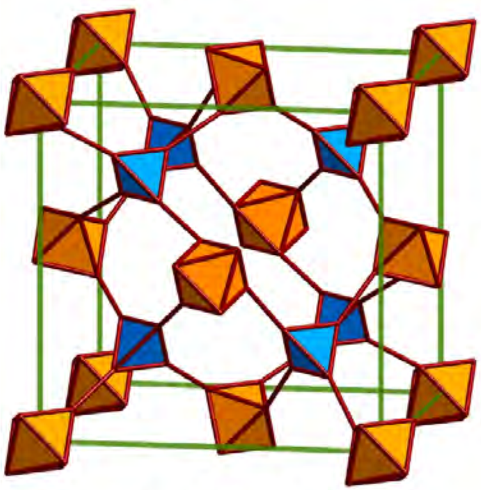
scu-a



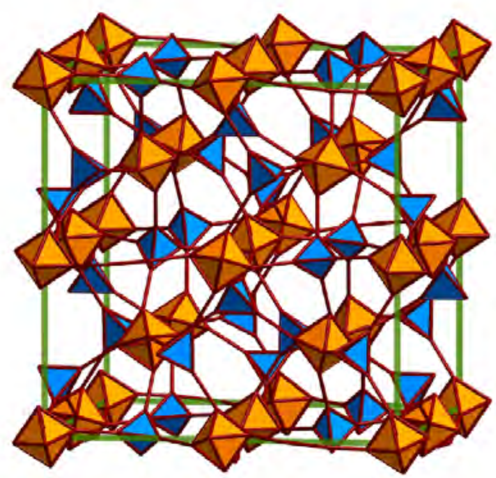
shp-a



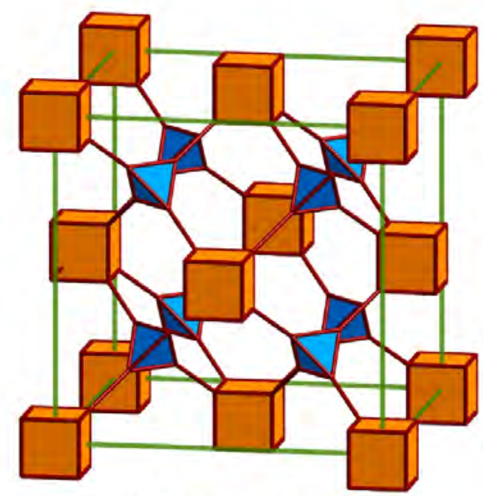
ftw-a



toc-a

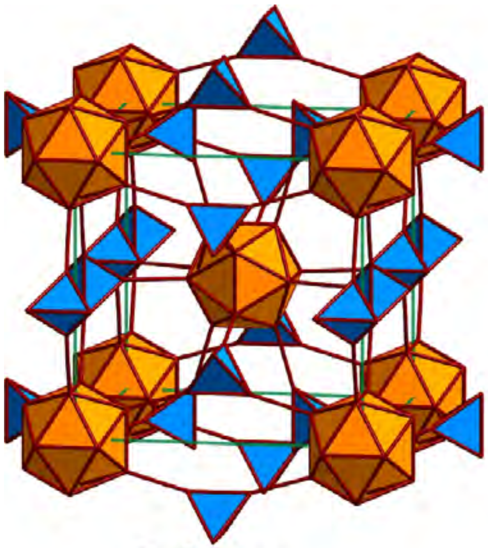


gar-a

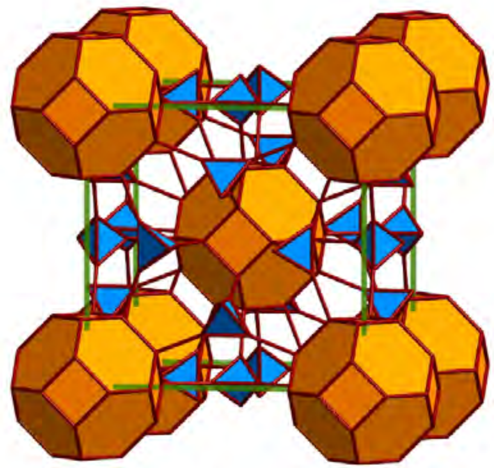


flu-a

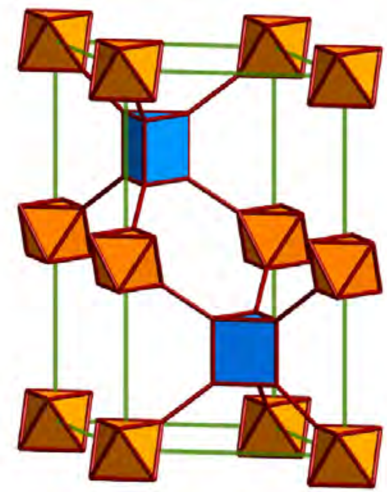
Edge-transitive binodal nets - summary 4



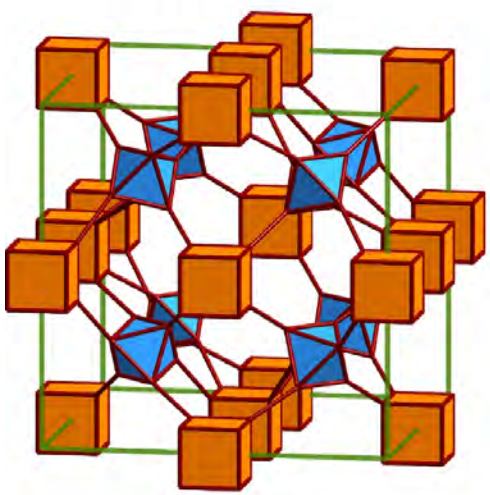
ith-a



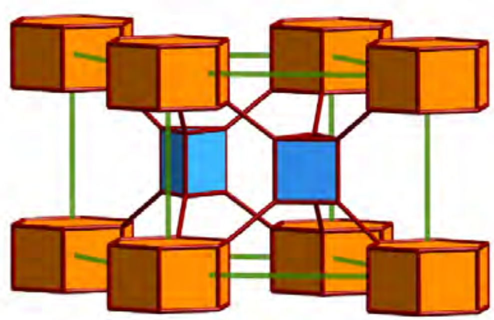
twf-a



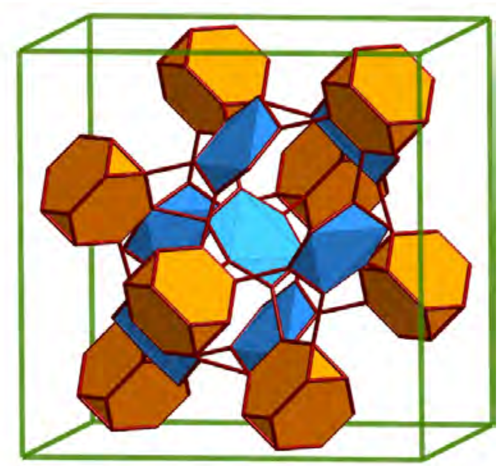
nia-a



ocu-a

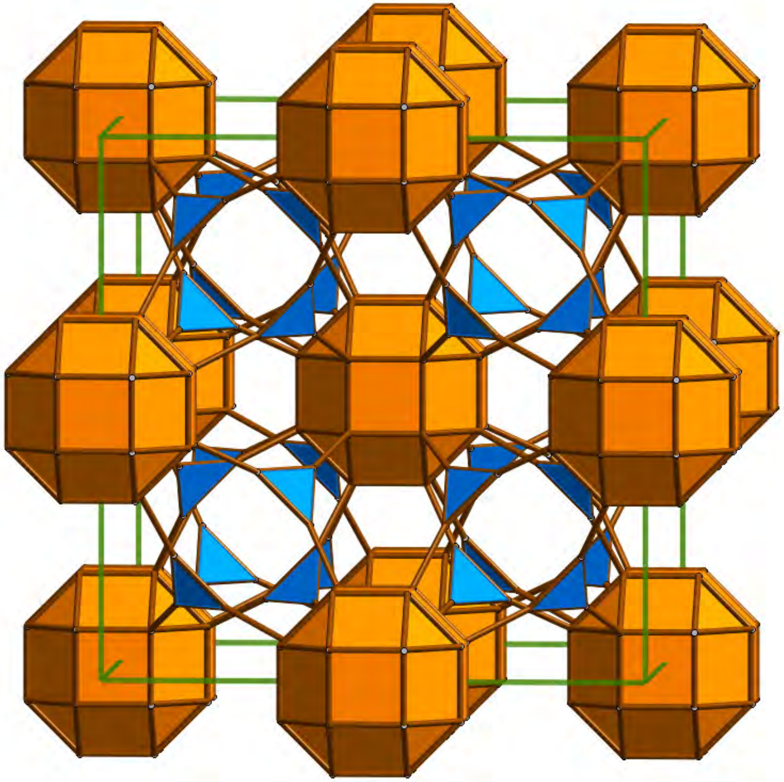


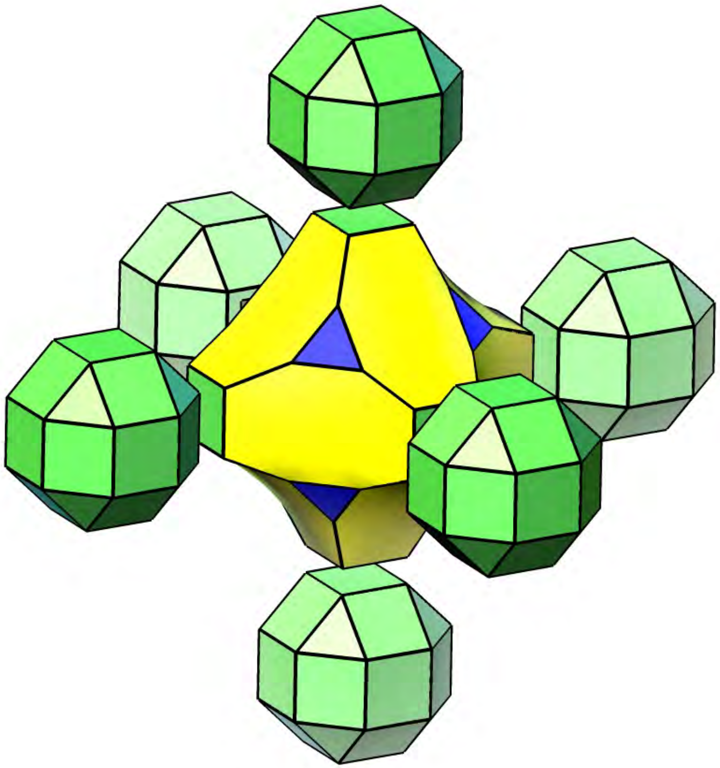
alb-a



mgc-a

oops





forgot (24,3)-connected **rht** (shown here as **rht-a**)

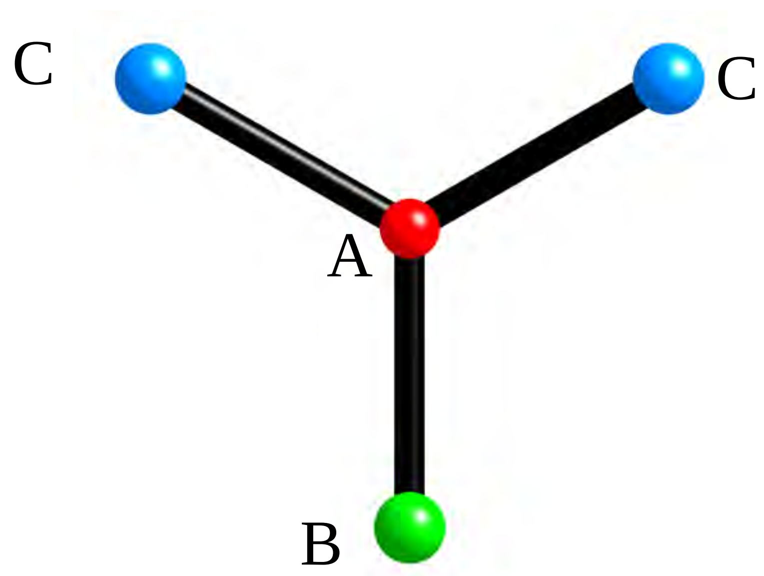
Results of enumerating face-transitive tilings

Table 1. Edge-transitive nets retrieved in this study listed by size of the Delaney-Dress symbol (D-symbol) of the proper tiling with smallest size. The 3-letter symbols are the RCSR (http://rcsr.anu.edu.au/) symbols.

D-symbol size	uninodal	binodal
1	**pcu**	
2	**bcu, dia, fcu, nbo**	**flu**
3	**reo, sod**	
4	**crs, hxg**	**ftw**
6	**acs**	
8	**rhr**	**bor, mgc, nia, ocu, rht, she, soc, spn, tbo, the, toc, ttt, twf,**
10	**lcs, lvt, lcy, srs**	**ith, scu, shp, stp**
12	**lcv**	**alb, pto**
14	**qtz**	**pts**
16	**bcs**	**sqc**
20	**thp**	**csq, ssa, ssb**
24	**ana**	**gar, iac, ibd, pyr, ssc**
28		**ifi**
32		**ctn, pth**

← **pcu** only regular tiling!

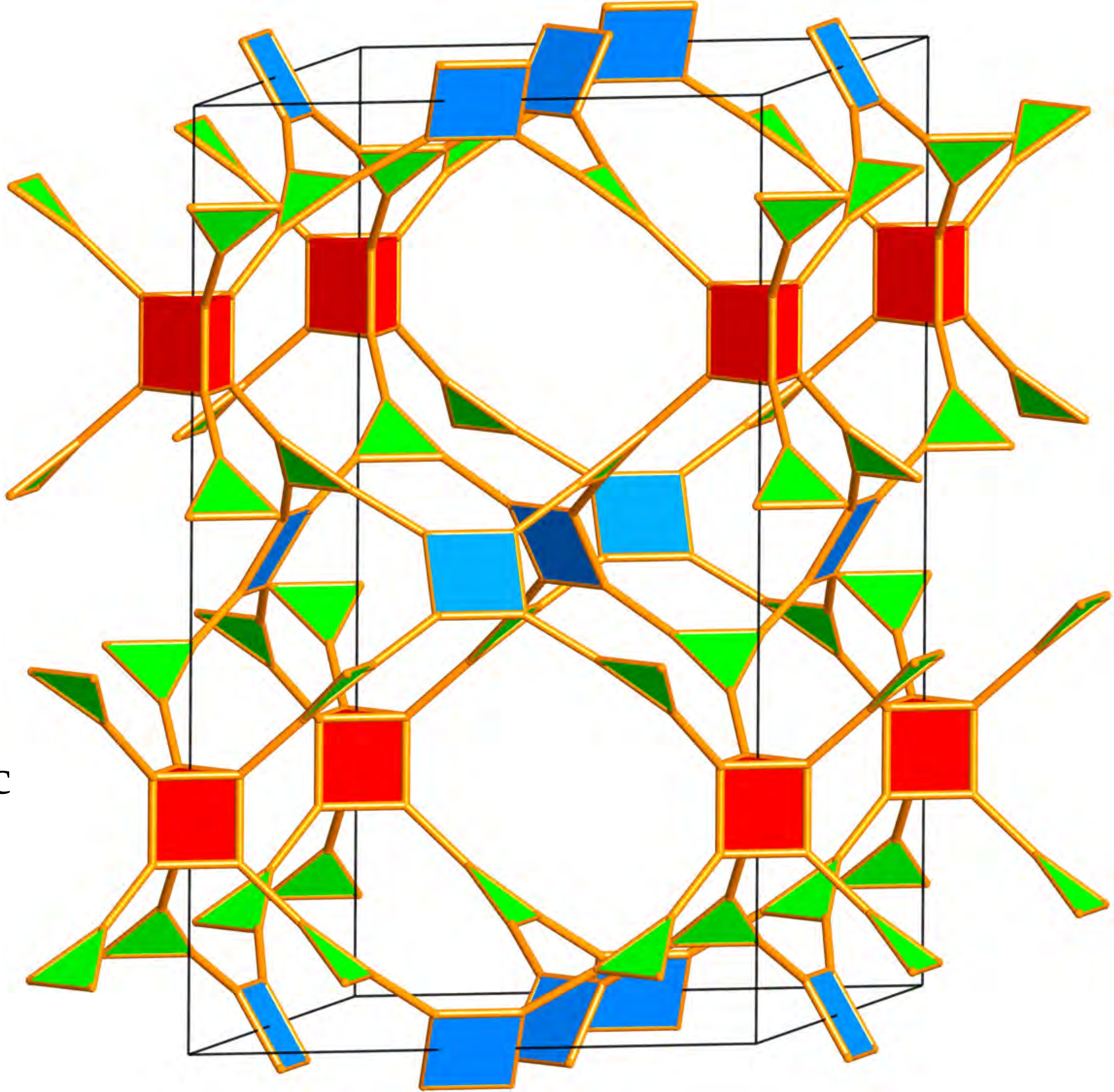
Nets with three kinds of vertex. Here must be at least two kinds of adge, e.g. A-B and A-C. many such have emerged in MOFs in the last few years.
For example a tritopic linker joined to two different SBUs

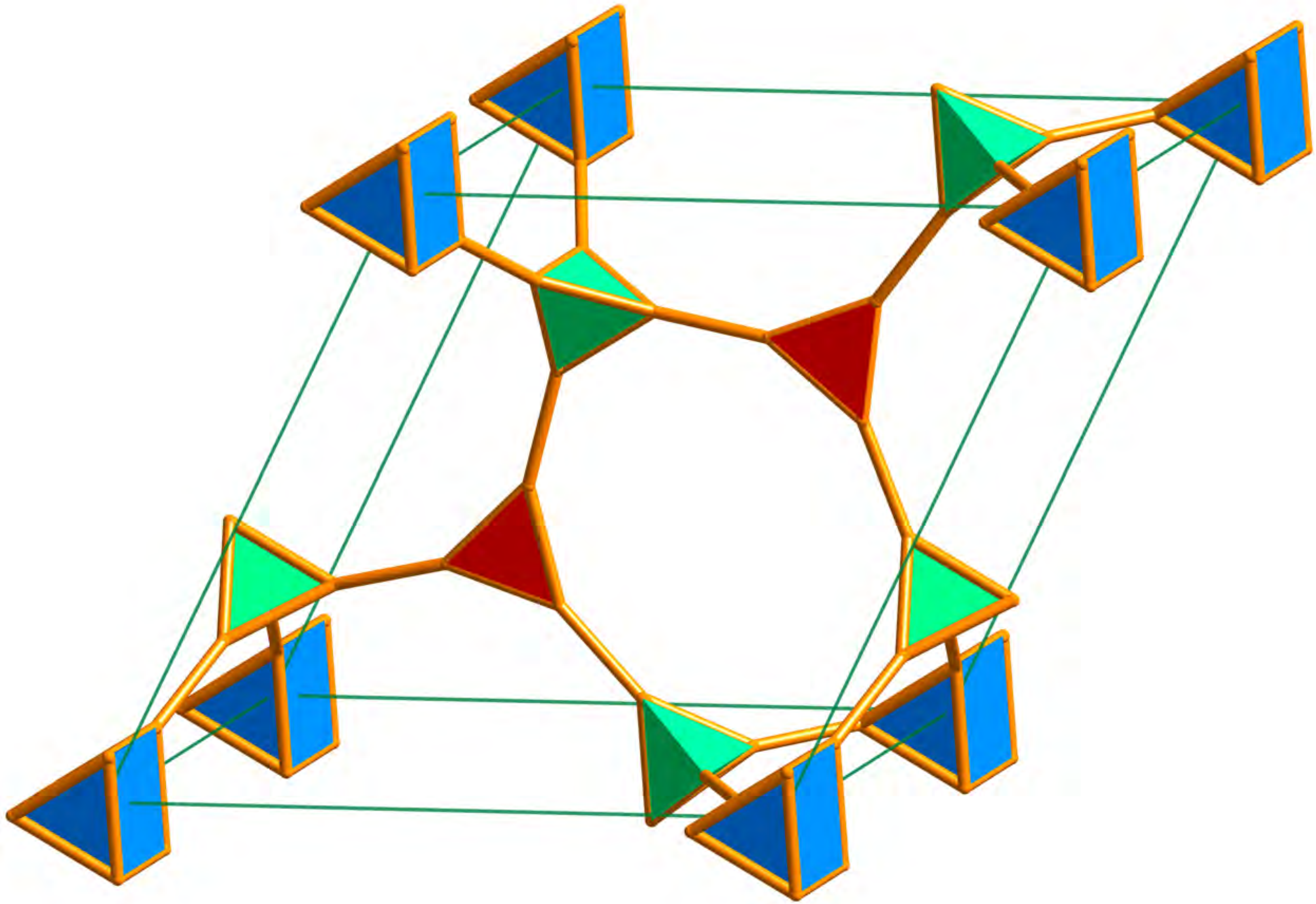


There are probably too many for systematic enumeration?

net **agw** shown as augmented net **agw-a**

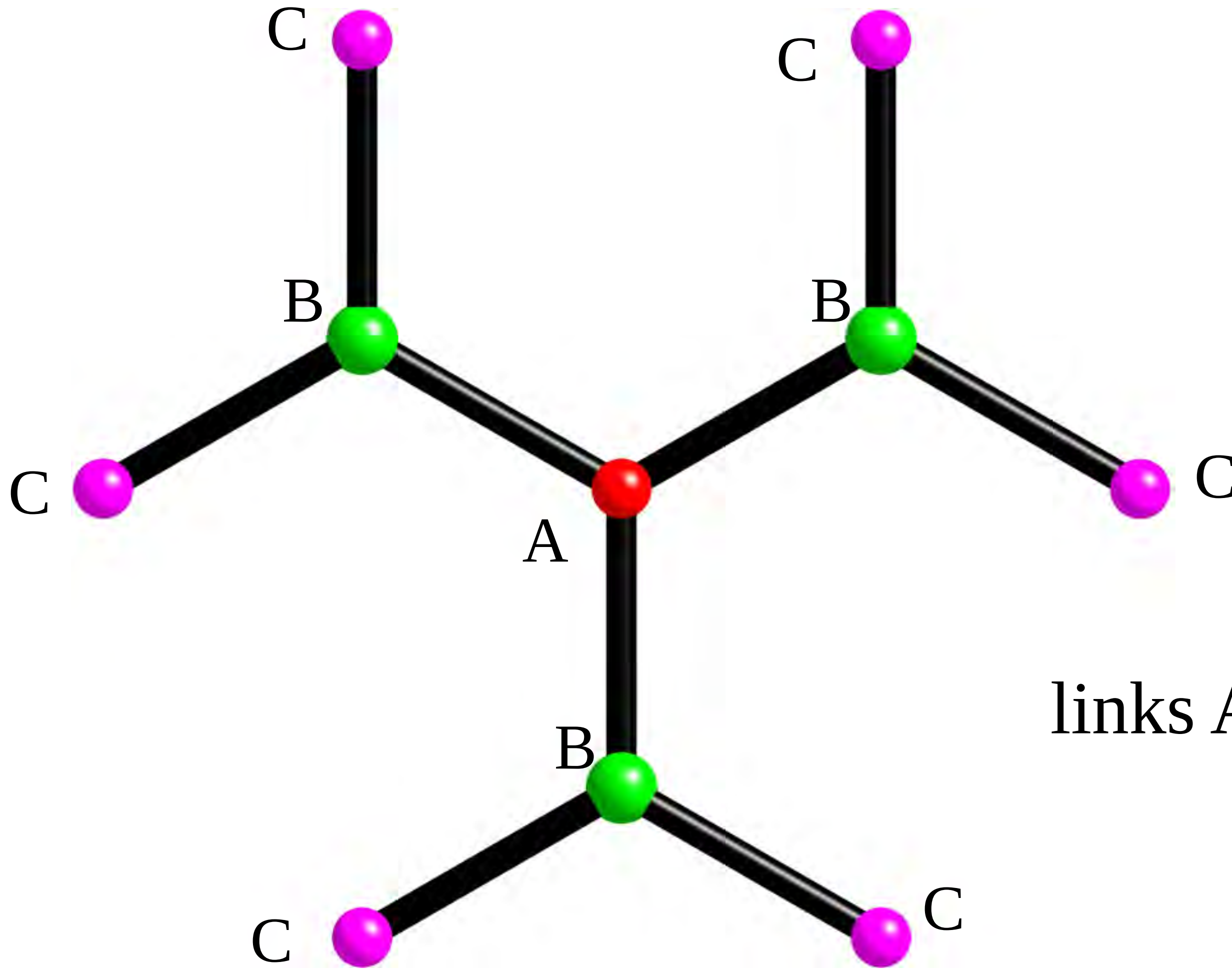
3-c node connected to one 6-c and two 4-c nodes





Net **asc** with transitivity 3 2 shown in augmented form **asc-a**
tetrahedral node linked to 2triangular and 2 tridonal prismatic nodes.

Another example with minimal transitivity 3 2 *r s*

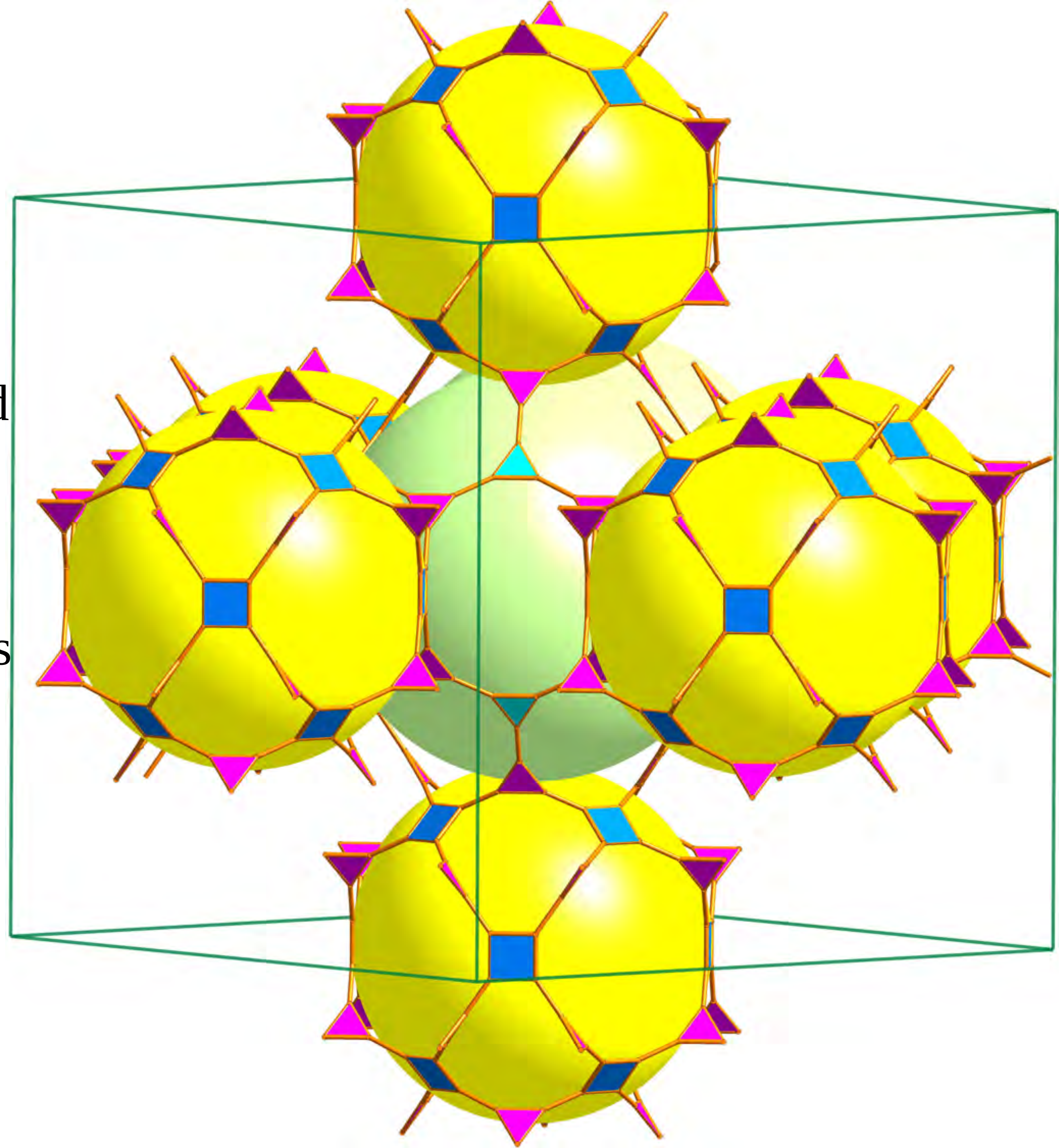


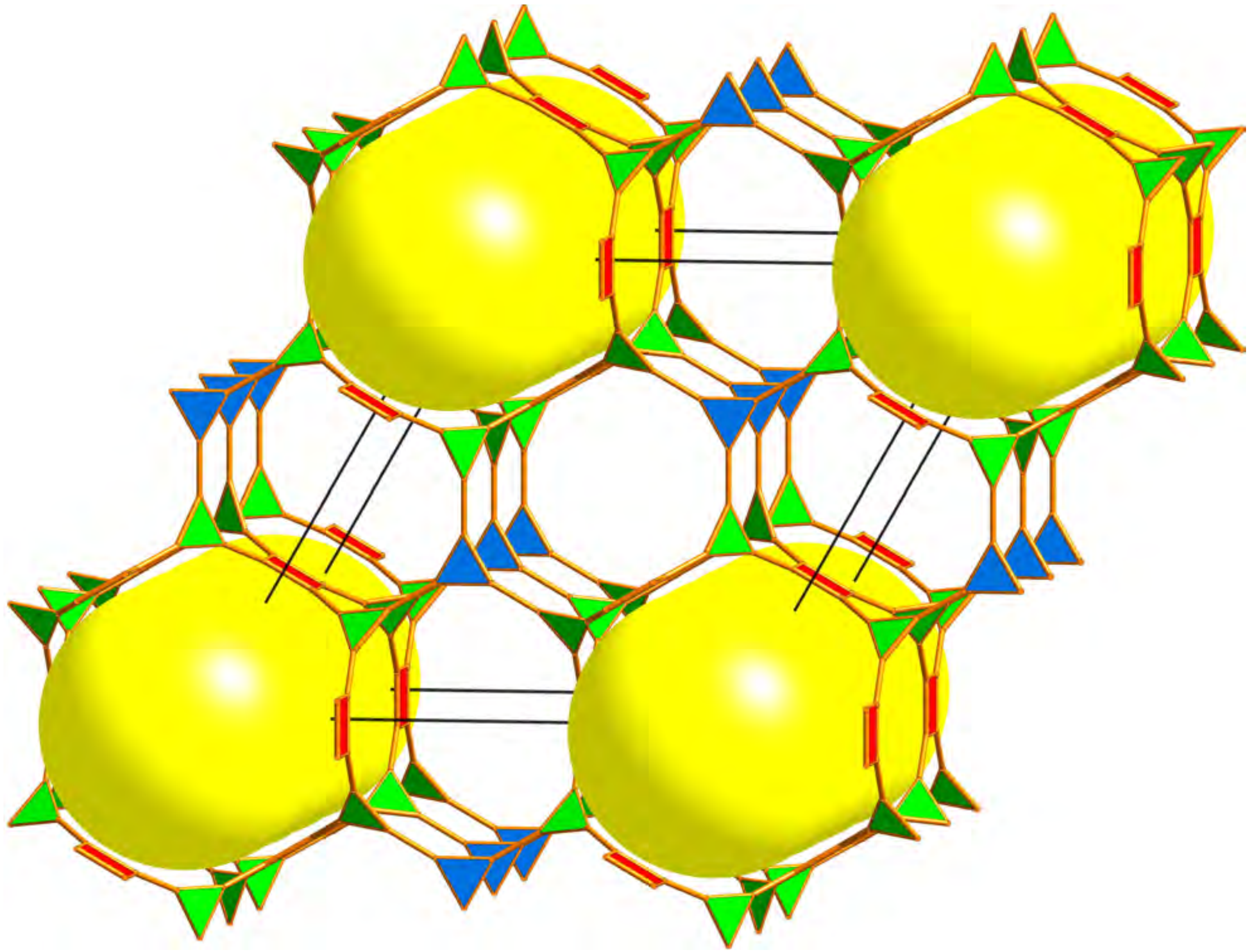
links AB and BC

The net **ntt** with transitivity 3 2 *r* *s*

shown in augmented form **ntt-a**.

Note the balls with 24 magenta triangles linked to a common green triangle.
The (3,24)-c net is edge transitive **rht**



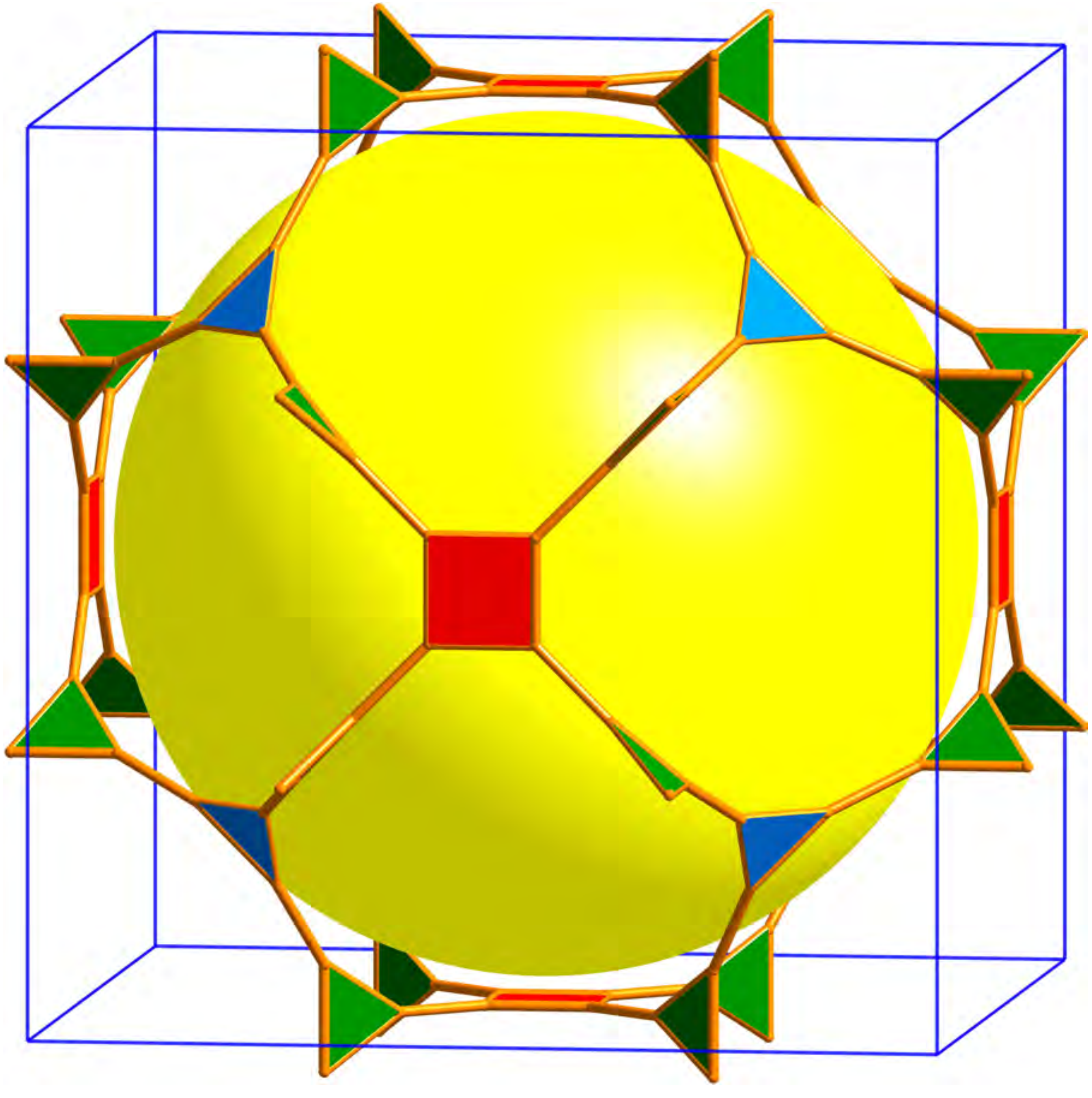


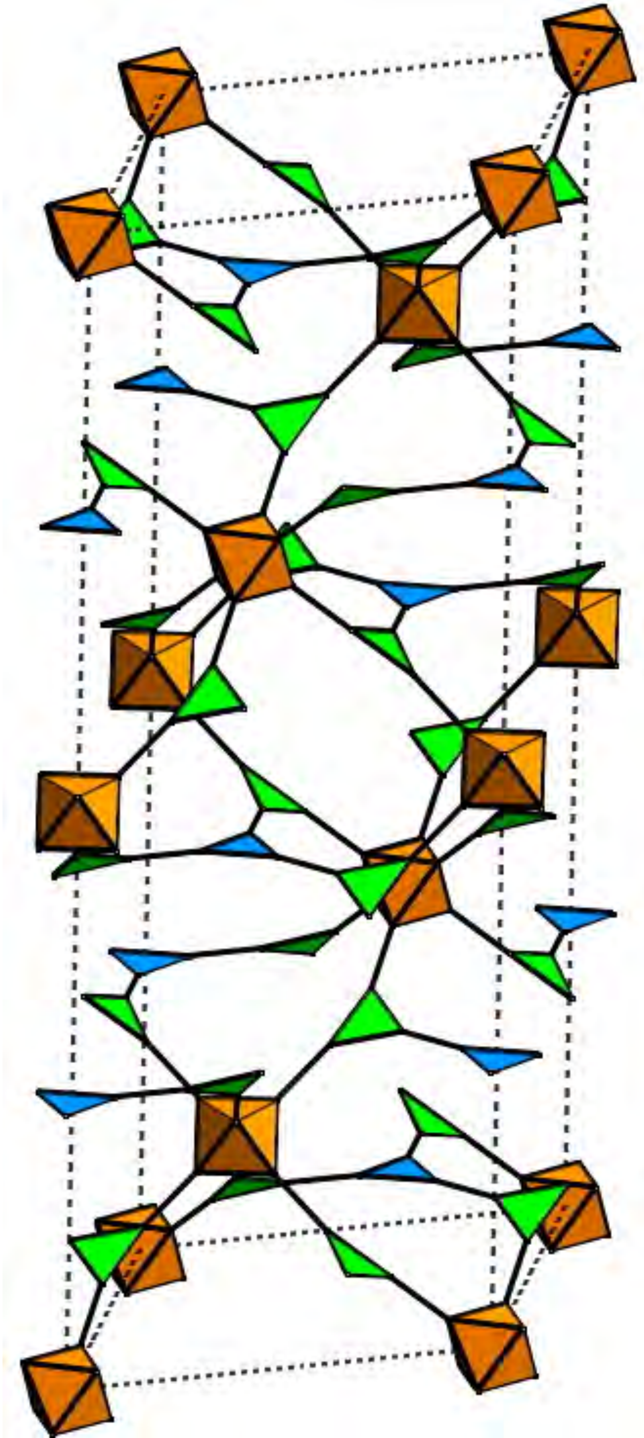
The net **zyg** with transitivity 3 2 *r s*. Note that the four triangle group is non-planar in contrast to previous (**ntt**) but same proportion of 3-c and 4-c nodes.

The net **tfe** with transitivity 3223 shown in augmented form **tfe-a**

Note that the groups of four triangles are not co-planar

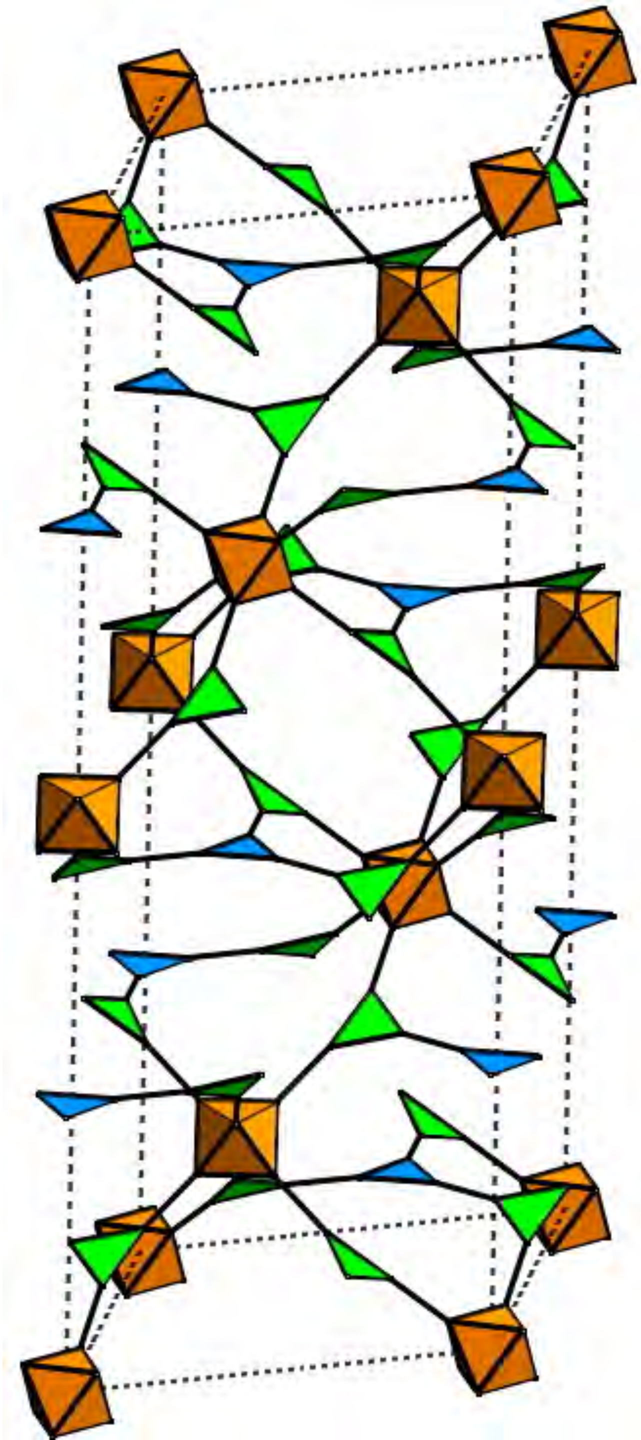
this has a different ratio of 3-c to 4-c vertices





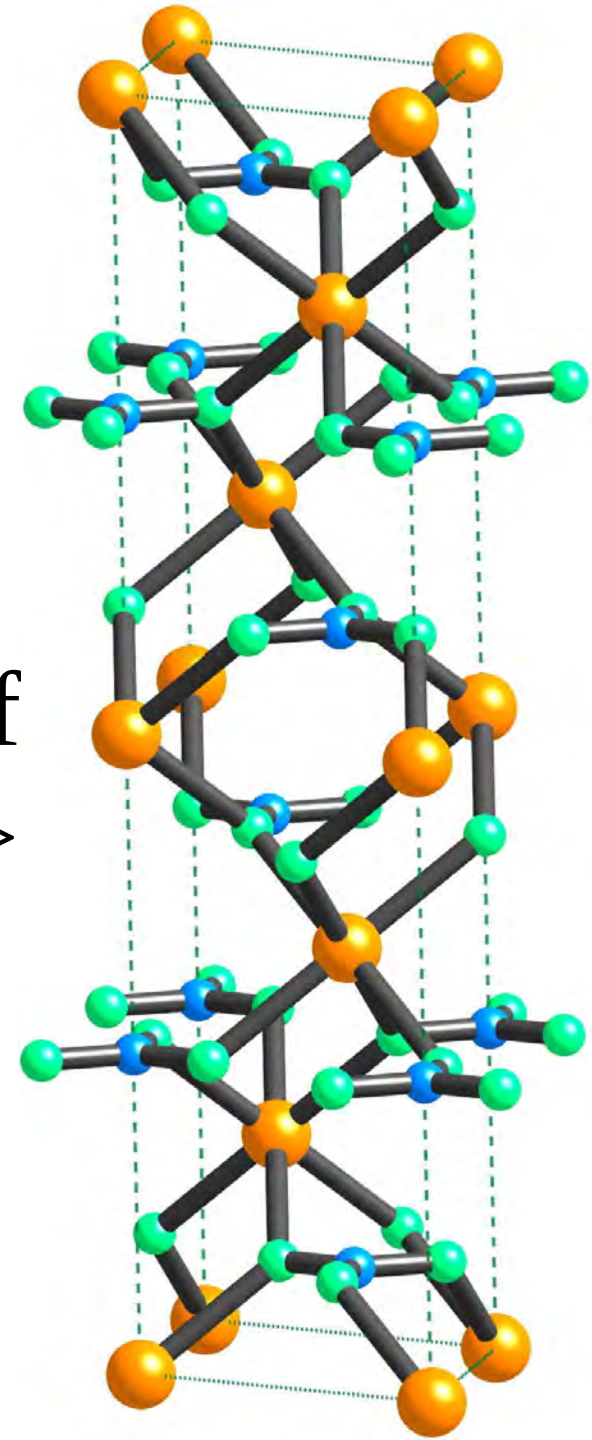
net is **zxc**

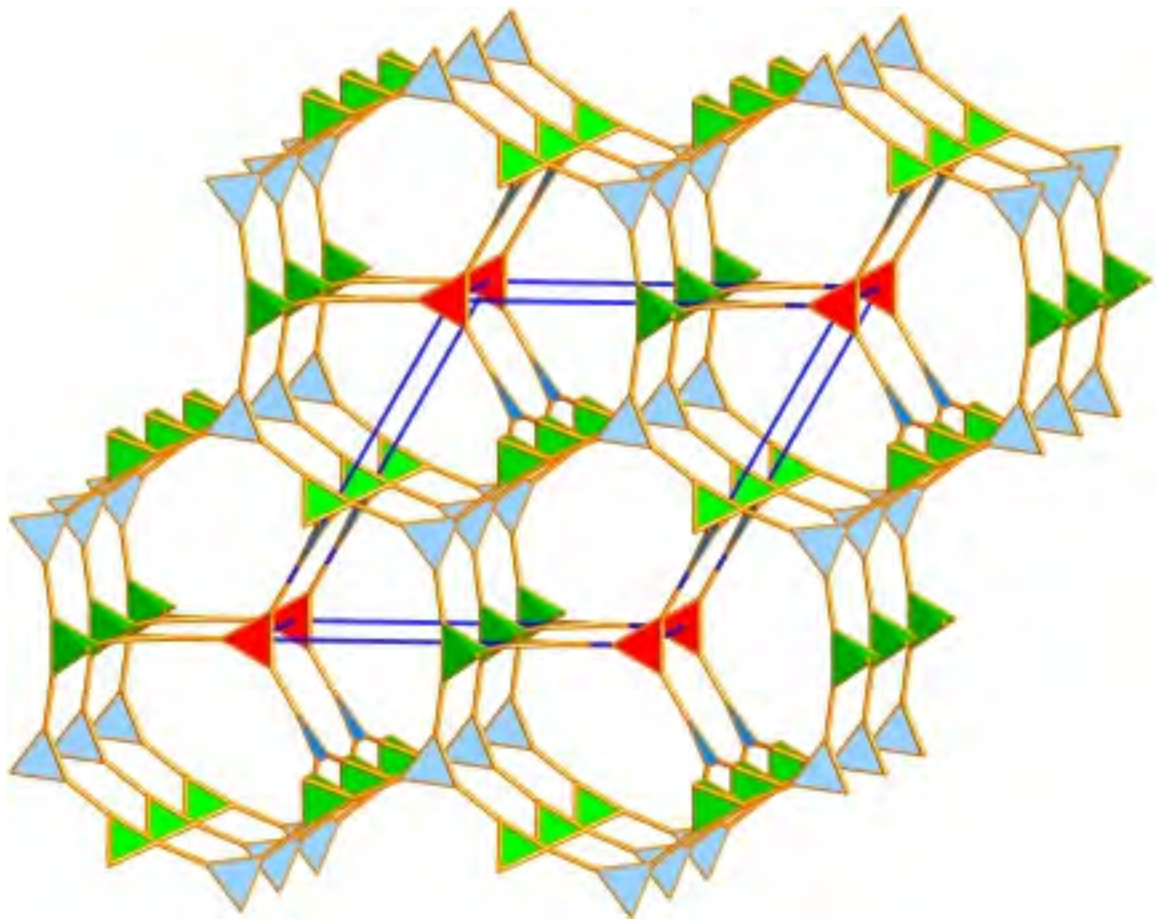
<-



net is **zxc**
<-

structure of
$CaCO_3$! ->





mco (ransitivity 4 3) shown in augmented form

This is **xbo** the net of the dual ting of **fte** (previous slide. black and blue vertices are 6-c, red is 12-c These are the atom positions in perovskite ABX_3 (X is blue) e.g. $SrTiO_3$. Nodes are in fixed positions of *Pm*-3*m*:

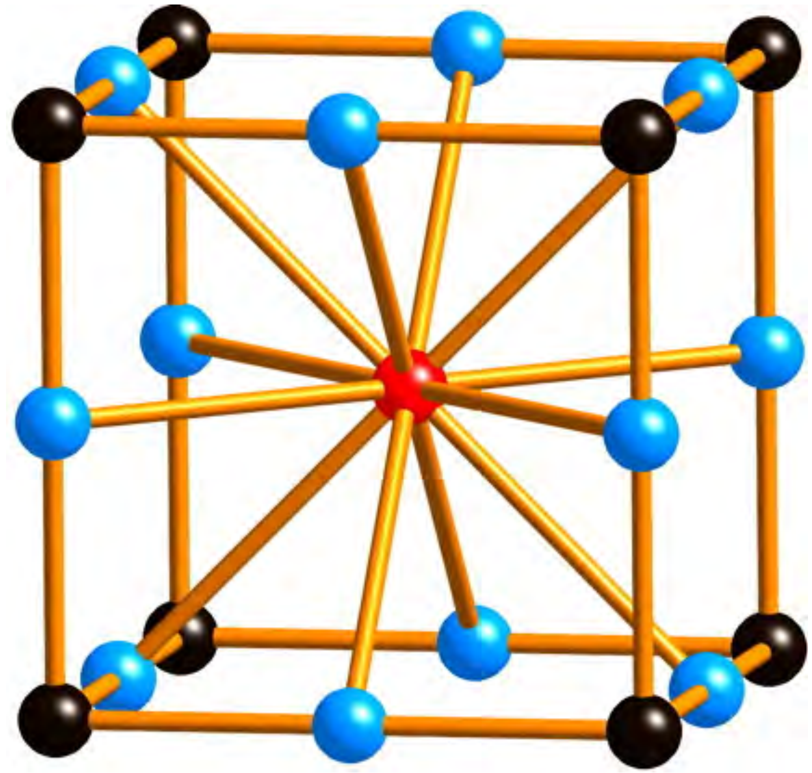
Black 0, 0, 0

blue ½, 0, 0

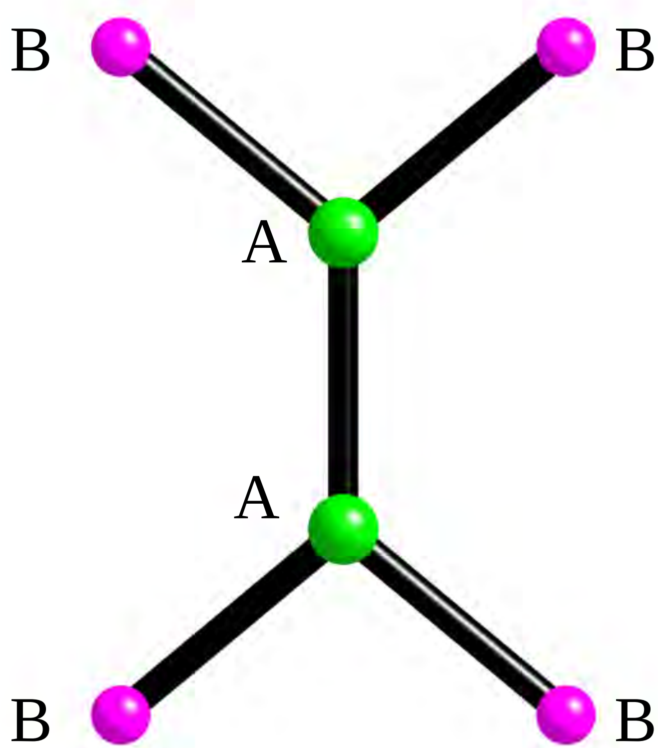
red ½, ½, ½

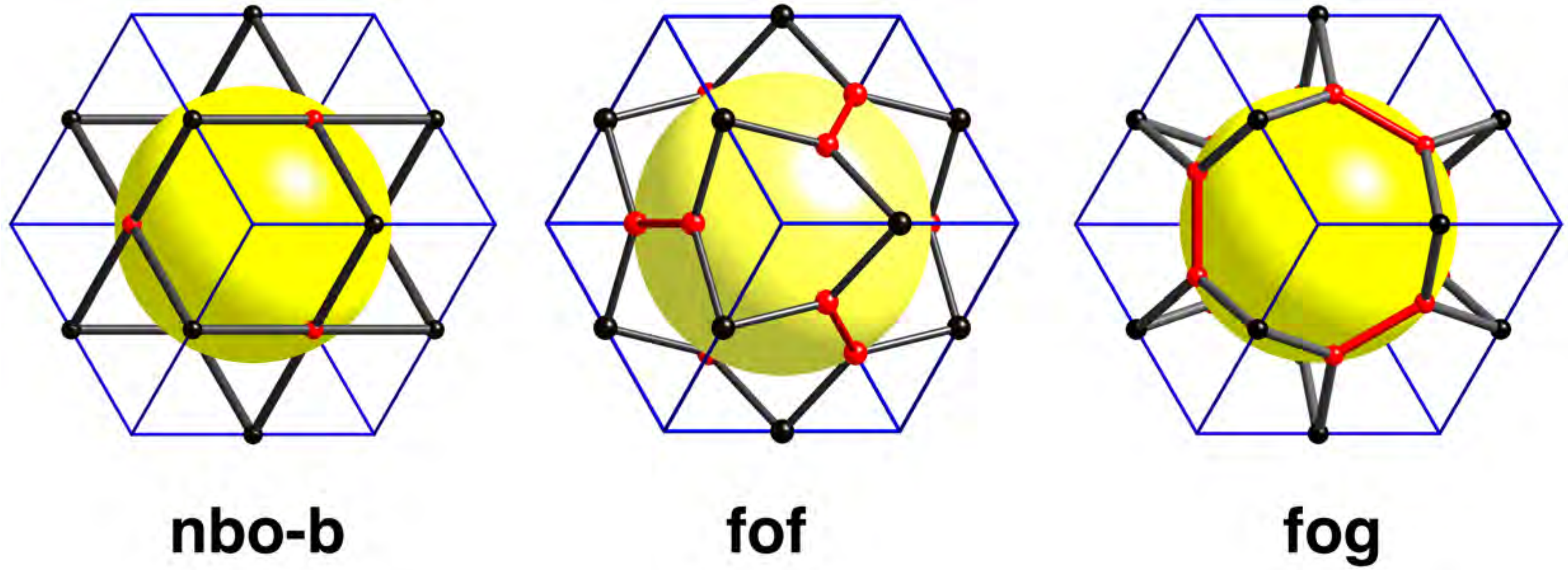
Two links: blue – red and blue – black whose lengths must be in the ratio 1: √2.

i.e. can't be made with any other ratio (such as equal)



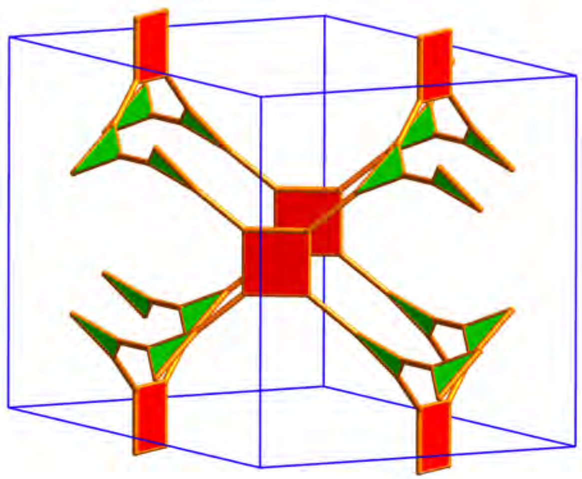
Derived nets. E.g. replace a 4-c node by two 3-c nodes
Must be A-A and A-B links. Minimal transitivity 2 2 *r s*

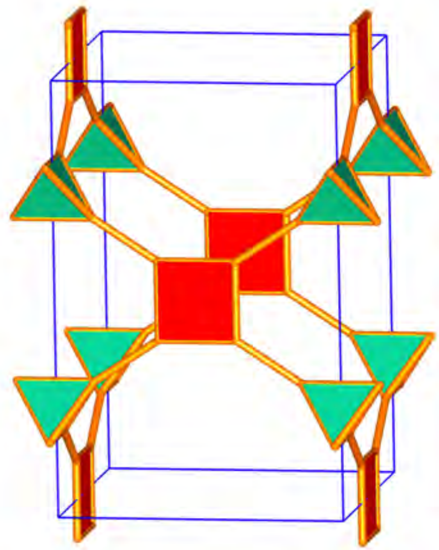


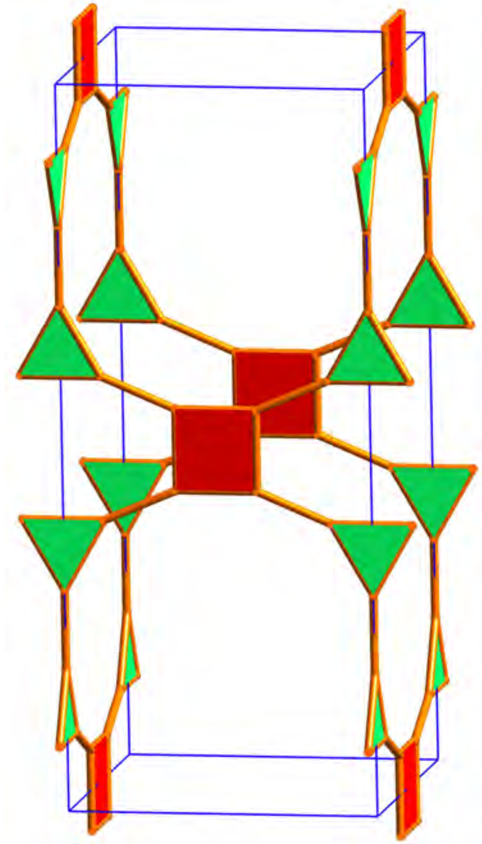


Replace one half 4-c nodes of **nbo** (red) with
to 3-c nodes (red) to produce nets like **fof** and **fog**
with transitivity 2 2 *r s*.

pts – derved nets – splitting tetrahedron



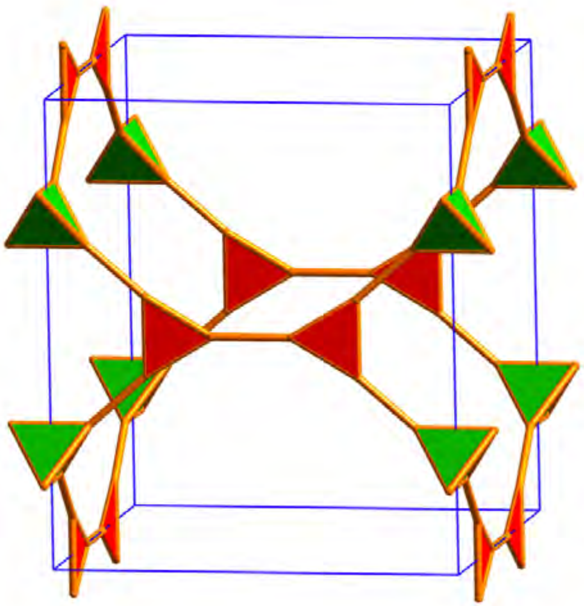




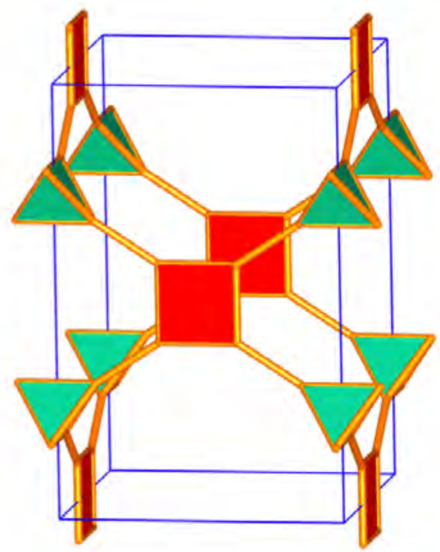
sur-a **pts-a** **tfk-a**

all have transitivity 2 2 *r s*

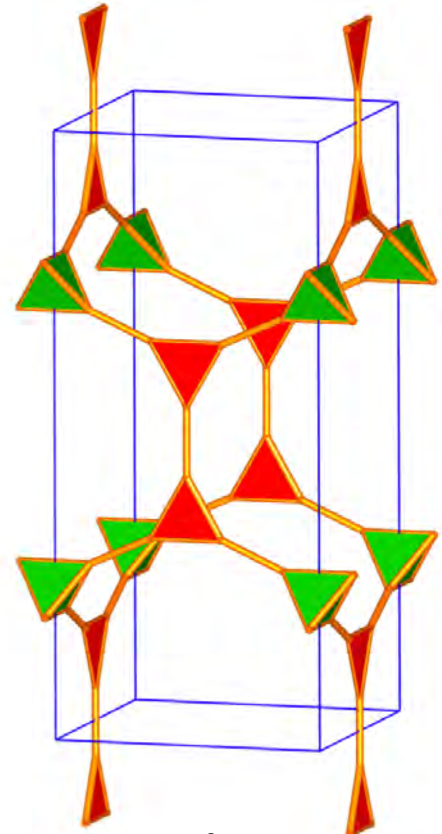
pts – derved nets – splitting square



dmd-a



pts-a



tti-a

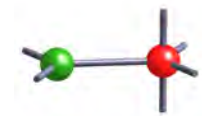
all have transitivity 2 2 *r s*

Minimal nets (genus 3). There are 15, of which 7 have collisions. The collision-free nets are:

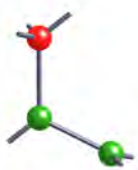
pcu self-dual net of P

dia self-dual net of D

cds self-dual net of CLP

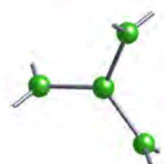


hms self-dual net of H

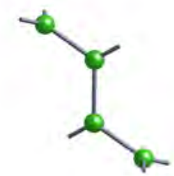


tfa
dual is **dia**

tfc
dual is **pcu**



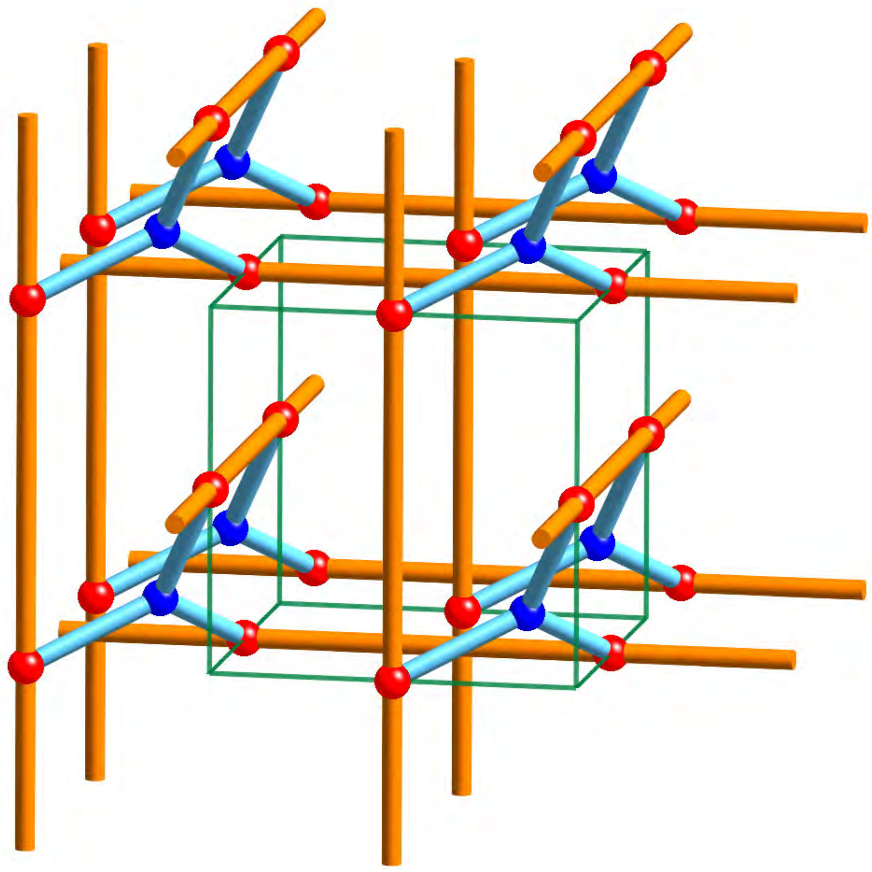
srs self-dual net of G

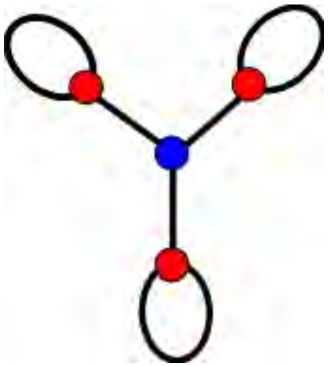


ths
dual is **dia**

C. Bonneau *et al. Acta Cryst* **A** **60**, 517 (2004). A. Beukemann & W. E. Klee, Z. Krist. **201**, 37 (1992).

a minimal net with collisions.





quotient graph

Vertex-transitive naturally self-dual nets
(nets with self-dual natural tilings):

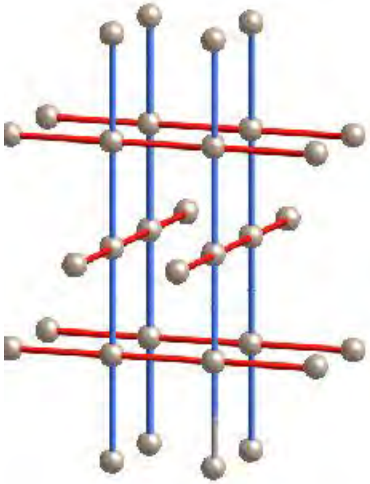
srs	1111
dia	1111
pcu	1111
cds	1221

These account for most topologies found in crystal structures based on interpenetrating nets.

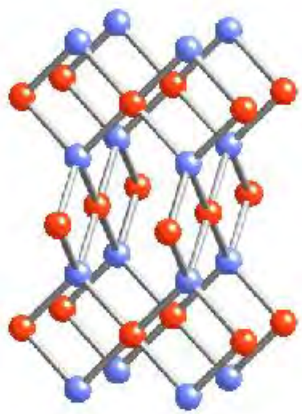
~ 80% see V. A. Blatov *et al*. *CrystEngComm*. 2004, *6*, 377.

These are all minimal (genus 3) nets

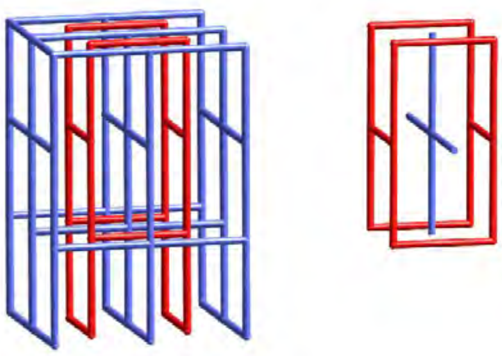
Aspects of the $CdSO_4$ net:
A self-dual minimal net.
Labyrinth of CLP surface.
Transitivity 1221.



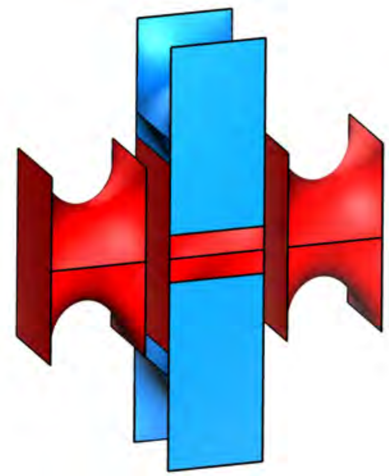
$CdSO_4$ net



PtS net (edge net)

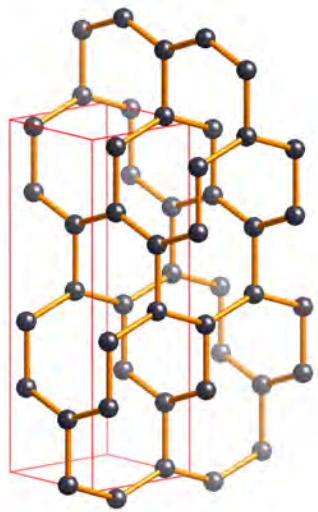


Two interpenetrating $CdSO_4$ nets



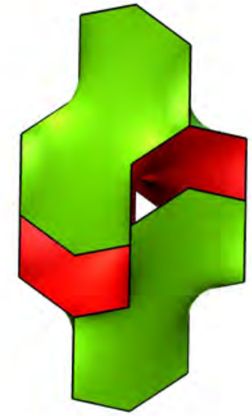
natural tiling $[6^2.8^2]$

Aspects of the $ThSi_2$ (**ths**) net, symmetry $I4_1/amd$



Net with unit cell

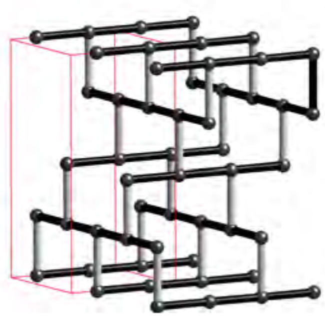
Natural tiling [10^4] transitivity 1211



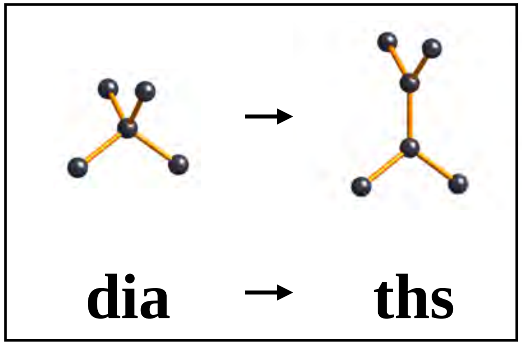
red faces are not formed by strong rings

Dual tiling is diamond tiled by half-adamantane tiles. Transitivity 1121

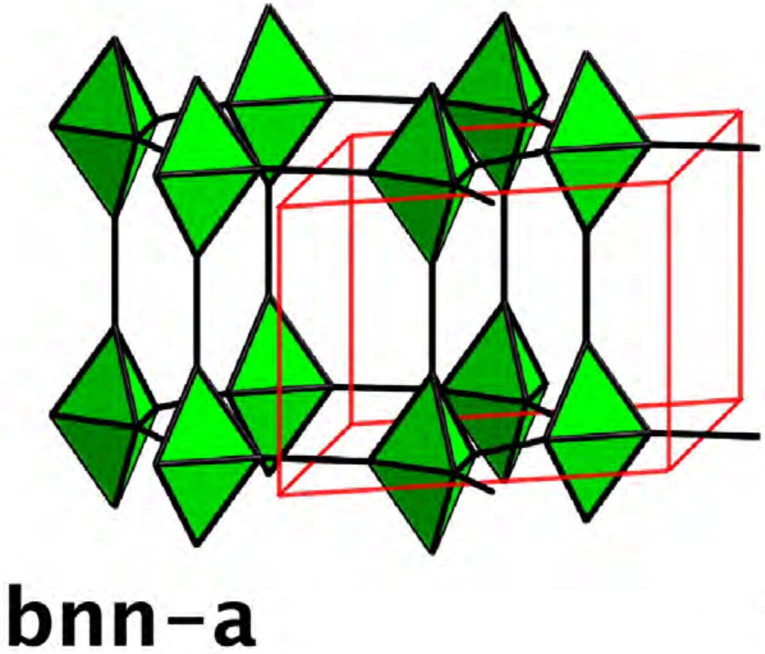
Self-dual tiling of **ths**. Transitivity 1221 (*not* natural)

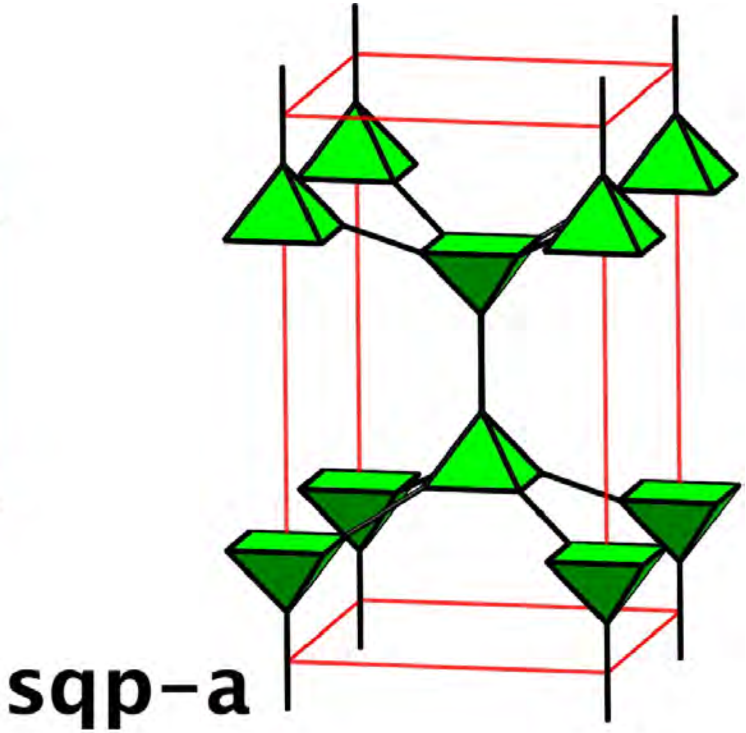


As the net of a rod packing (**ths-z**)



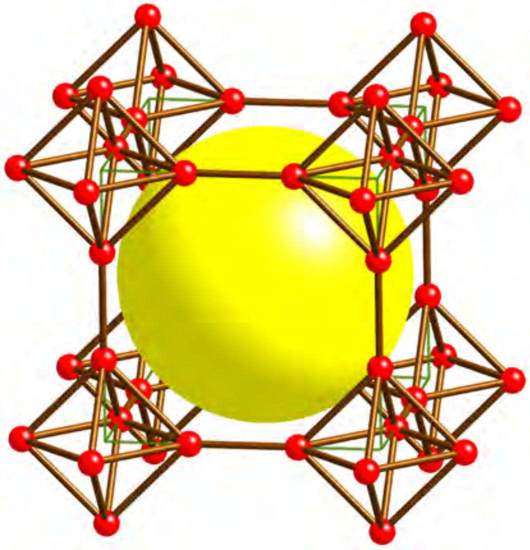
Simple nets for 5-coordination. Vertex figure must be square pyramid or trigonal bipyramid. Must be at least two kinds of edge.

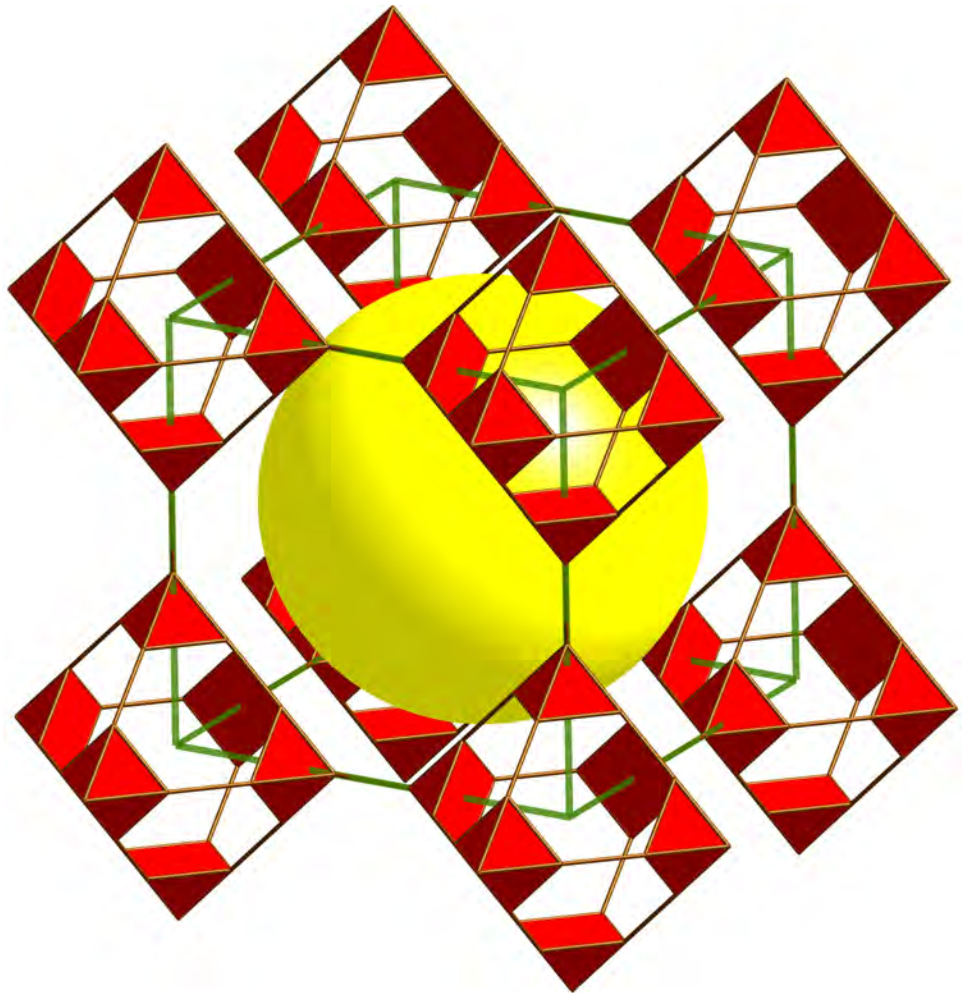




bnn transitivity 1221

sqp transitivity 1222



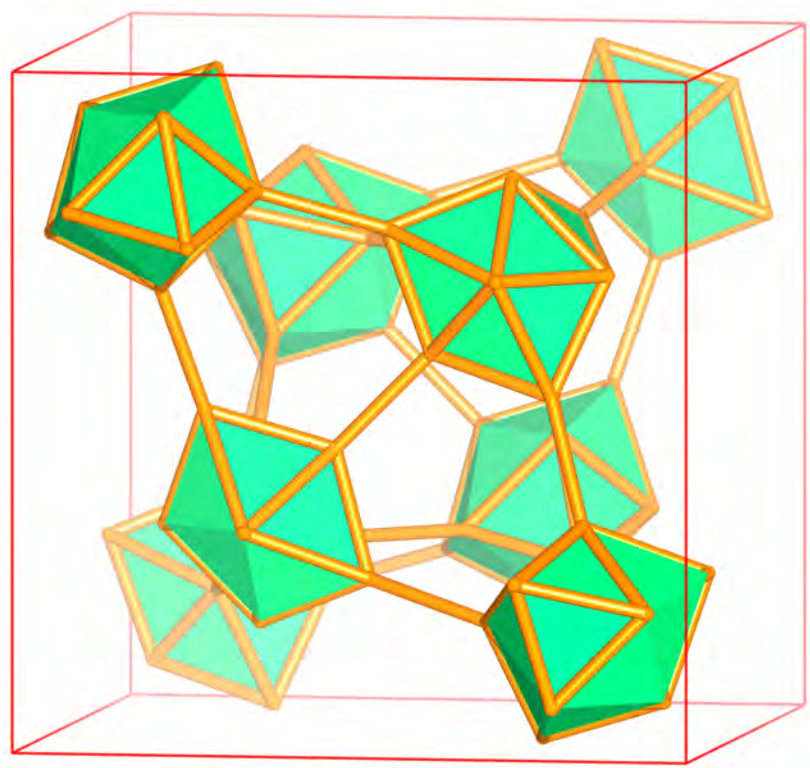


cab

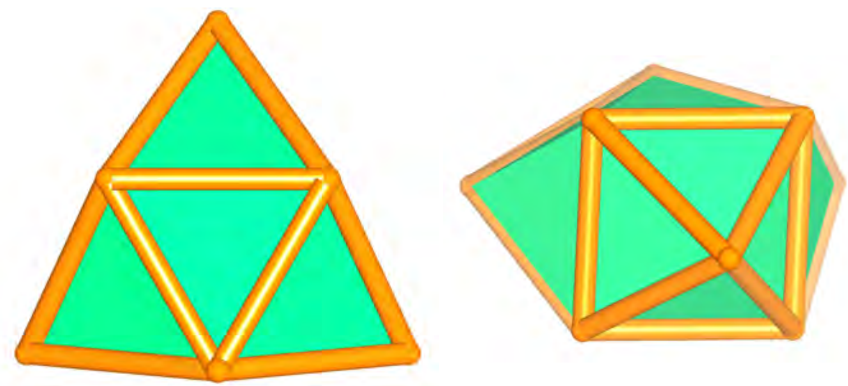
transitivity 1 2 2 2

cab-a

what about 9-c nets? Again must have at least two kinds of link. There are three 9-c nets with transitiity 1 2 *r s*. The most symmetrical is **ncb**



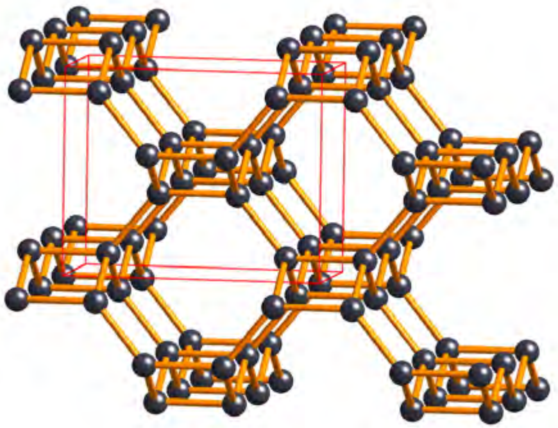
ncb-a



coordination figure is tricapped trigonal prism

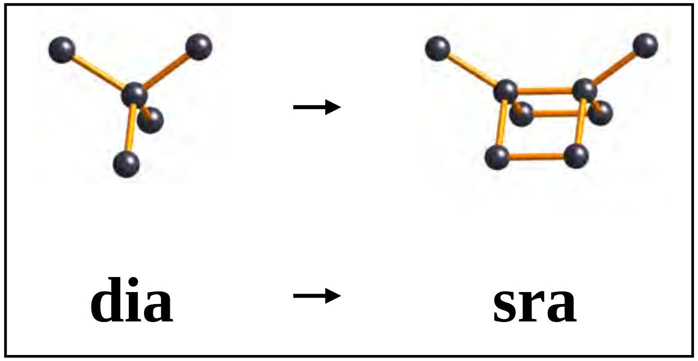
Many isoreticular MOFs XiaoMing Chen group *Nature Comm.*, **3**, 642 (2012)

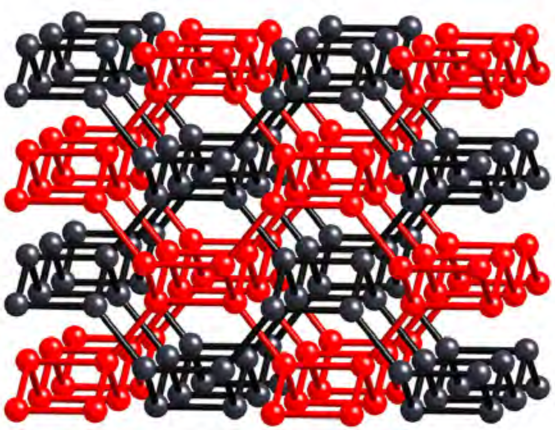
Aspects of the $SrAl_2$ (**sra**) net, symmetry *Imma*
The simplest way of linking ladders



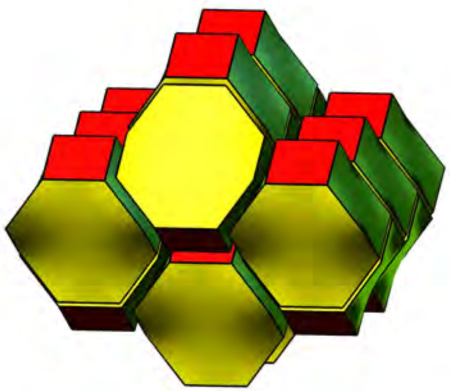
sra

zig-zag ladder

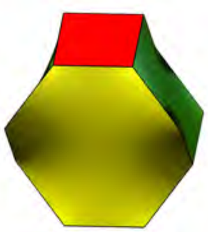




sra-c, symmetry *Cmma*

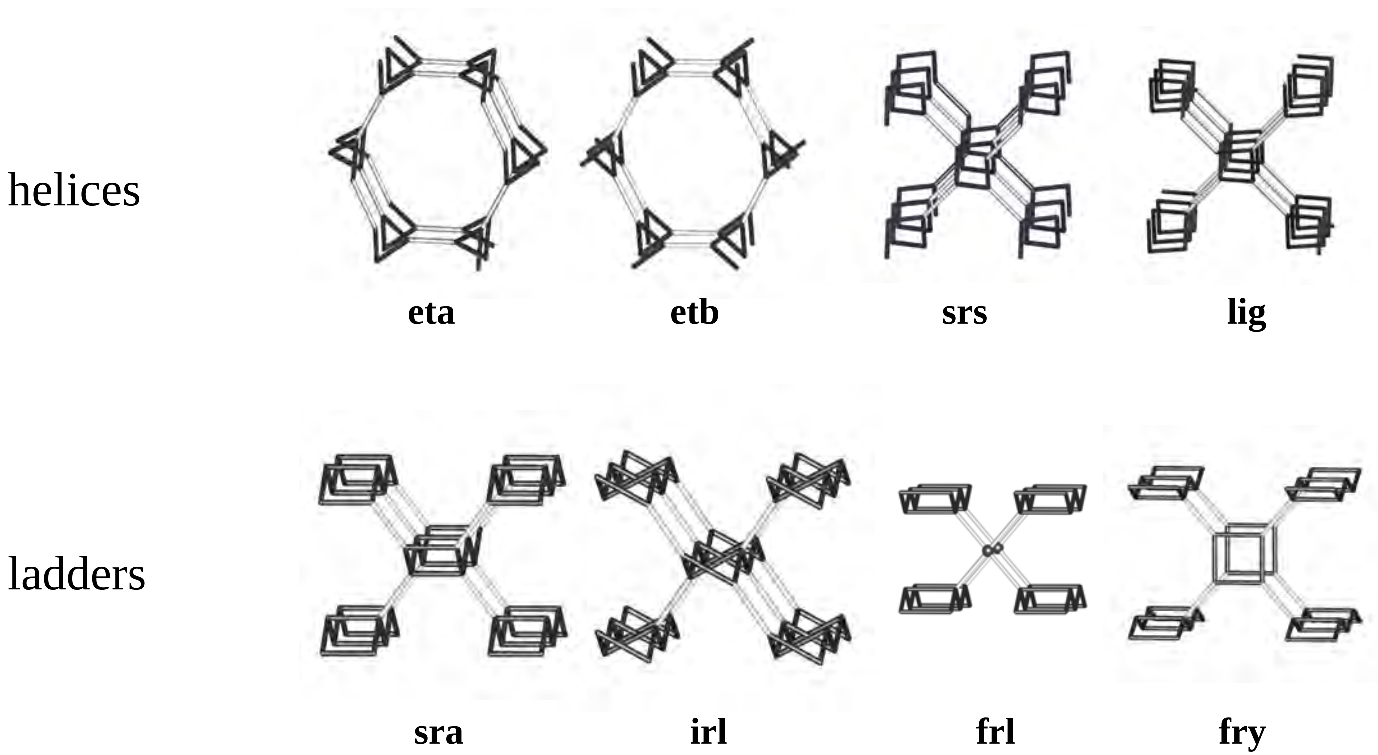


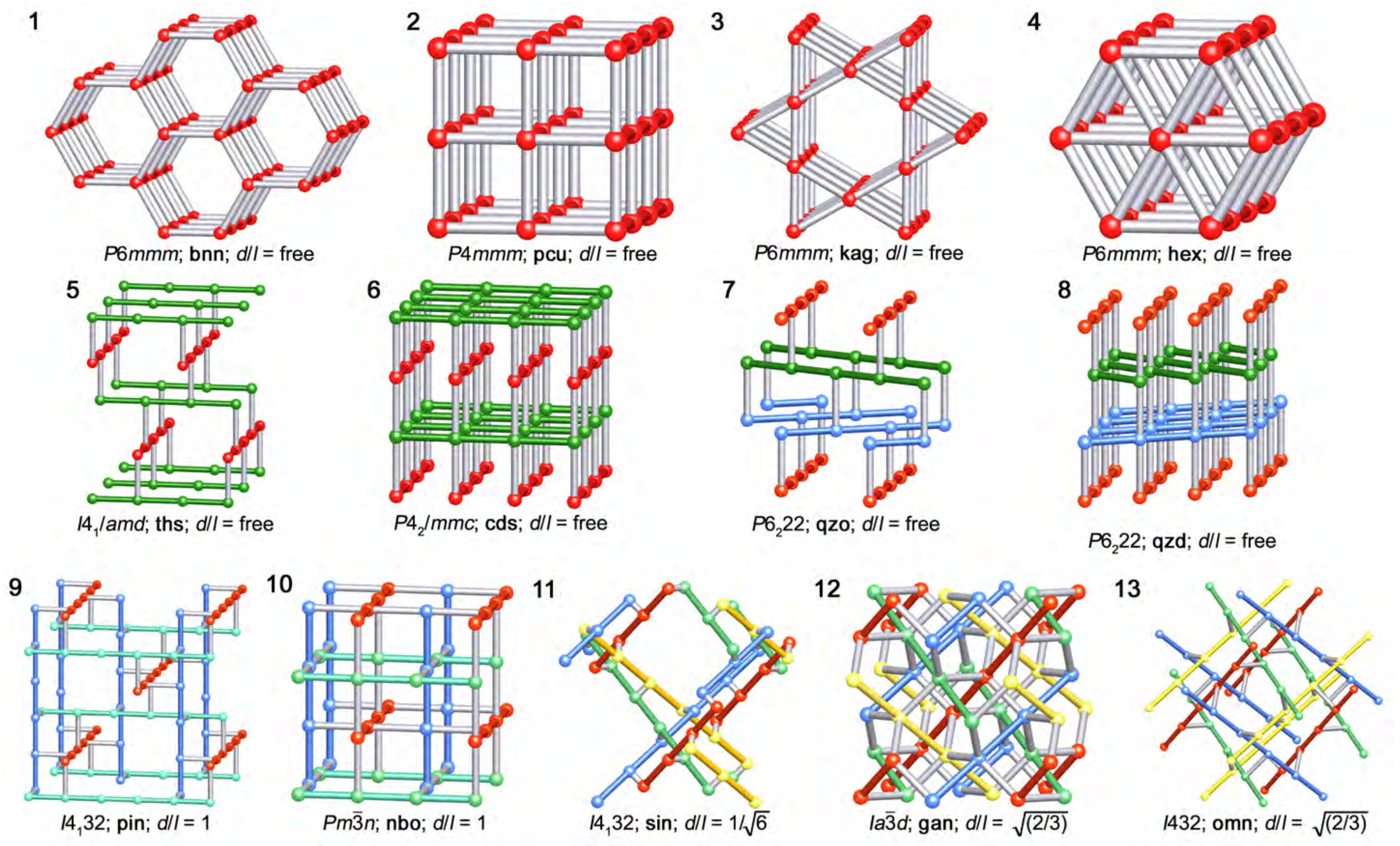
tiling, 1331
(not self-dual)



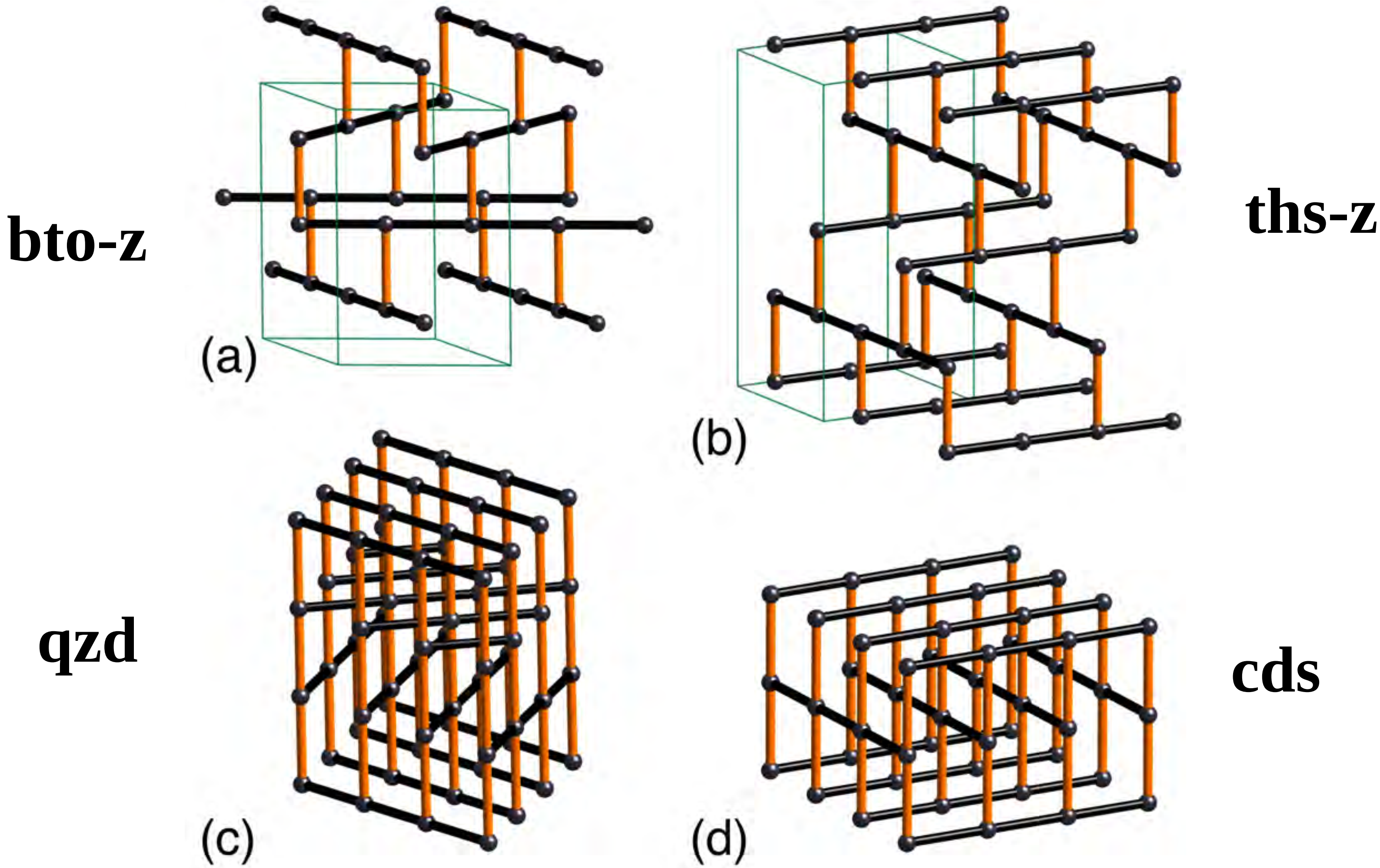
tile is an expanded version of adamantane with 4 inserted edges

simple nets formed by linking helices and ladders.

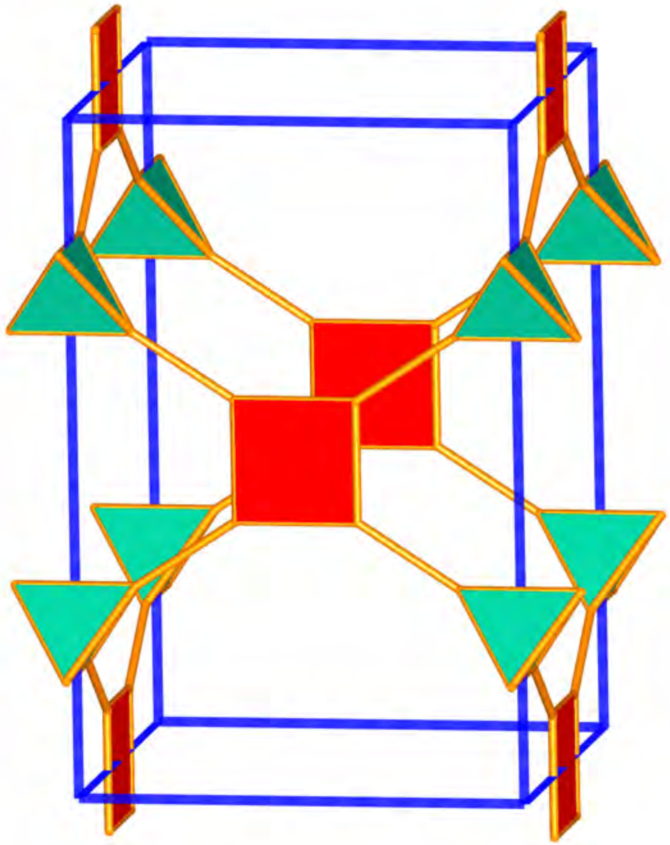


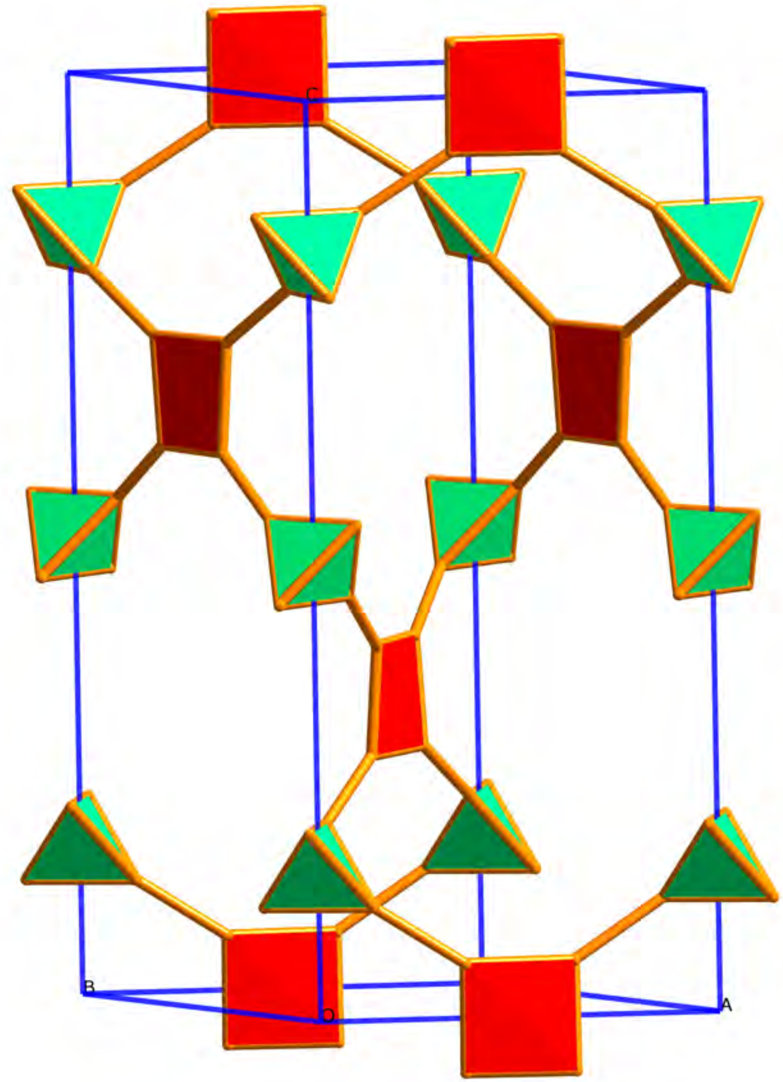


the invariant rod (cylinder) packings as nets JACS **2007**, *127*, 1504



Nets of parallel layer rod packings. symmetries (a) $P6_222$ (b) $I4_1/amd$ (c) $P6_222$ (d) $P4_2/mmc$



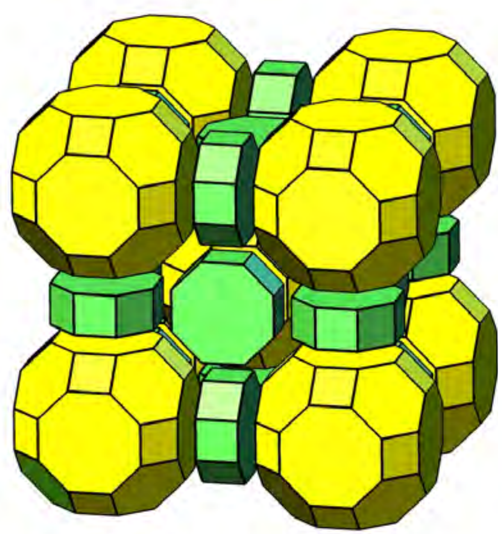


Example of a tetragonal – hexagonal pair

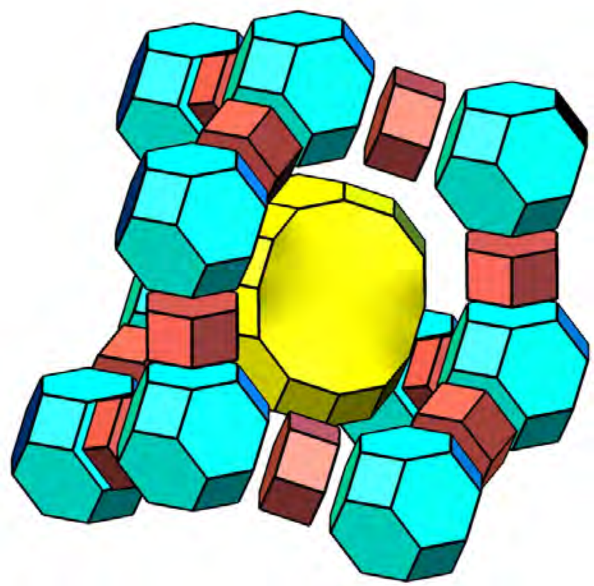
pts-a ($P4_2/mmc$) **pth-a** ($P6_222$)

Nets of simple tilings (duals of tlings by tetrahedra)

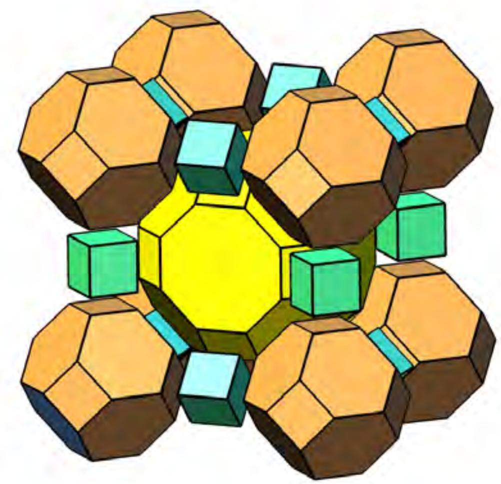
There are 9 vertex-transitive simple tilings (Delgado, Huson)
We have met **sod** (sodalite) already. Some of the others
are important zeolite nets:



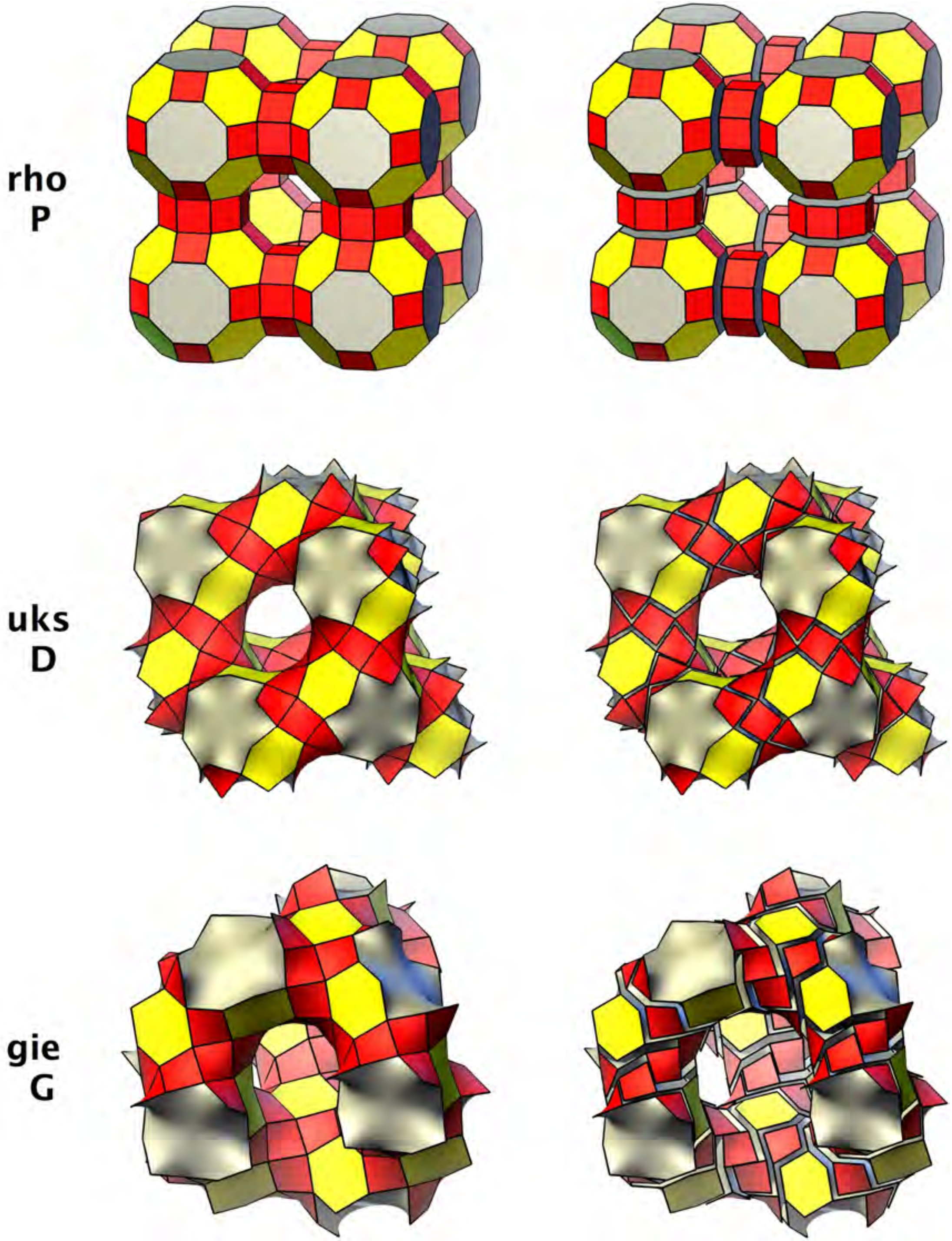
rho



fau (faujasite)

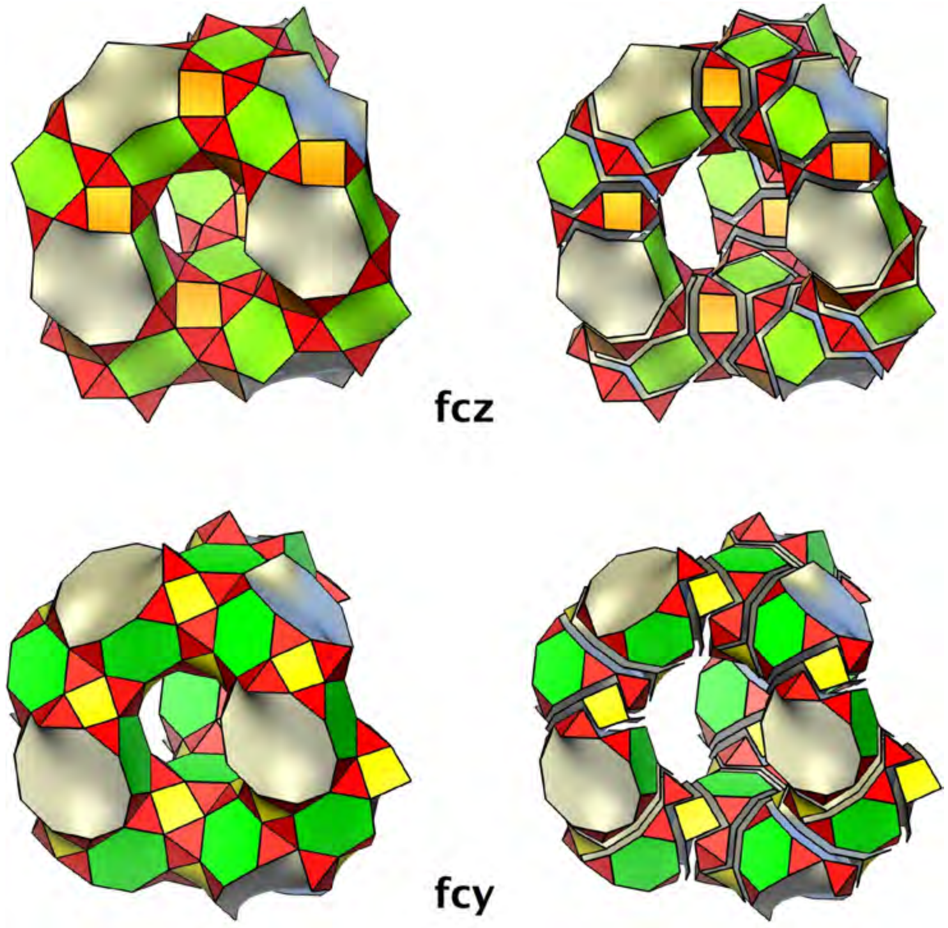


lta



Nets as tilings of minimal surfaces.
On the left $4^3.6$ tilings of P, D and G surfaces.
On the right as tilings E^3.

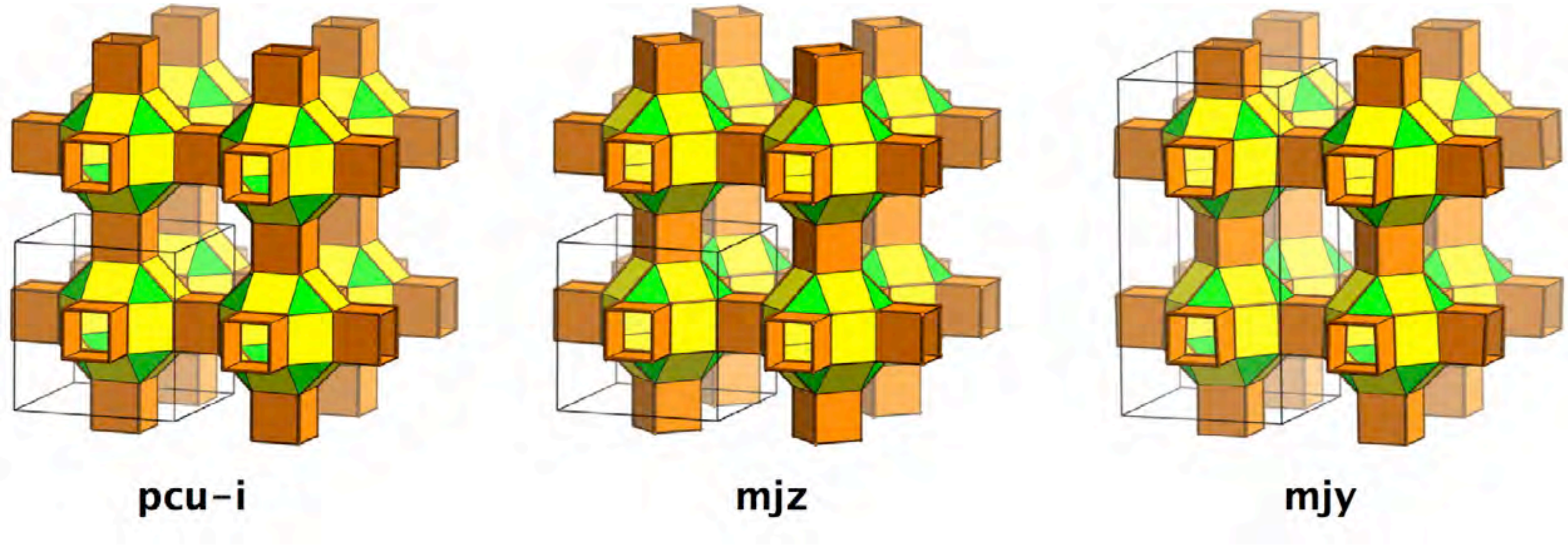
The epinet project **epinet.anu.edu.au** of S. T. Hyde et al. derives net as projections from H^2 onto P, G, and D.



There are two distinct $3^2.4.3.6$ tilings of G

One of these (**fcz**) is the underlying topology of a germanium oxide with a giant unit cell (a = 53 Å)
X. Zou, T Conradsson. M. Klingstedt. M. S. Dadachov, M. O'Keeffe, *Nature*, **437**, 716 (2005)

examples 3.4^4 tilings of *P* surface - an infinite family
but only **pcu-i** is vertex transitive
(recall two polyhedra 3.4^3)



for MOF with **mjz** structure see M. J. Zaworotko, *J. Am. Chem. Soc.* **129**, 10076 (2007) vertex transitive high-coordination sphere packings

12-coordinated (2)
fcu, hcp

11-coordinated (6)
ela, elb, elc, eld, ele, elf

10-coordinated (14)
bct, cco, chb, feb, gpu, mob, tca,
tcc, tcd, tce, tcf, tcg, tch, tci

12-coordinated sphere packings (closest packings) and 6-coordinated relatives in RCSR

c 12-c goes to octahedral 6-c
h 12-c goes to trigonal prismatic 6-c

	12-c	6-c	
c	**fcu**	**pcu**	
h	**hcp**	**acs**	
hc	**tcj**	**nia**	(NiAs)
hcc	**tck**	**sta**	
hhc	**tcl**	**stb**	
hhcc	**tcm**	**stc**	

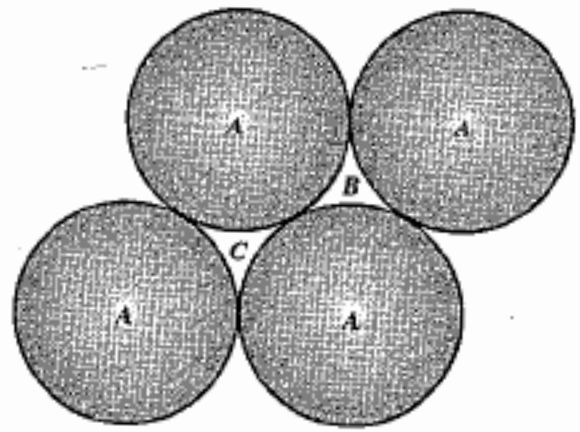


Fig. 6.1. Part of a layer of close-packed spheres. *A* marks the corners of a unit cell.

A *h* layer has similar layers both sides as in the sequence *A**B**A*

A *c* layer has different layers both sides as in the sequence *A**B**C*

h AB… (i.e. *ABABAB*….)
c ABC… (i.e. *ABCABC*….)
hc ABAC (i.e. *ABACABAC*….)
hcc ABACBC

how many 3-periodic structures are there?

minimal-density vertex-transitive sphere packings:

49 3-coordinated*
~160 4-coordinated
probably ~2000 in total

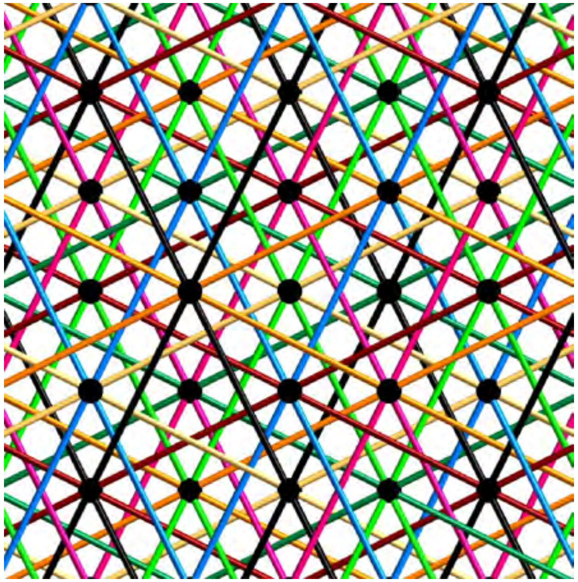
For symmetry *P*6/*mmm* and 6 kinds of vertex, there are 18,400,408 nets that are potential zeolite frameworks. Treacy & Foster, 2004
The most complicated zeolite has 99 kinds of vertex.
* Koch & Fischer, 1995 (+ 2005)

Infinite families of nets

2-D example. Symmetry *p*4*mm*

one vertex / unit cell bonded to vertex in cell *u*, *v*

i.e. links to vertices at ±*u*, ±*v* ; ±*v*, ±*u*. (8-coord)



So a lot of possible nets...

But < 100 edge transitive with edges as shortest distances

Interpenetrating nets

in special cases there are extra symmetry elements

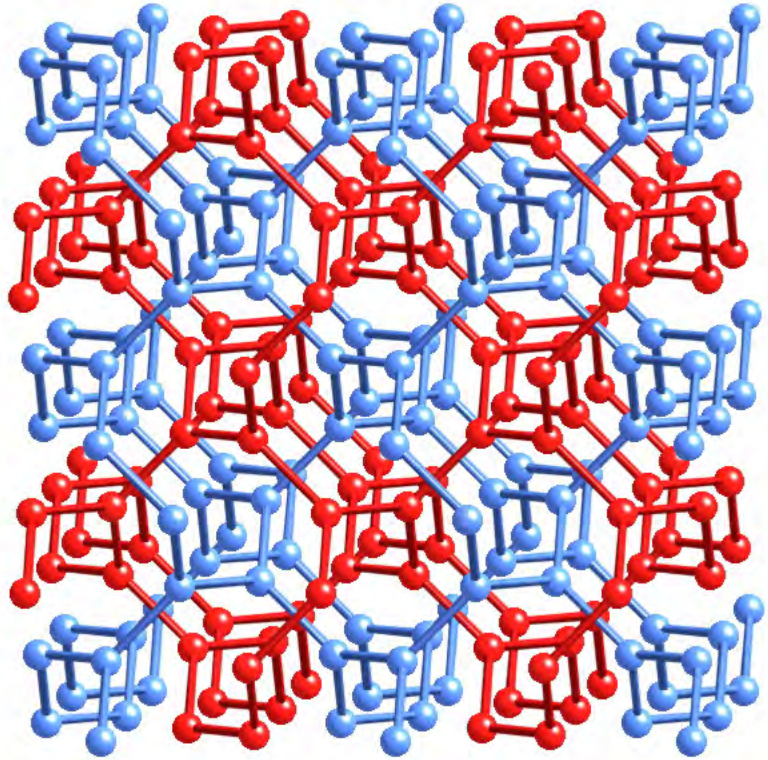
these can be extra translations Class I

or point operations such as inversion Class II

or both Class III

Recent reference on embeddings of interpenetrating nets

Bonneau, C.; O’Keeffe, M. *Acta Cryst. A* **2015**, *71*, 82



The **srs** net is chiral (symmetry $I4_132$).
The dual is the enantiomorph. Here two **srs** nets of opposite hand are intergrown to form a centrosymmetric structure (symmetry *Ia*-3*d*). The surface separating the two nets is the *G* minimal surface (*gyroid*)

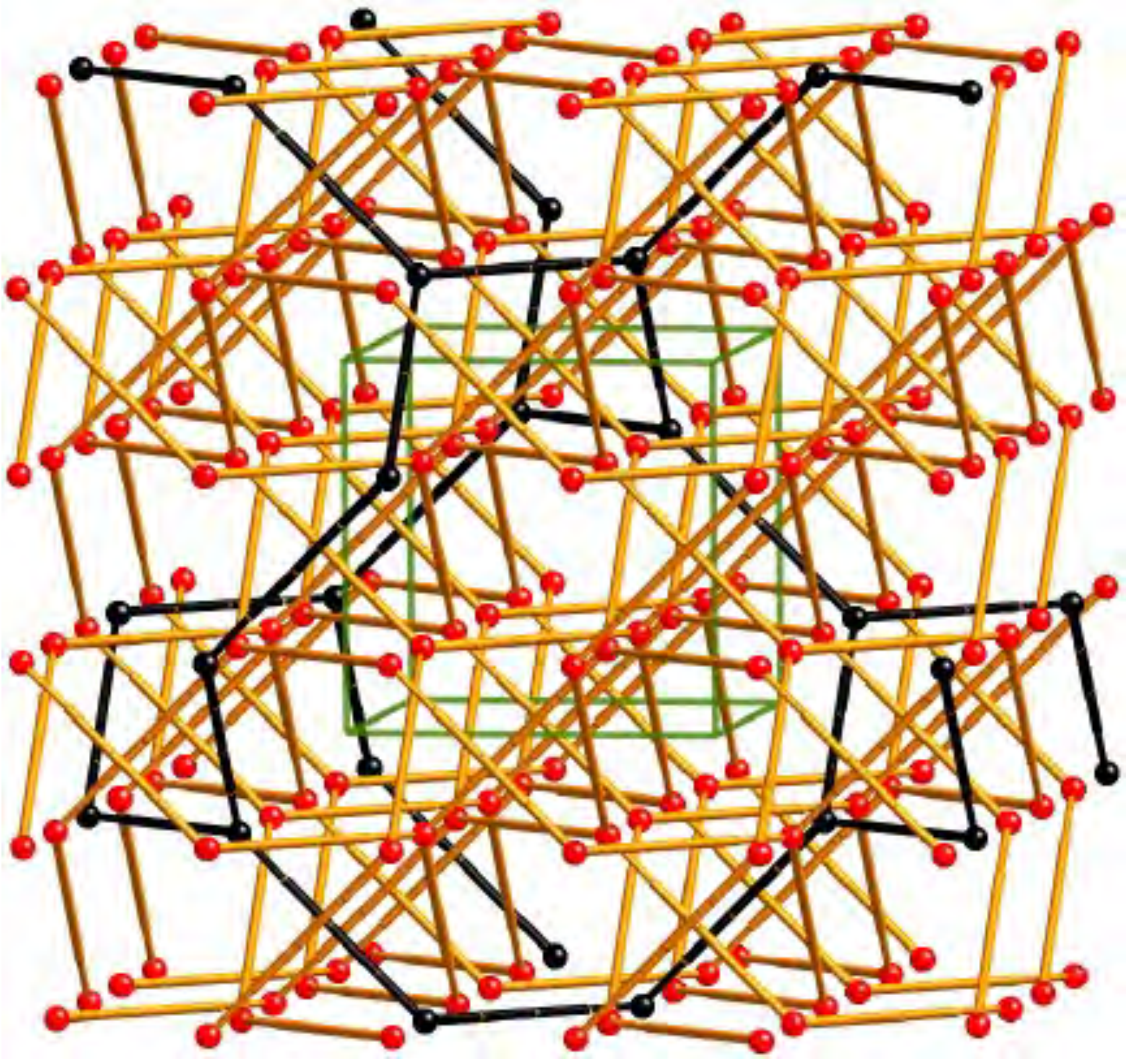
interpenetrating **srs** nets (symmetry $I4_132$) in RCSR

(a) net has full symmetry

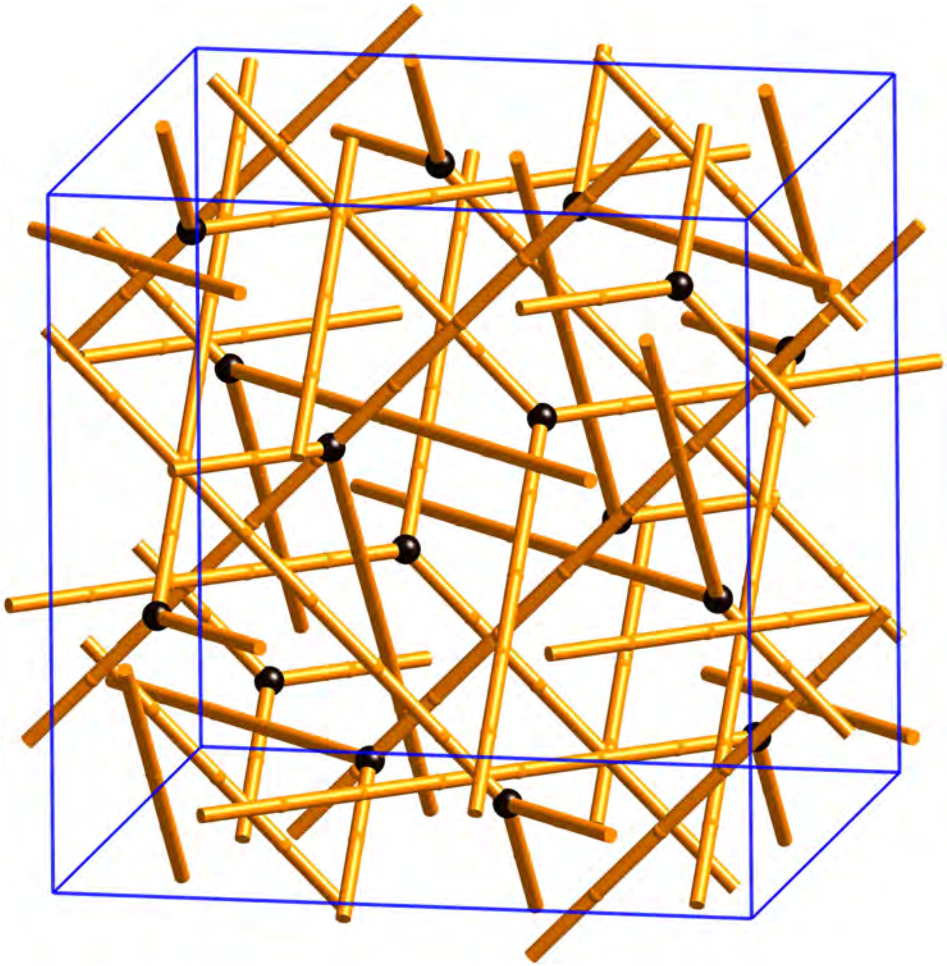
srs-c	*Ia*-3*d*	one *L* and one *R*	inversion
srs-c4	$P4_232$	four *L* or four *R*	translation
srs-c8	*I*432	eight *L* or eight *R*	rotation
srs-c54	*Ia*-3*d*	*27 L and 27 R*	

(b) net has lower symmetry

srs-c2*	$P4_222$	two *L* or two *R*
srs-c3	$I4_132$	three *L* or three *R*
srs-c4*	$P4_2/nbc$	two *L* and two *R*



srs-c8 symmetry *I*432
8 vertices in cubic cell, 4 in primitive cell

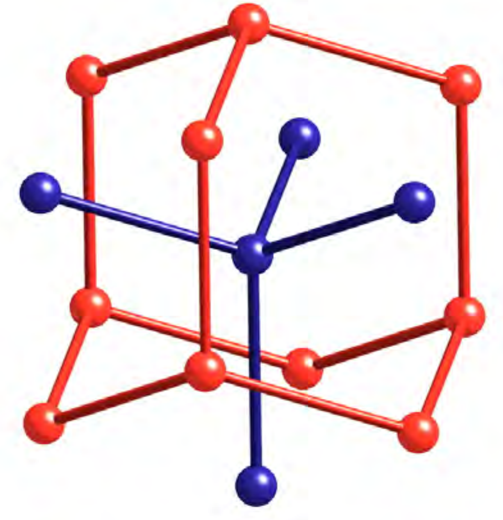


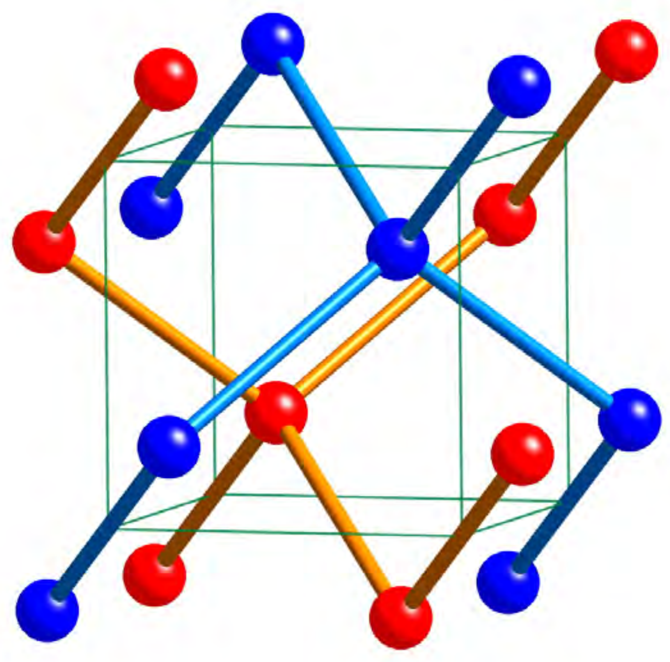
one can have 54 full-symmetry **srs** nets interpenetrating (27 left and 27 right). this shows one unit cell (*Ia*-3*d*)
Actually made! Wu, H., Yang, J., Su, Z.-M., Batten, S, R. & Ma, J.-F. (2011). *J. Am. Chem. Soc*. **133,** 11406-11409

Each ring catenated with 634 others!

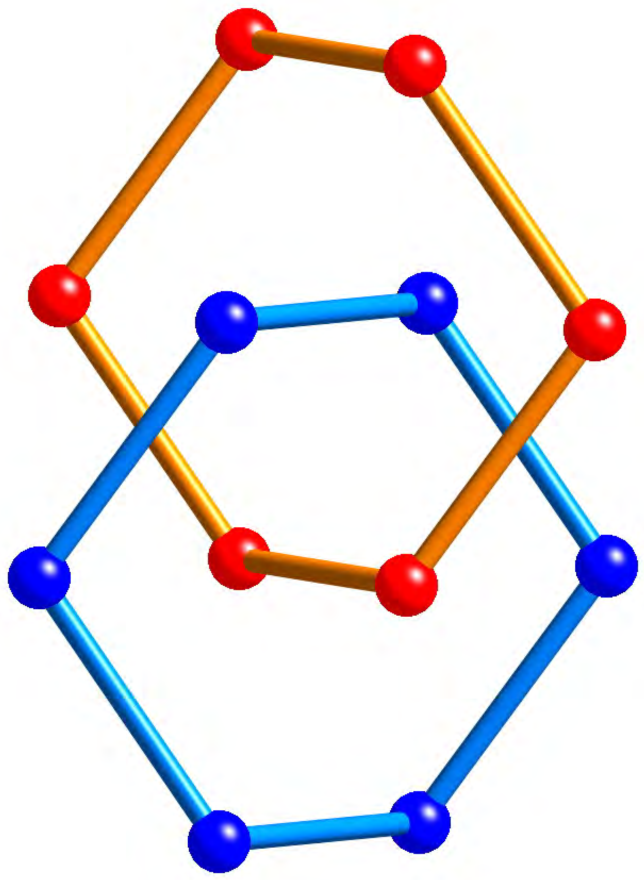
diamond (**dia**) symmetry *Fd*-3*m*
two vertices in primitive cell

dia-c symmetry *Pn*-3*m*
two vertices in primitive cell
two nets related by translation





dia-c symmetry *Pn*-3*m*
two vertices in primitive cell
two nets related by translation

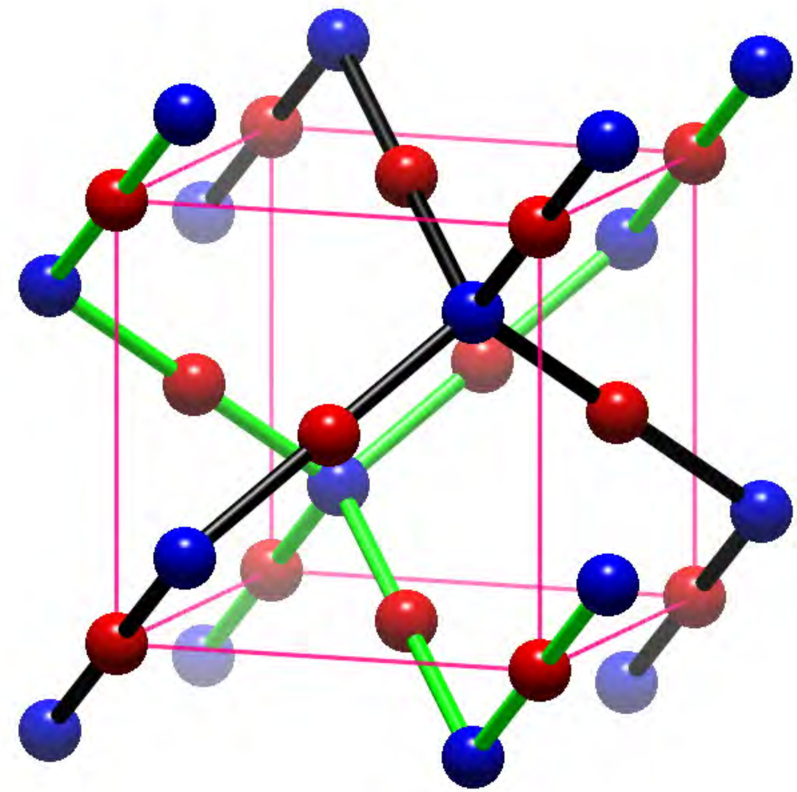


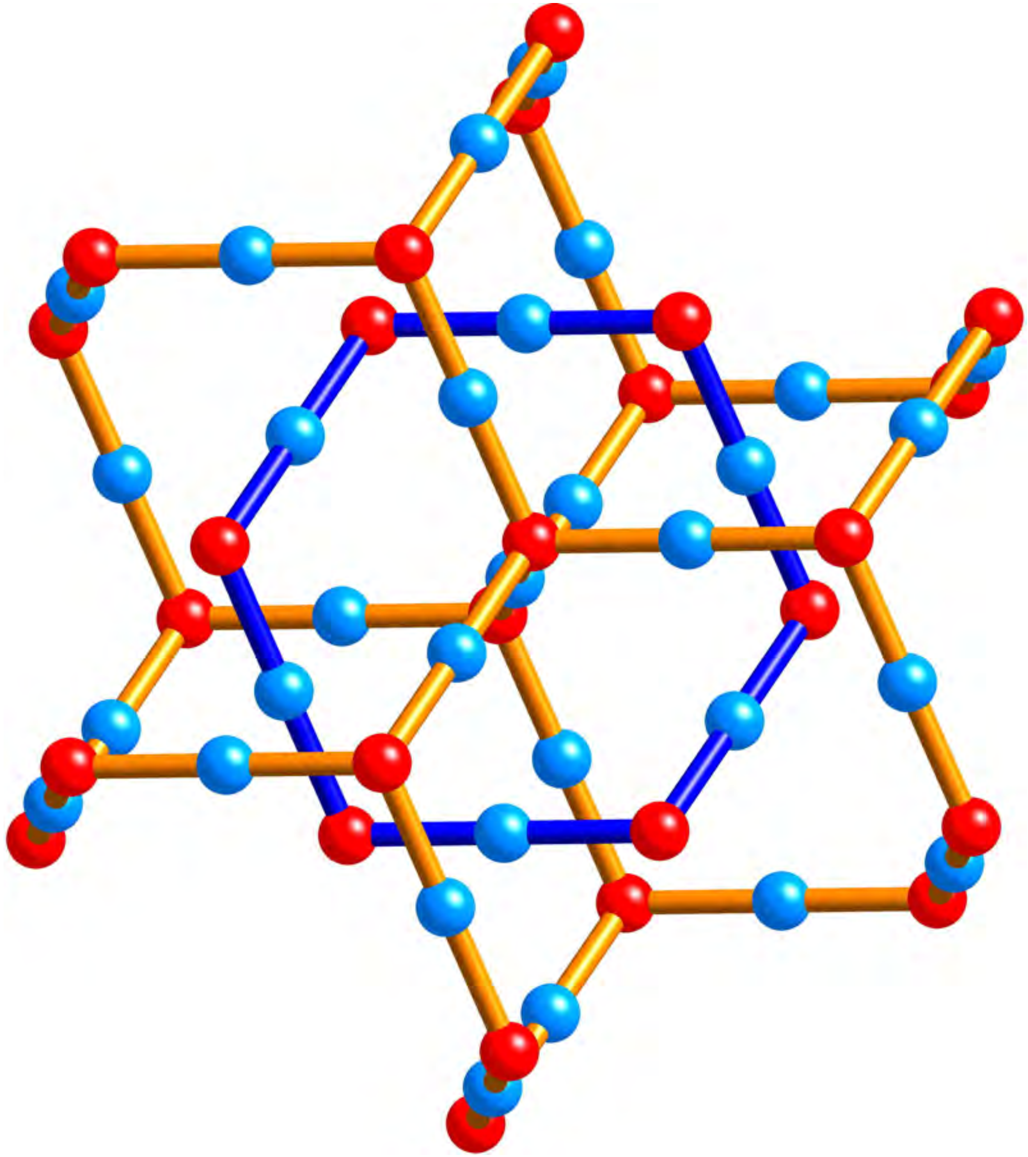
rings are catenated

Cuprite (Cu_2O) - one of the very first crystal structures Bragg (1915)

Note the two nets related by a unit cell edge (a translation)

Blue spheres are Cu at vertices of **dia** nets edges are -O- links (O red)





Showing one Cu_6O_6 ring in Cu_2O catenated with 6 others

Multiple **dia** nets related by translation

Table 1. Crystallographic Data for the Ideal Geometry of *N*-Fold Interpenetrated Diamond Nets

N^a	crystal system	space group	a^b	c^b	a/c
1	cubic	$Fd\bar{3}m$	$4/\sqrt{3}$	a	1
2	cubic	$Pn\bar{3}m$	$2/\sqrt{3}$	a	1
$2n+1$	tetragonal	$I4_1/amd$	$\sqrt{8}/\sqrt{3}$	$4/\sqrt{3}N$	$N/\sqrt{2}$
$4n$	tetragonal	$P4/nbm$	$2/\sqrt{3}$	$4/\sqrt{3}N$	$N/2$
$4n+2$	tetragonal	$P4_2/nnm$	$2/\sqrt{3}$	$4/\sqrt{3}N$	$N/2$

[a] N = Interpenetration number, n is any integer > 1. [b] Cell parameters are in units of the edge length (distance between linked vertices).

see **dia-3***, **dia-c4**, **dia-c6** in RCSR.
Primitive cell in each case contains 2 vertices

F. Uribe-Romo, M. O'Keeffe, O. M. Yaghi, *et al*. *J. Am. Chem. Soc.* **131**, 4570 (2009)

Interpenetrating quartz (**qtz**) nets - non-intersecting edges

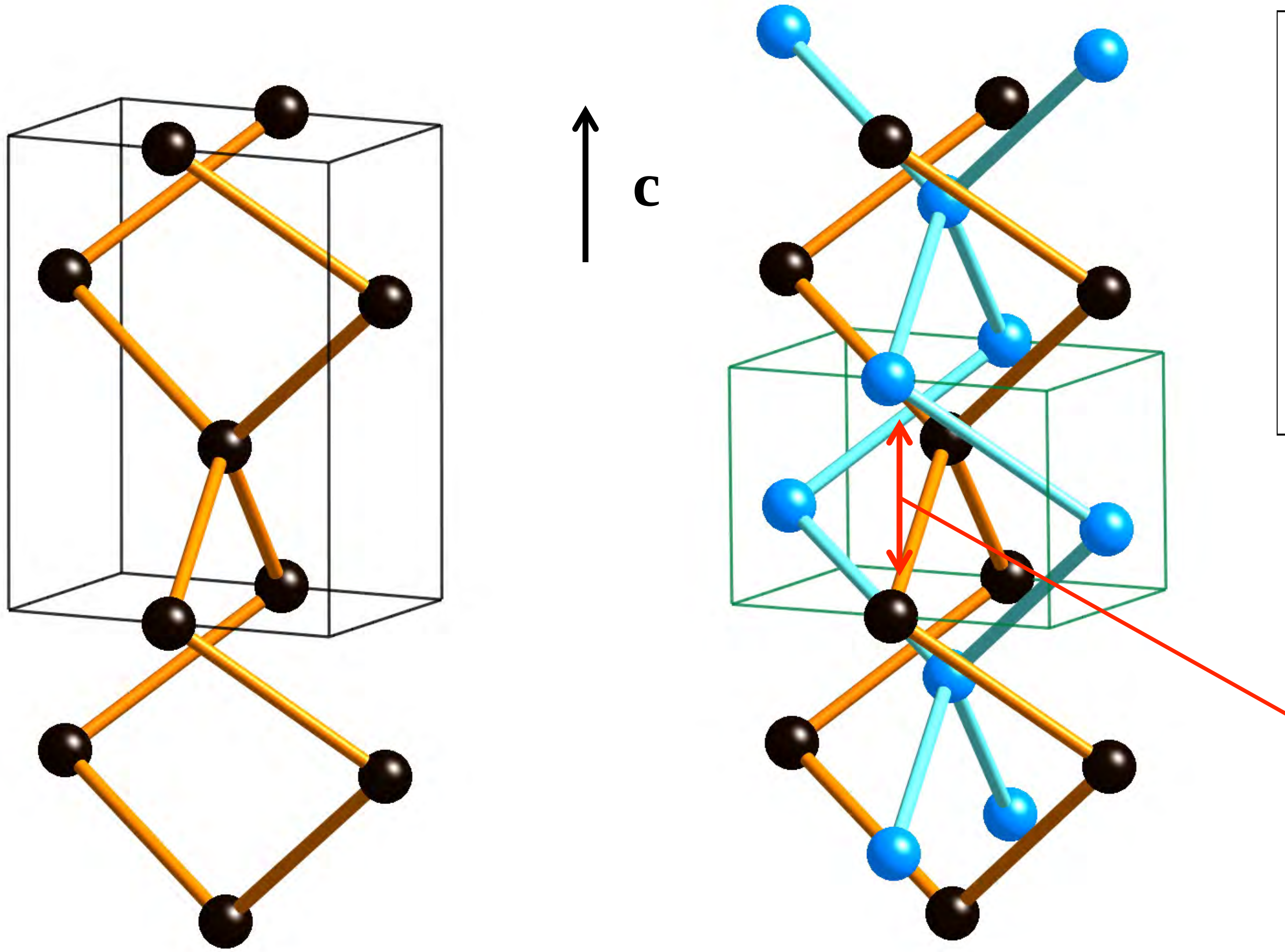
"ideal" **qtz** net $P6_222$ (or $P6_422$) $a = a_q = \sqrt{(8/3)}$, $c = c_q = \sqrt{3}$

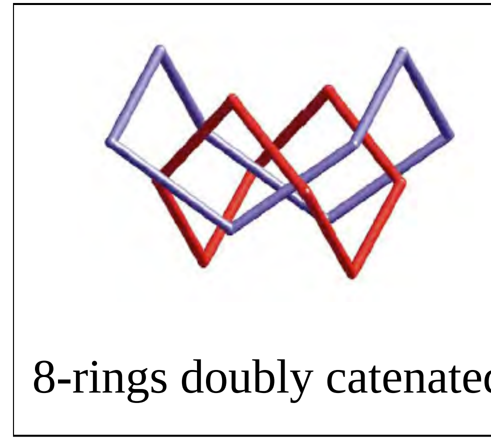
a. qtz-n, *n* not a multiple of 3, related by translations along *c*
$a = a_q$, $c = c_q/n$

b. qtz-n, $n = 3$, related by translations along *a*.
$a = a_q/\sqrt{3}$, $c = c_q$

c. qtz-n, $n = 3$ times (not a multiple of 3),
related by translations along *a* and *c*
$a = a_q/\sqrt{3}$, $c = 3c_q/n$

possibilities for *n*: 2(a),3(b),4(a),5(a), 6(c),7(a),8(a),9 (not possible)



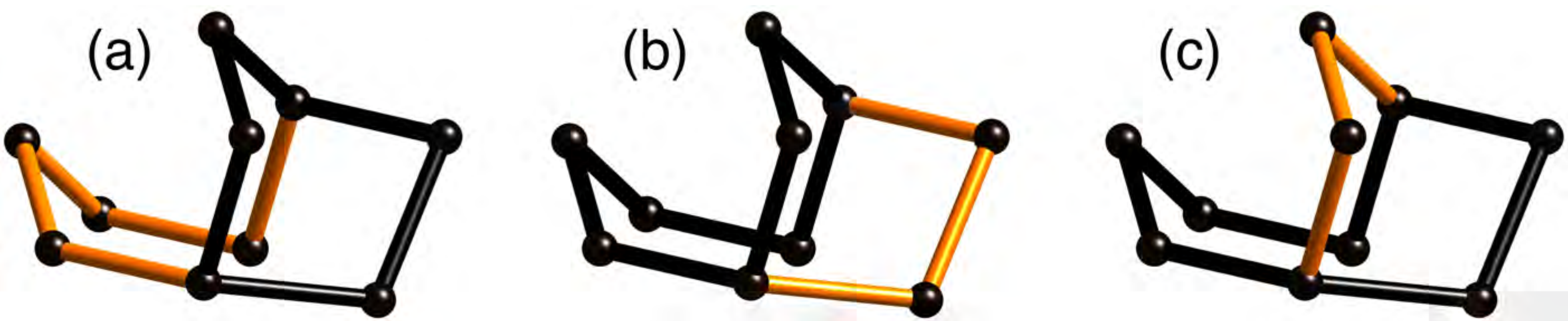


two nets
related by
translation
along **c**

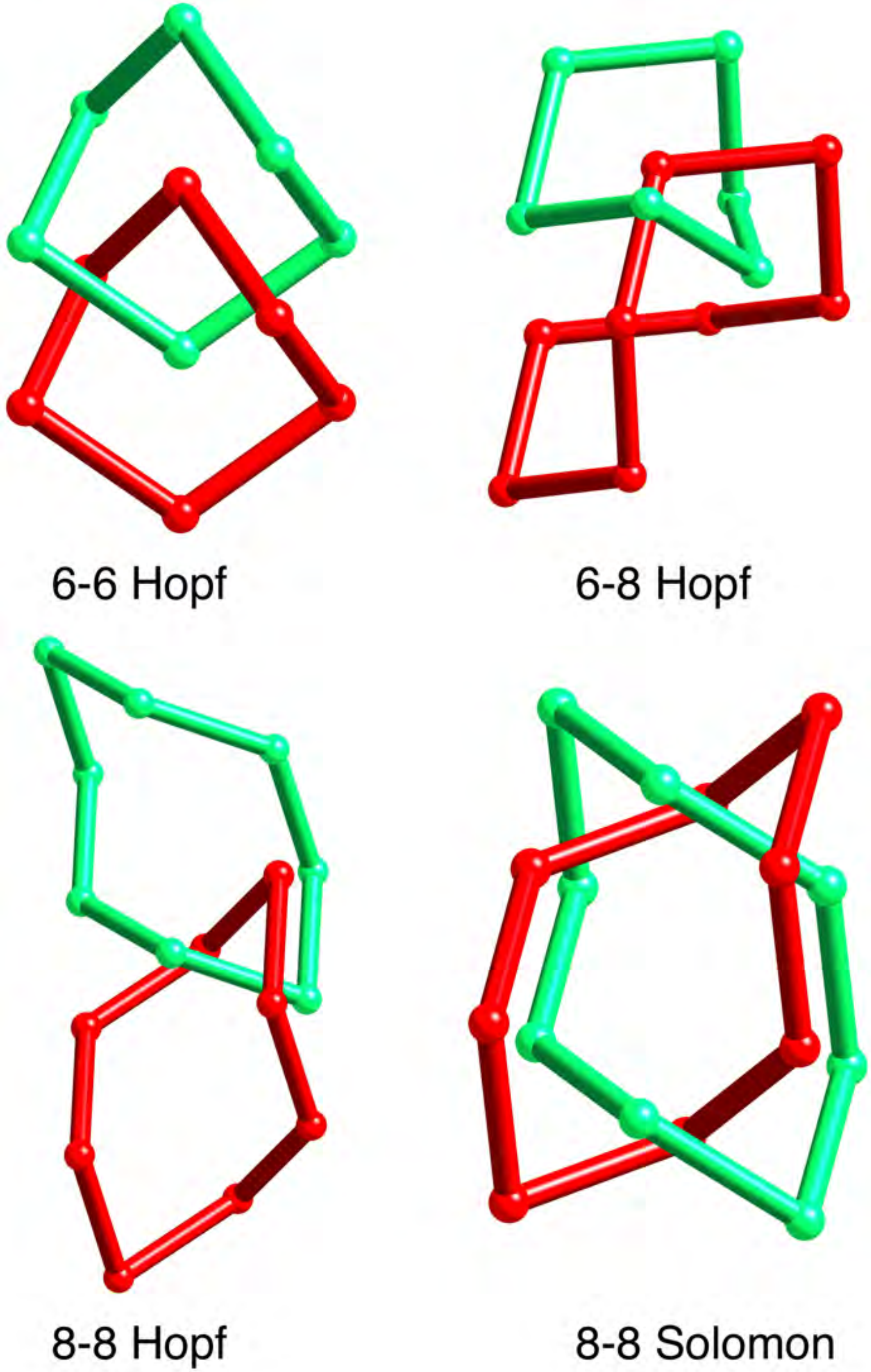
qtz $P6_222$ **qtz-c** $P6_422$

note that space group changes "hand", not the net!

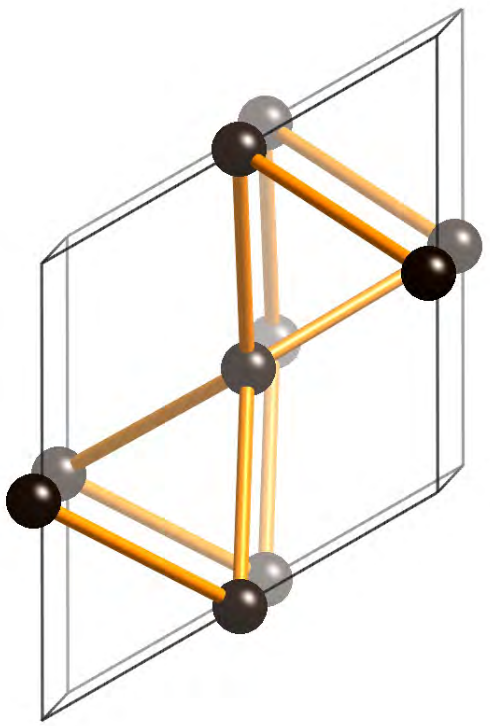
natural tile for **qtz** 1-skeleton of tile one 8-ring



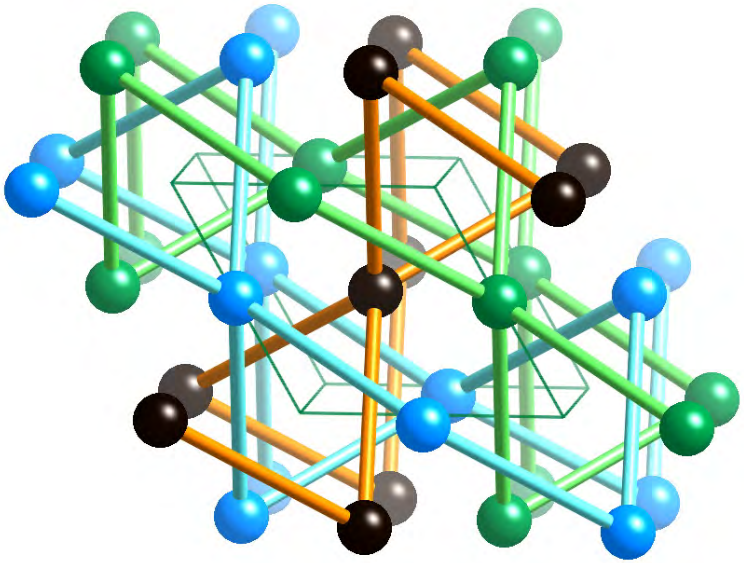
The tile faces are essential rigs. In **qtz** other 8-rings (c) are sums of essential ring (a) and (b)



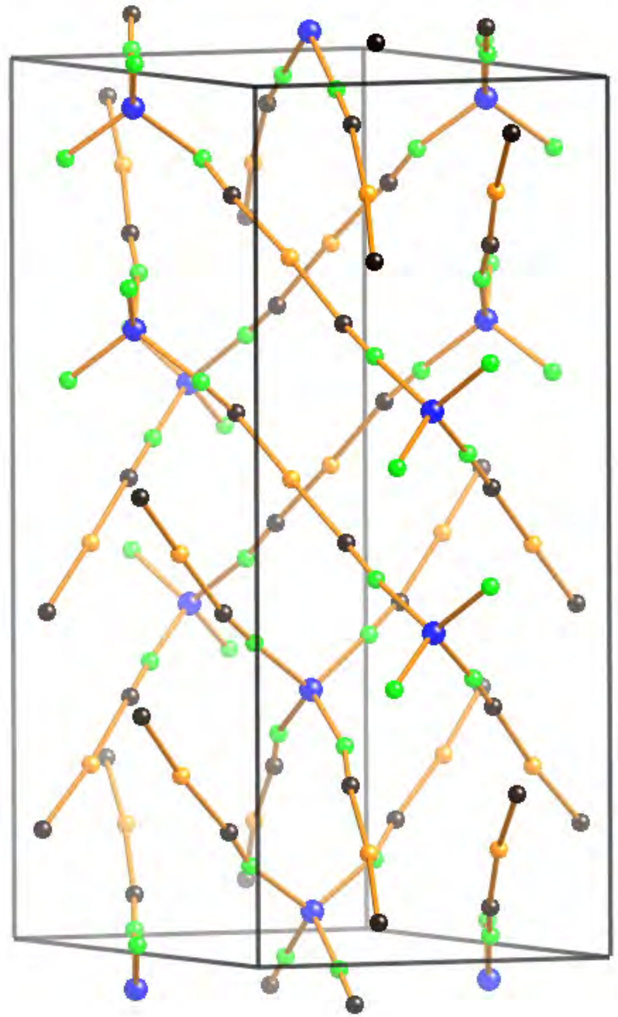
The four kinds of catenation in **qtz-c**



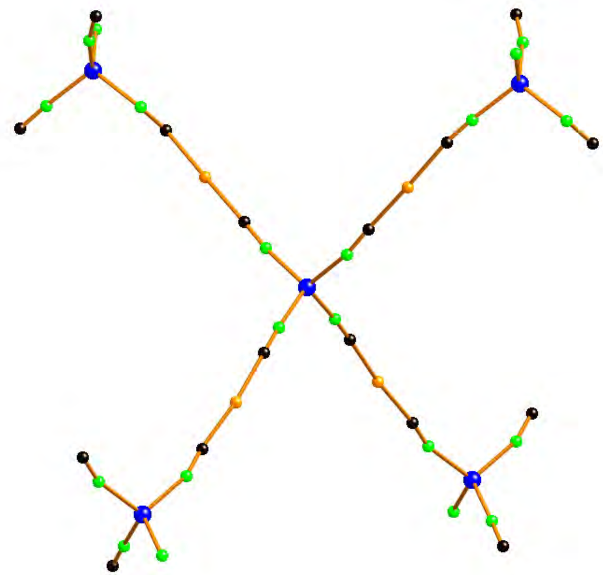
qtz - view down **c**
$P6_222$



qtz-c3 - view down **c**
$P6_222$, $a' = a/\sqrt{3}$
nets related by **a'**

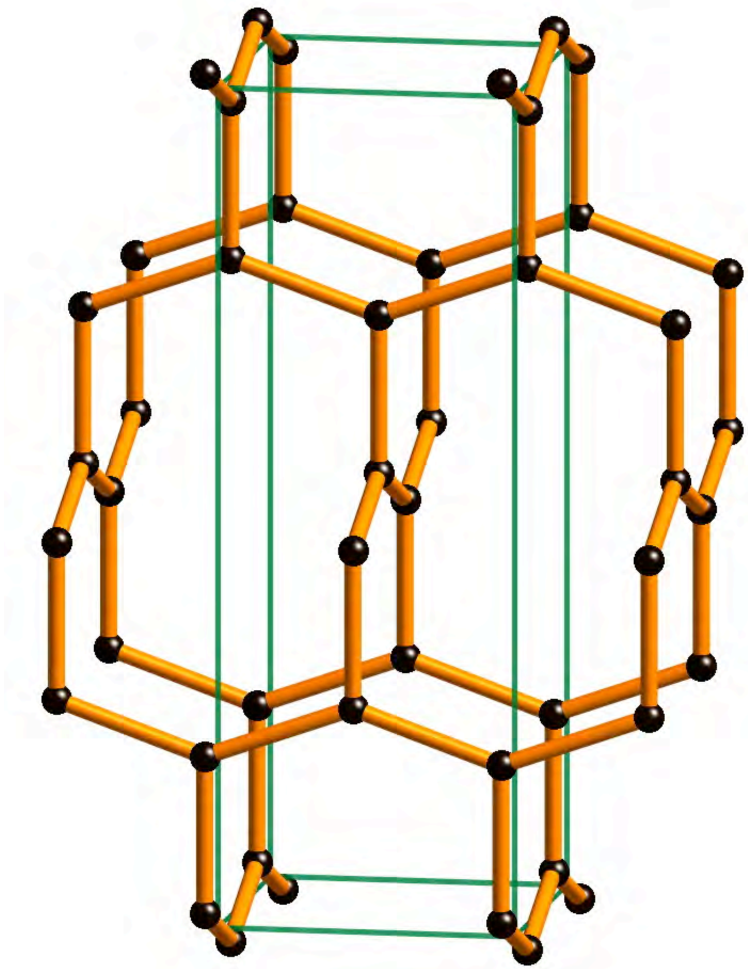


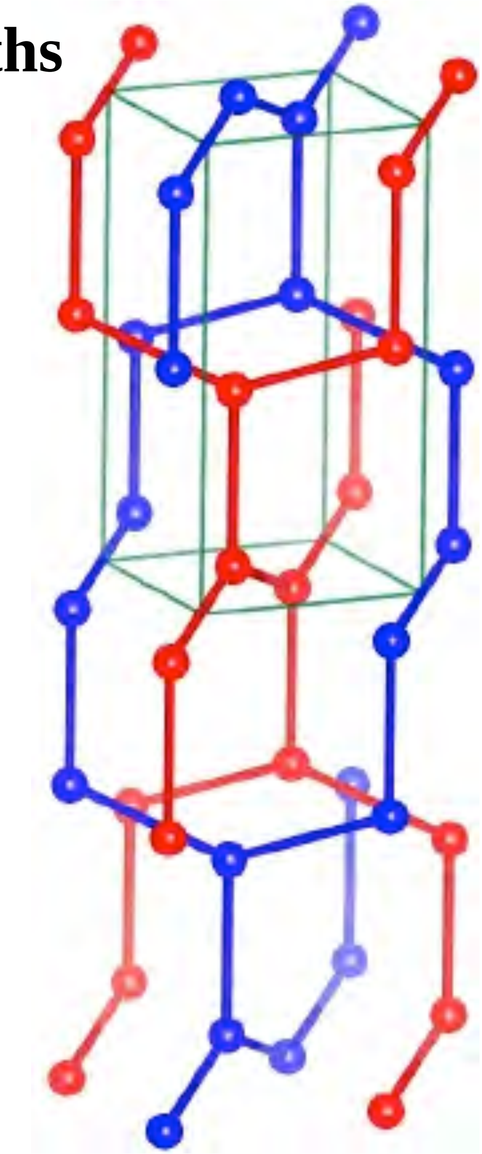
example of **qtz-c6** (both modes of interpenetration)



$Co[Au(CN)_2]_2$ S. C. Abrahams et al. *J. Chem. Phys.* **76**, 5458 (1982)

Another common intergrowth **ths**





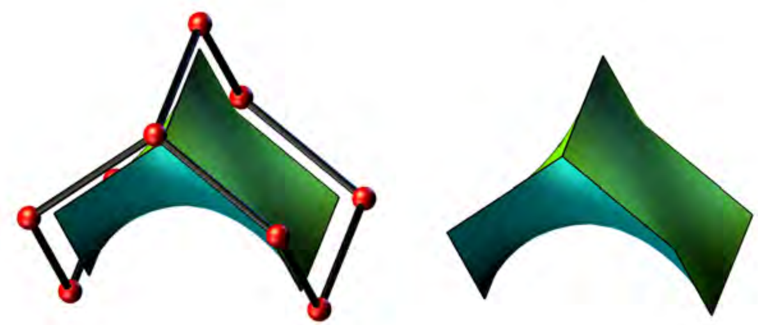
dia

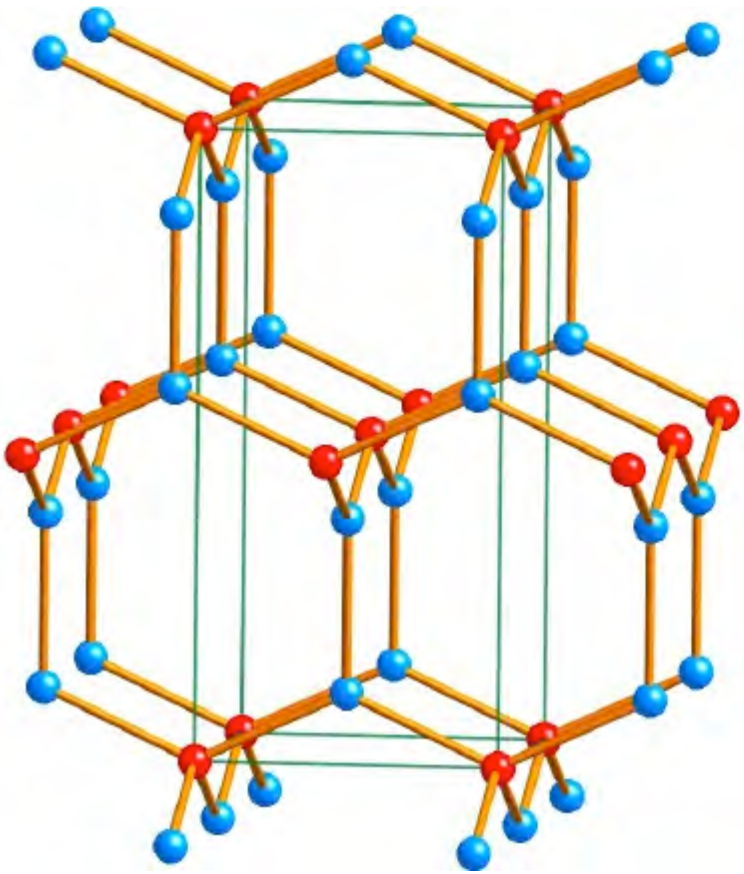
ths

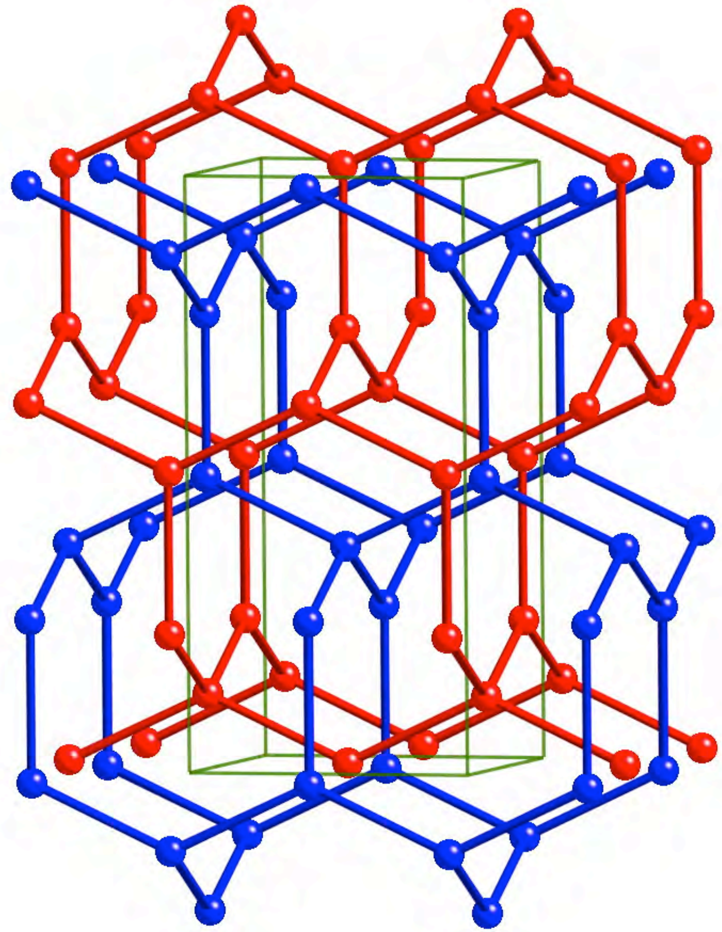
ths $I4_1/amd$
4 vertices in primitive cell

ths-c $P4_2/nnm$, $a' = a/\sqrt{2}$, $c' = c/2$
4 vertices in primitive cell

note that **ths** has a natural tiling [10^4]. So dual is 4-coordinated and is in fact **dia**. But the dual tile must have only 3 faces and is the "half-adamantane"tile [$6^2.8$]







dia

tfa

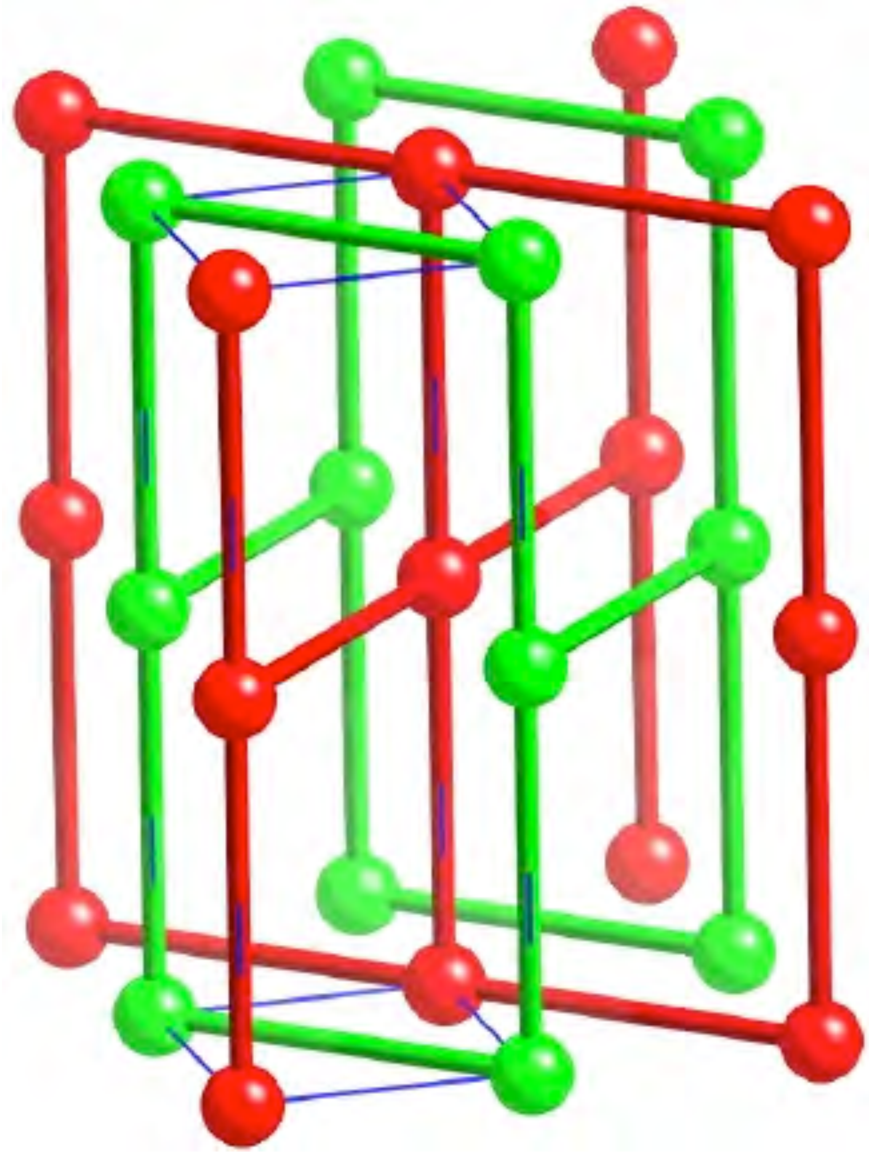
tfa *I*-4*m*2

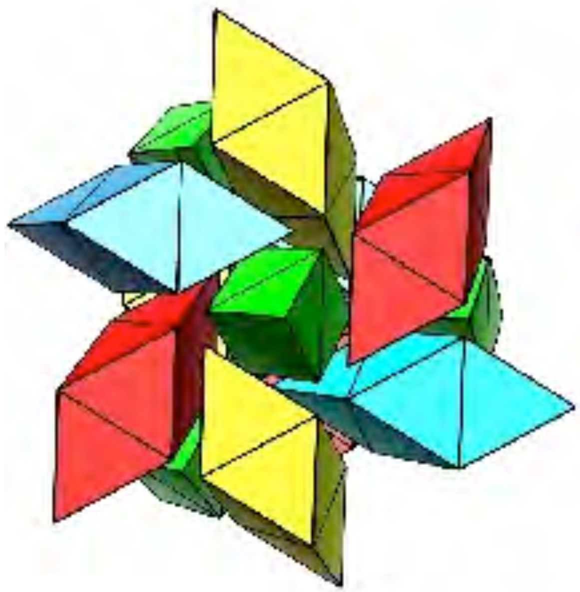
tfa-c $I4_1/amd$

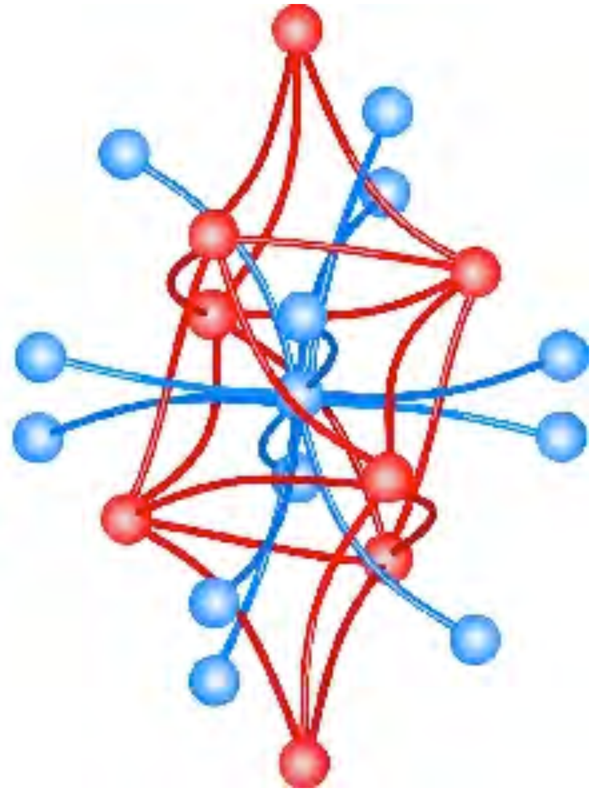
cds is naturally self-dual

cds $P4_2/mmc$

cds-c $P4_2/mcm$.
$a' = a/\sqrt{2}$
nets related by a'

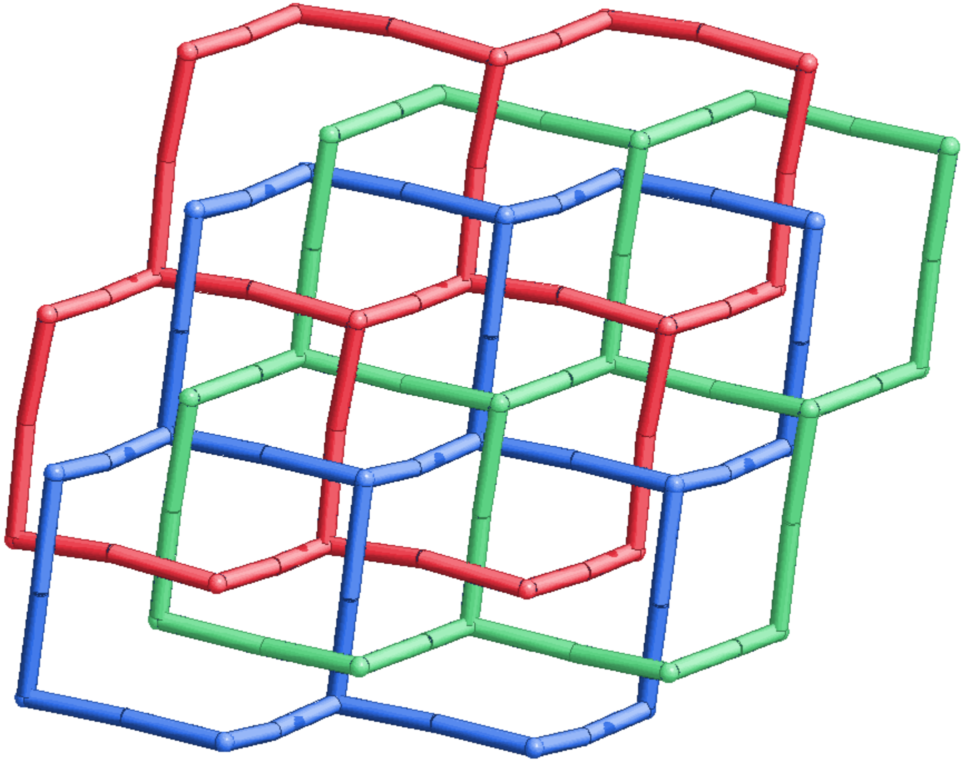






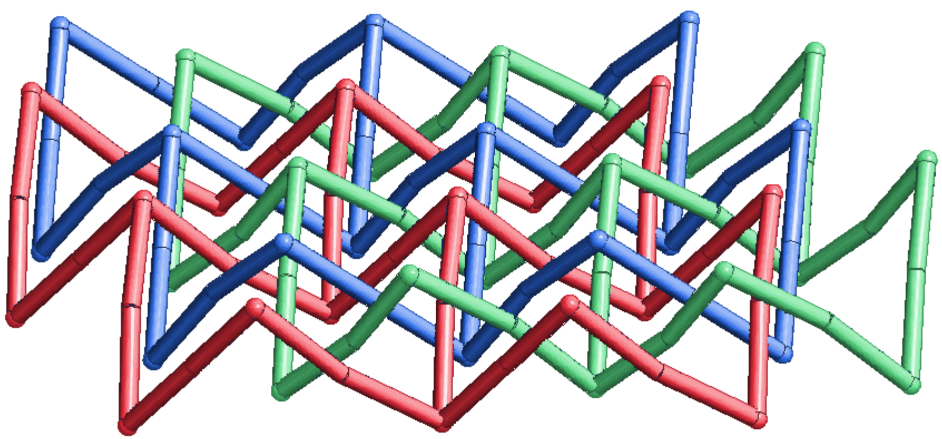
An oddity: a self-dual tiling of **fcu** symmetry *Pa*-3 transitivity 1111

two interpenetrating **fcu** nets with bent edges, symmetry *Ia*-3

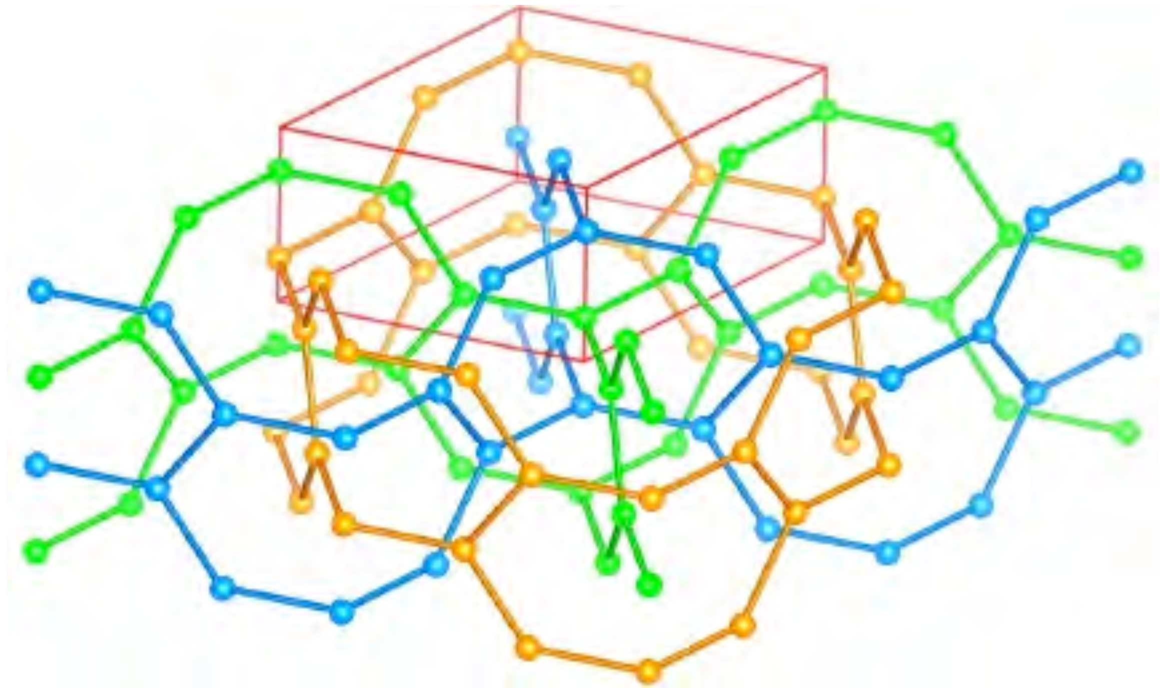


Borromean

red > green
green > blue
blue > red



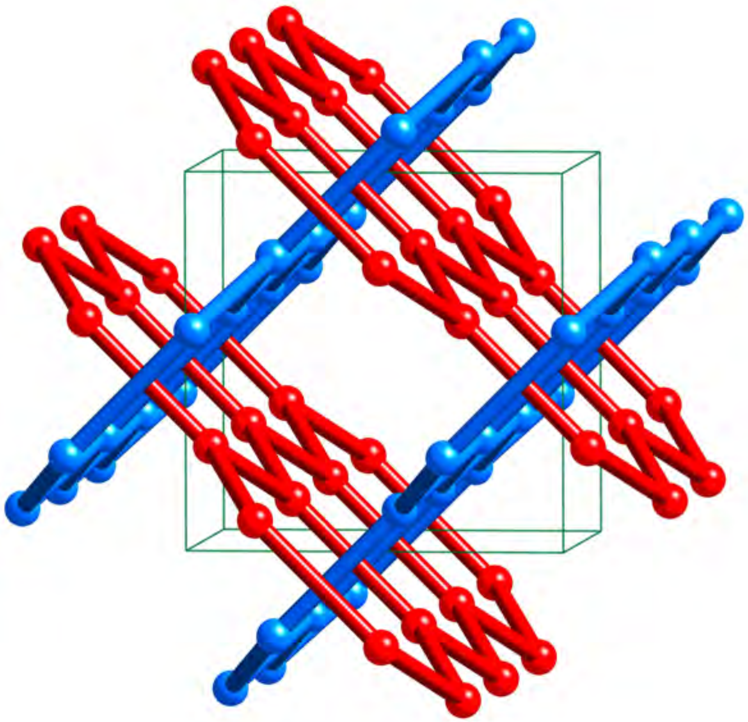
etc-c3 discussed first by S. T. Hyde *et al.* [*Austr. J. Chem.* ***56***, 981, (2003)]



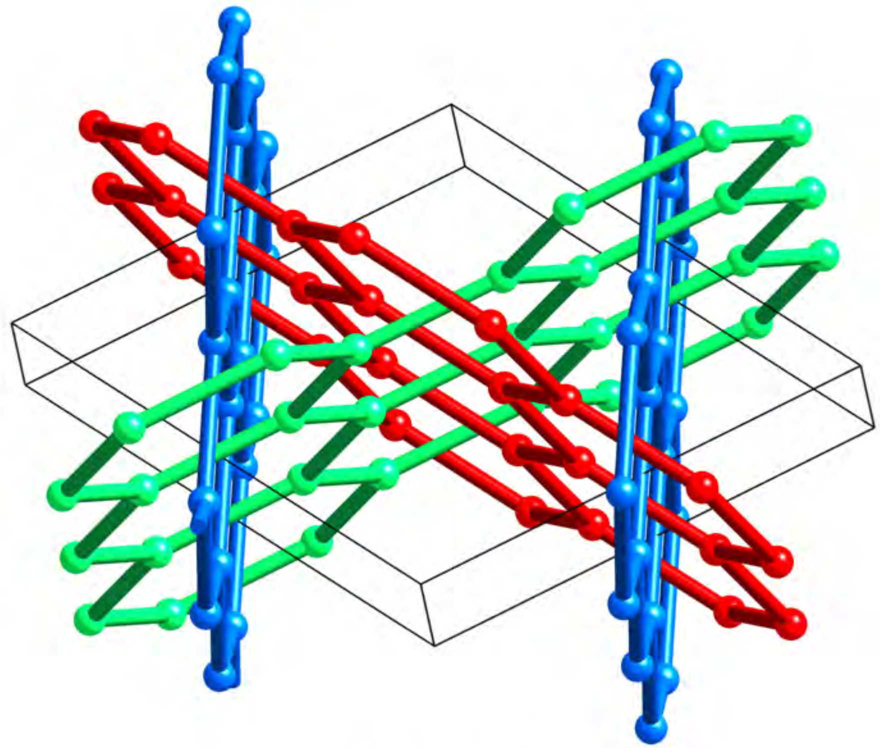
A tri-continuous mesoporous material with a silica pore wall following a hexagonal minimal surface

Yu Han[1†‡], Daliang Zhang[2,3‡], Leng Leng Chng[1], Junliang Sun[2], Lan Zhao[1], Xiaodong Zou[2*] and Jackie Y. Ying[1*]

Nature Chemistry **1**, 123 (2009)

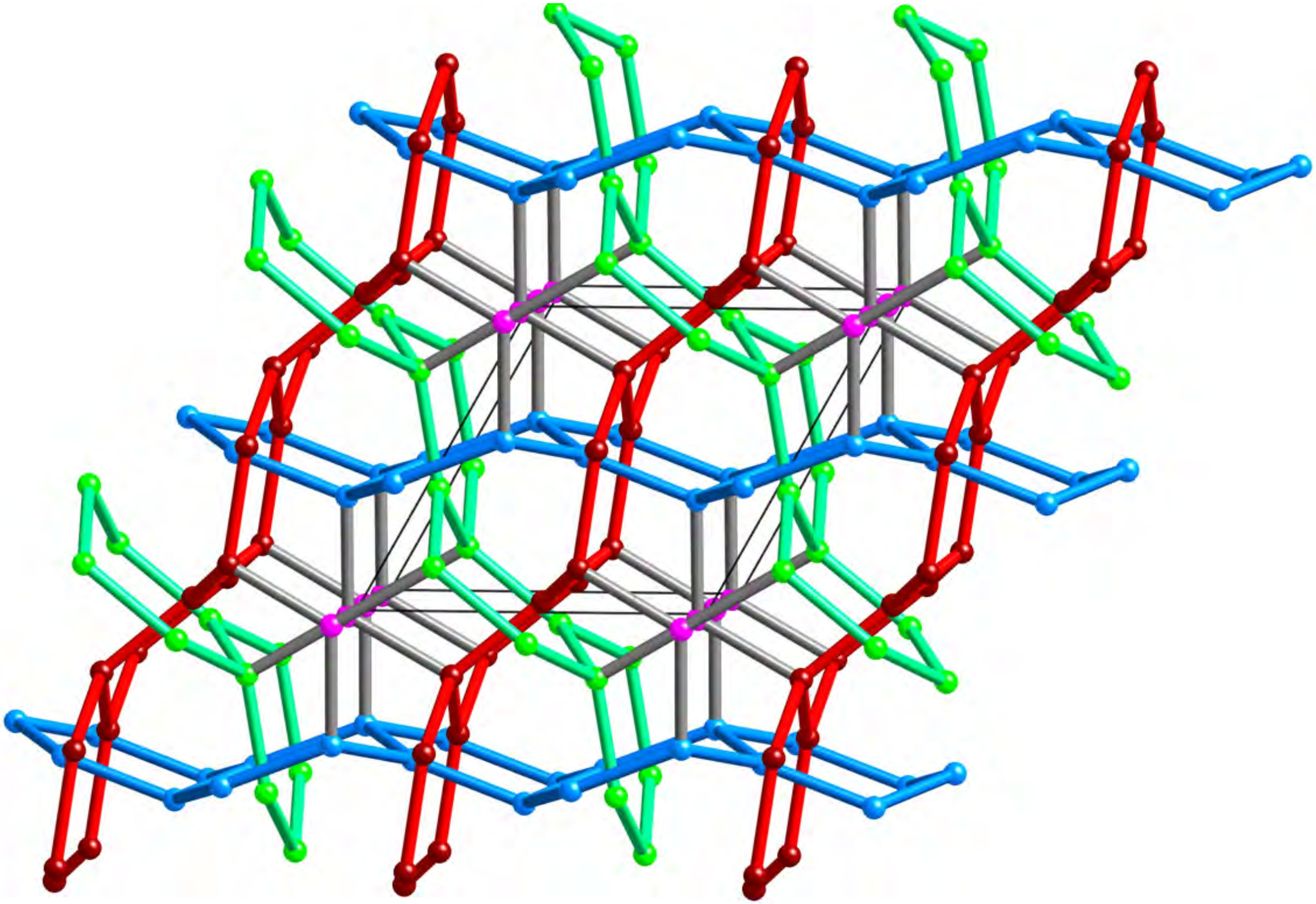


hcb-c

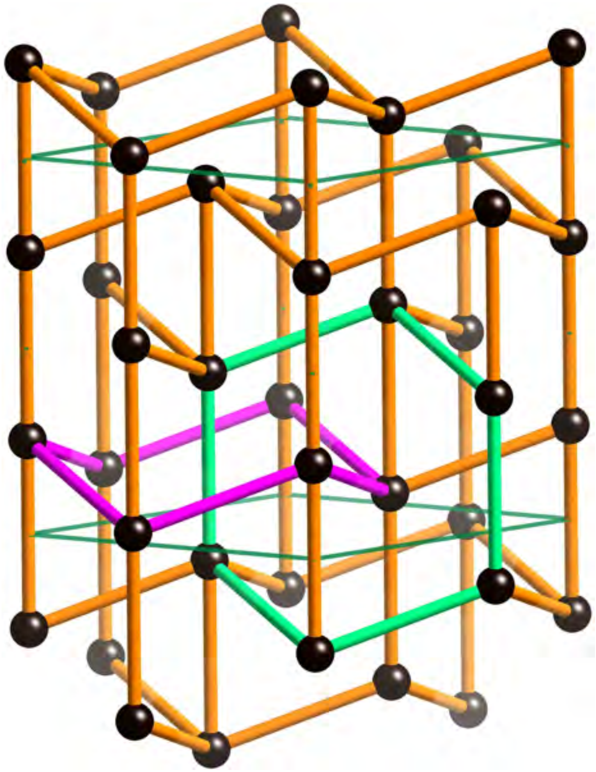


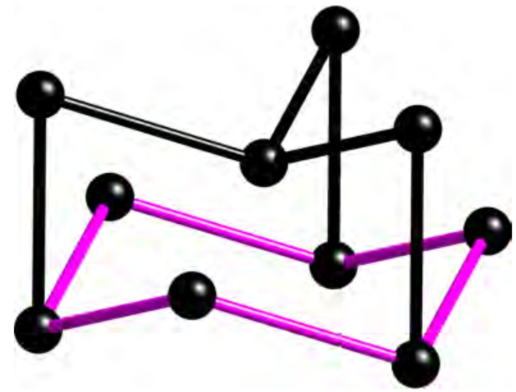
hcb-c3

Example of 2D nets -> 3D structure “polycatenation”

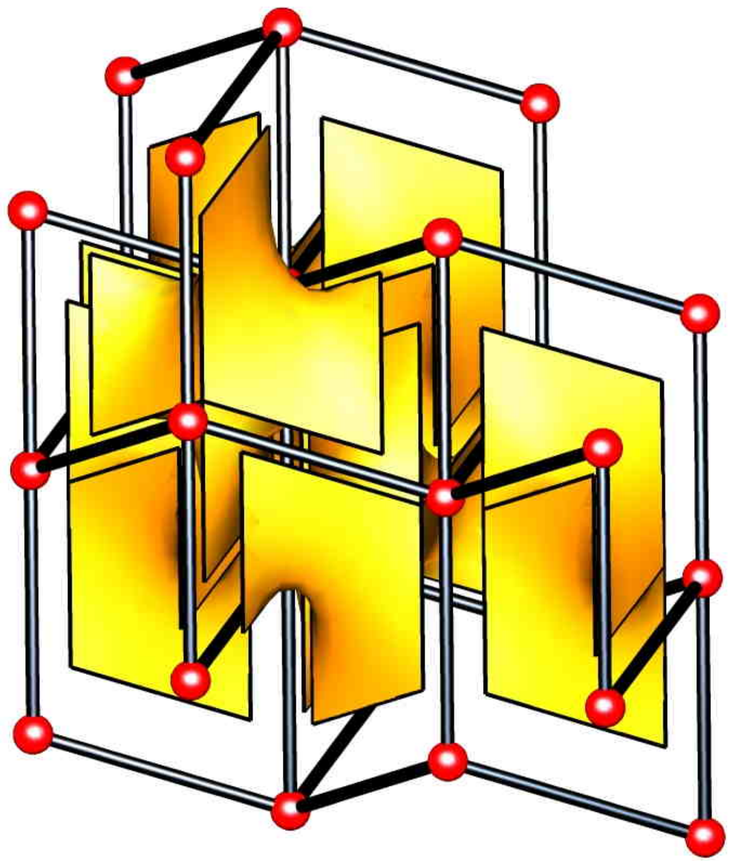


The net **jcy** formed by linking **hcb-c3**. Every ring in the structure is catenated with others ("self-catenated"). occurs in a MOF. M.O'Keeffe, banglin chen *et al.* *Angew. Chem. Int. Ed.* **2012,** 51**, 10542.**





The net **fnu**. has all 6-rings (8 per vertex (**dia** has 2 per vertex)
vertex symbol 6_3. 6_3. 6_3. 6_3. 6_3. 6_5. 6_5. 6_5. 6_7. $_7$. 6_7
Note some are catenated 9e.g. magenta and green
Bu not all rings independent magenta is sum of three others. So...



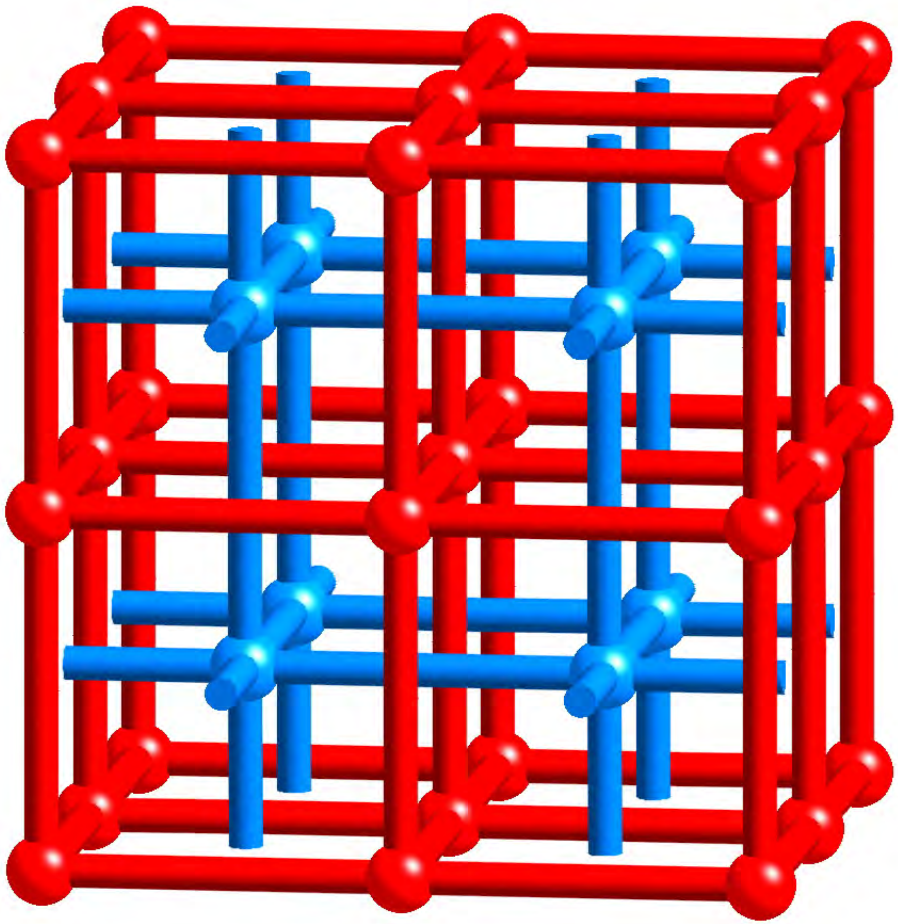
It turns out that **fnu** has a natural tiling
– so the essential rings are not catenated
-so net is not self-catenated?

Blatov, V. A.; Delgado-Friedrichs, O., O'Keeffe, M. & Proserpio, D. M. (2007). *Acta Cryst.* A**63**, 418-425.

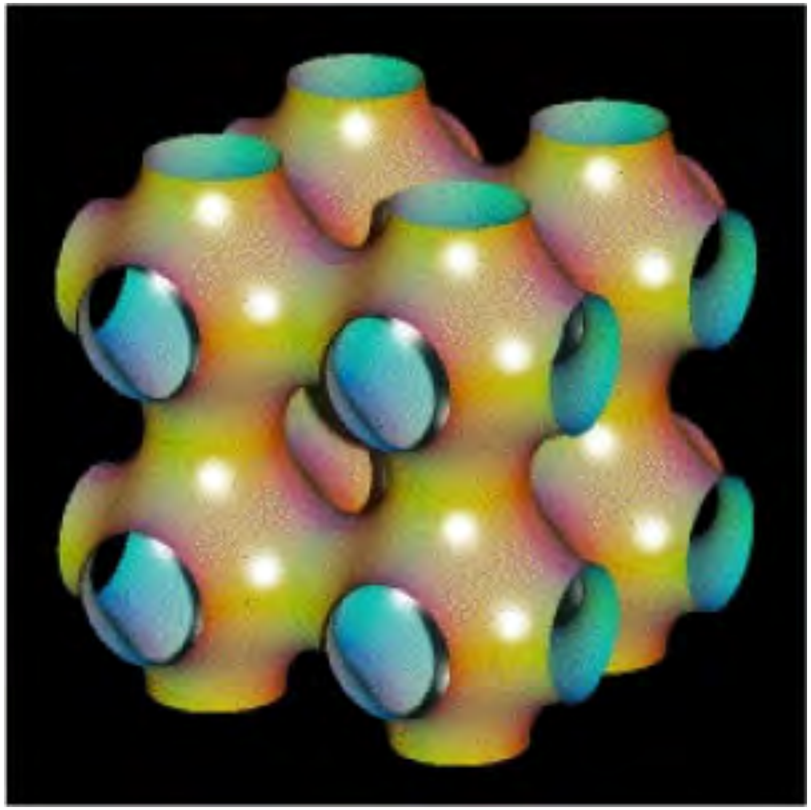
nets as surfaces - minimal surfaces

periodic minimal surface (PMS) divides space into two parts. The surface has zero mean curvature ($k_1 + k_2) = 0$), but negative Gaussian curvature ($k_1k_2 < 0$).
There are 5 PMS of genus 3. They divide two interpenetrating nets of genus 3

net	transitivity	surface
srs	1111	*G*
dia	1111	*D*
pcu	1111	*P*
cds	1221	*CLP*
hms	2222	*H*



Two interpenetrating **pcu** nets



The *P* minimal surface
separates the two nets.
Average curvature zero
Gaussian curvature neg.

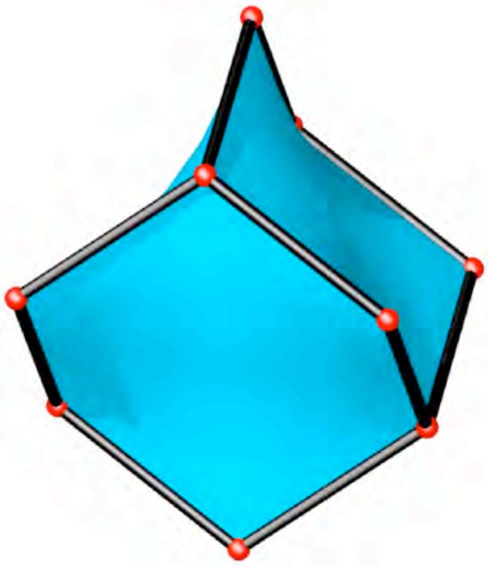
don't confuse two usages of the term "minimal"

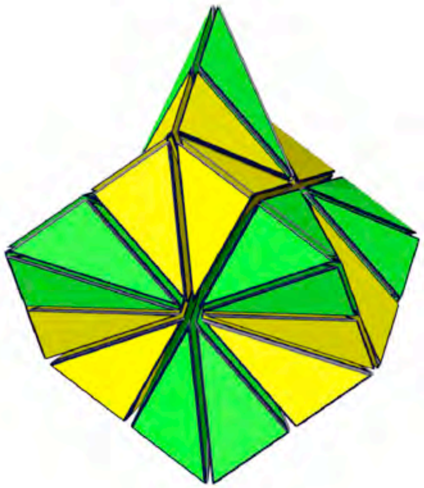
Minimal surface has zero mean curvature $(k_1 + k_2) = 0)$

Minimal net has genus = 3.

There are 5 Periodic Minimal Surfaces of genus 3
but more than five nets of genus 3

nets as surfaces:
the chambers of a tile for a net has vertices on the net and at the center of the tile. If the chambers are considered a tiling, the dual tiling has vertices in the centers of the chambers. I.e. between the net and its dual. We call such a net (derived from **xyz**) **xyz-t**.



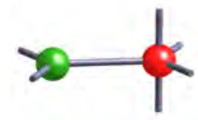


Minimal nets (genus 3). There are 15, of which 7 have collisions.
The collision-free nets are:

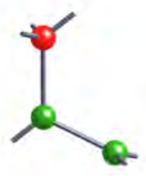
pcu self-dual
net of P

dia self-dual
net of D

cds self-dual
net of CLP

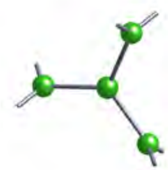


hms self-dual
net of H

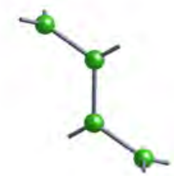


tfa
dual is **dia**

tfc
dual is **pcu**



srs self-dual
net of G



ths
dual is **dia**

BUT only five PMS of genus 3. Why?

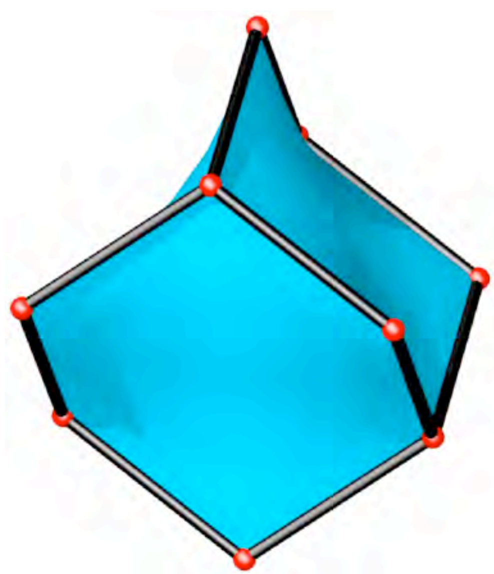
Reminder: periodic minimal surface have positive and negative curvature (or flat points) everywhere

The mean (average) curvature is zero

Reference

Delgado et al *Acta Cryst.* A69, 483 (2013)

We can construct a tiling that approximates
a surface associated with a net as follows.
For a net say **dia** find the tiling (see below) and then
find its chambers (blue and yellow below).
Now use the chambers as a tiling.
Now find the dual. The vertices of the dual are in the
centers of the chambers. I.e. on the surface separating
the original net from its dual.



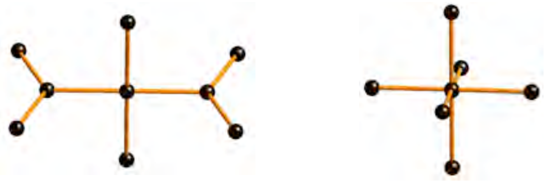
diamond tile

divided into chambers

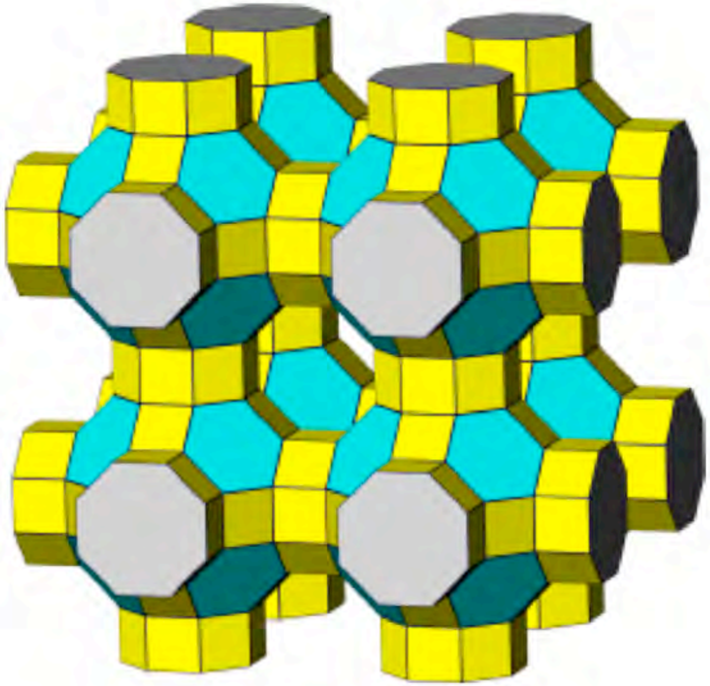
The answer is that more than one net may be the labyrinth of a given minimal surface!

nets ↔ surfaces

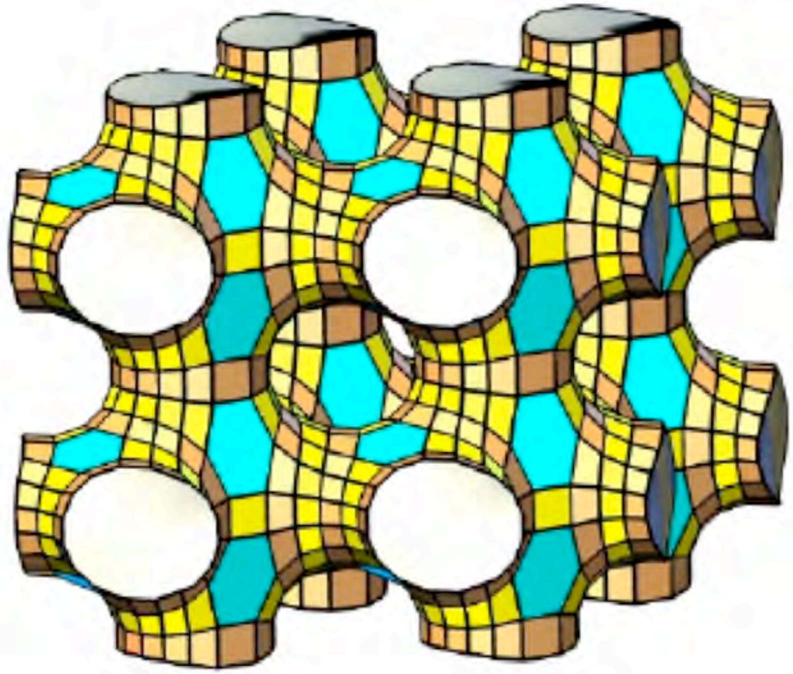
many ↔ one



tfc → pcu



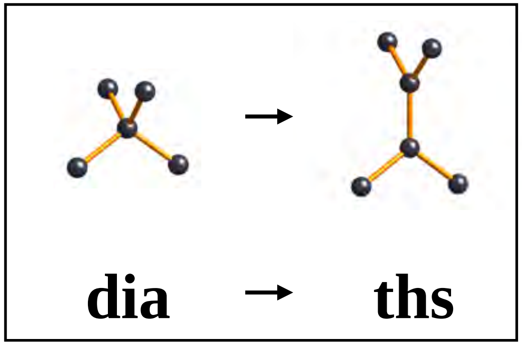
pcu-t = rho

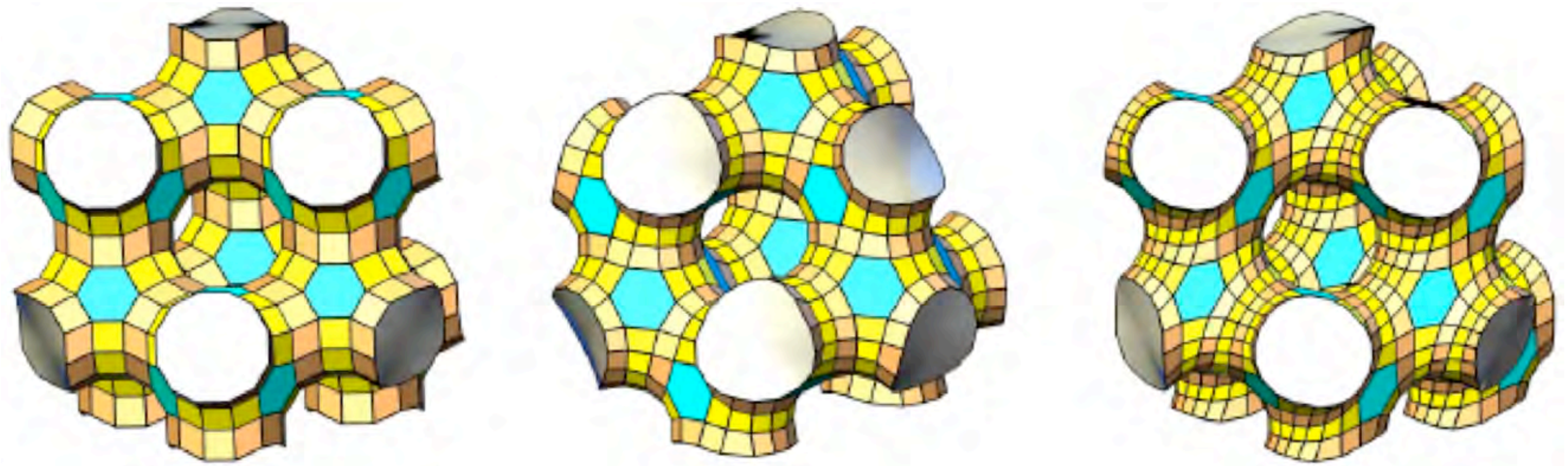


tfc-t

clearly surfaces of the same topology

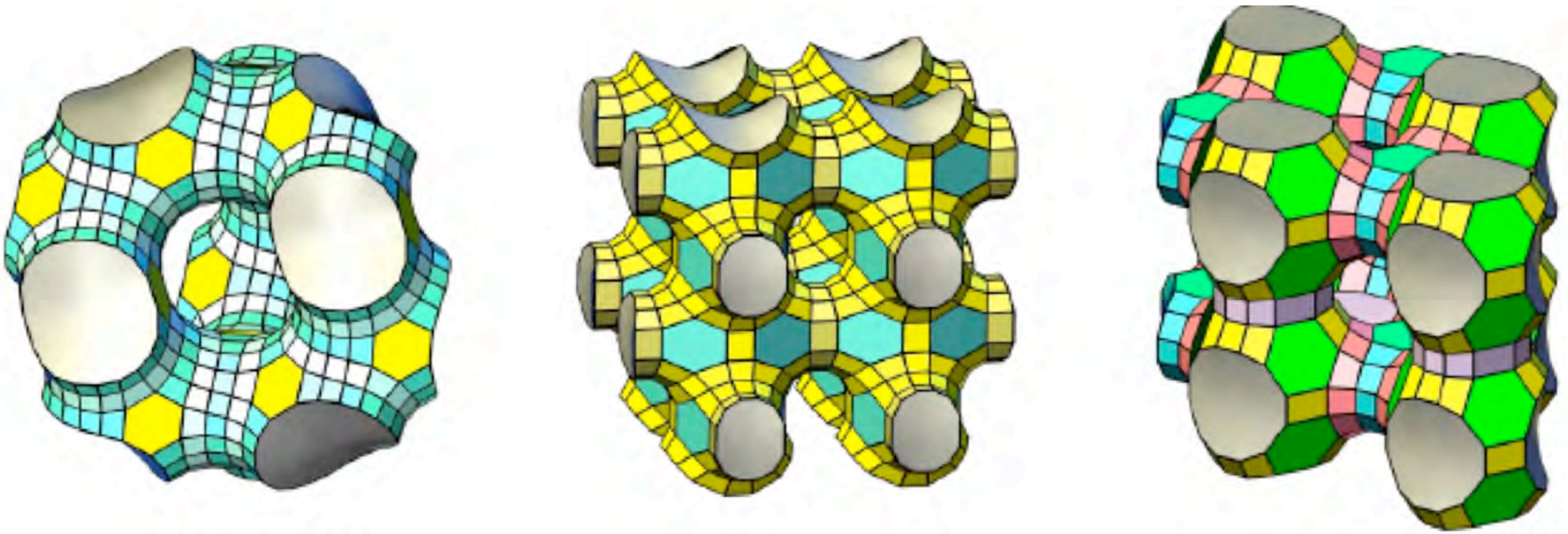
← adamantane unit





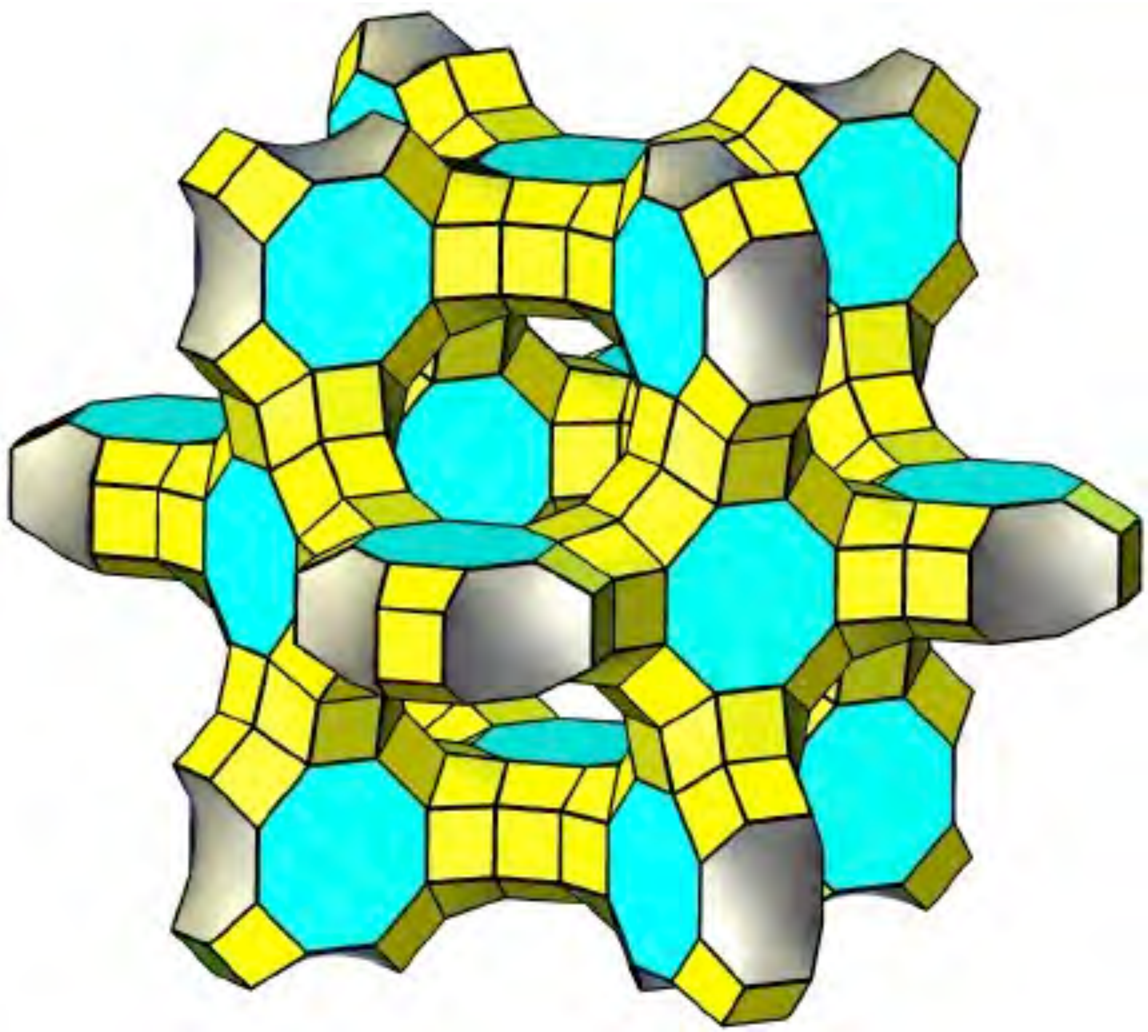
dia-t = fuf **tfa-t** **ths-t**

again surfaces of the same topology



srs-t (G) **cds-t** (CLP) **hms-t** (H)

Note: that *G* is the surface of most 3-periodic mesoporous materals (a few are *D*). but….



bcu-t = **nbo-t** surface is the *IWP* minimal surface of genus 4

Summary. Most important minimal surfaces

All minimum surfaces of genus 3

P	net **pcu** (also **tfc**)
D	net **dia** (also **tfa**, **ths**)
G	net **srs**
H	net **hms**
CLP	net **cds**

Genus 4

IWP nets **nbo**/**bcu**

Nets with collisions (unstable nets) and crystal chemistry

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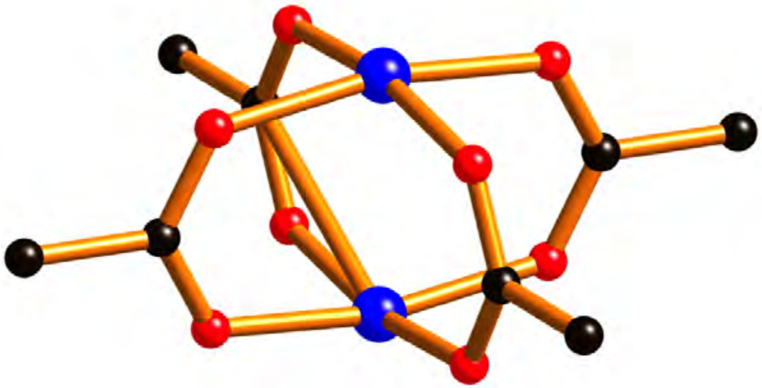
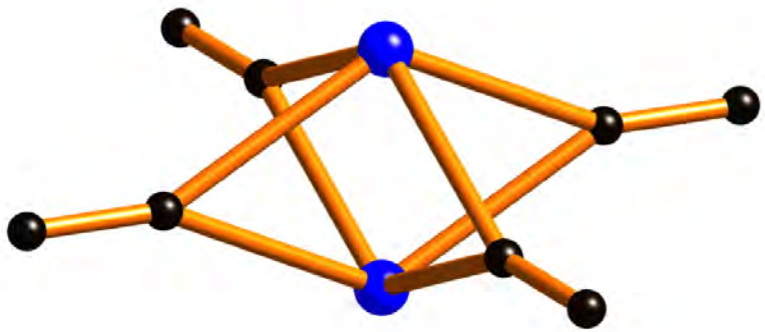
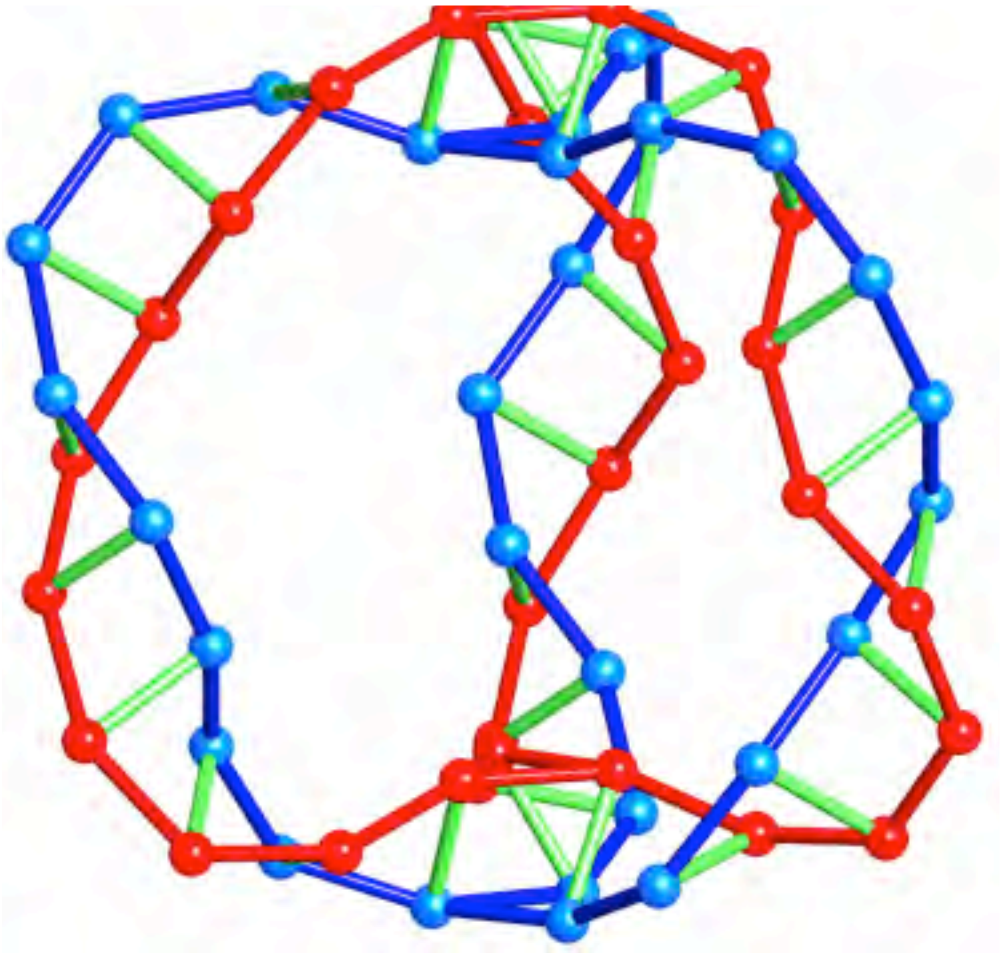
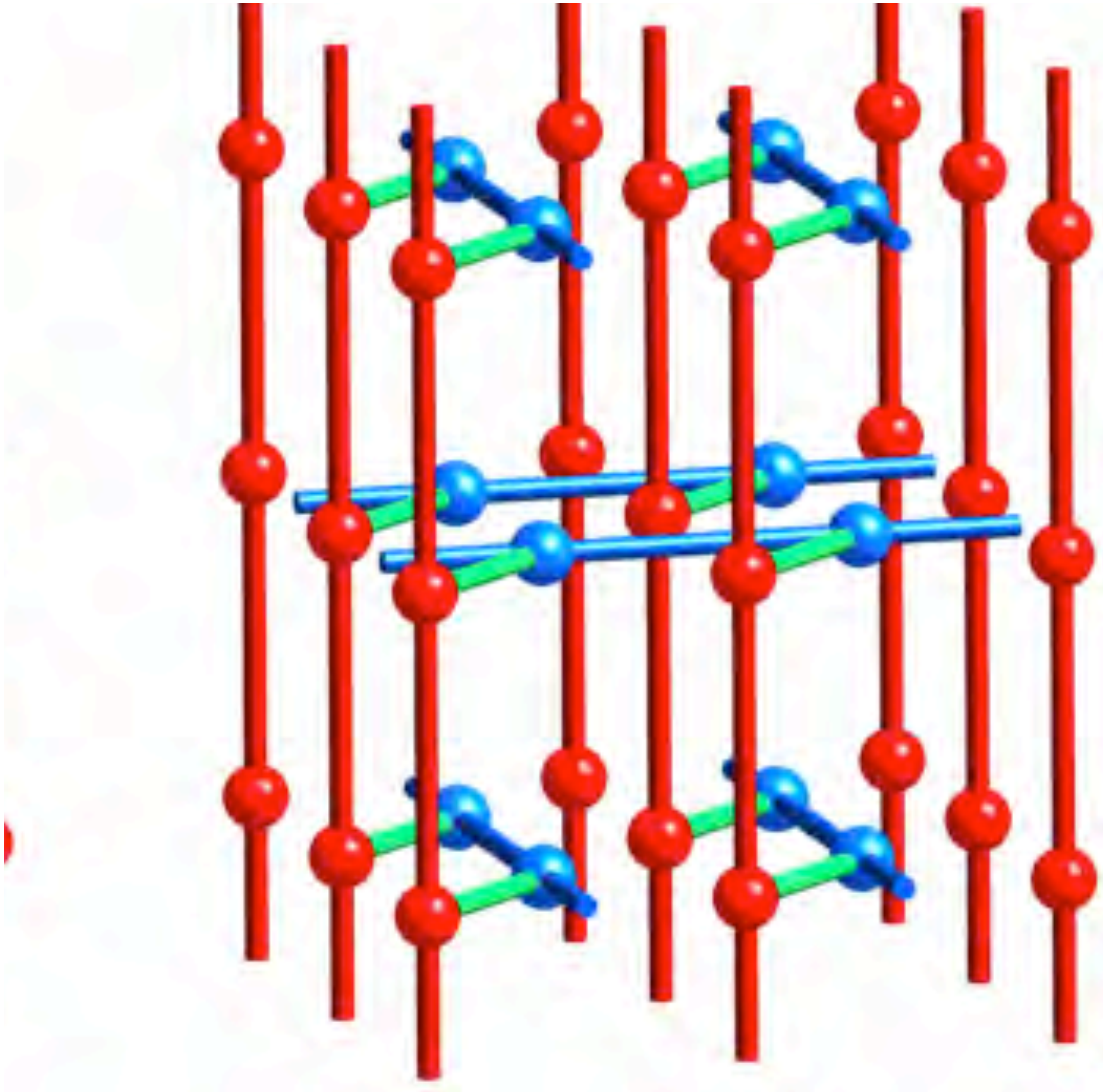
 

If we take net of all atoms, paddlewheel has collisions

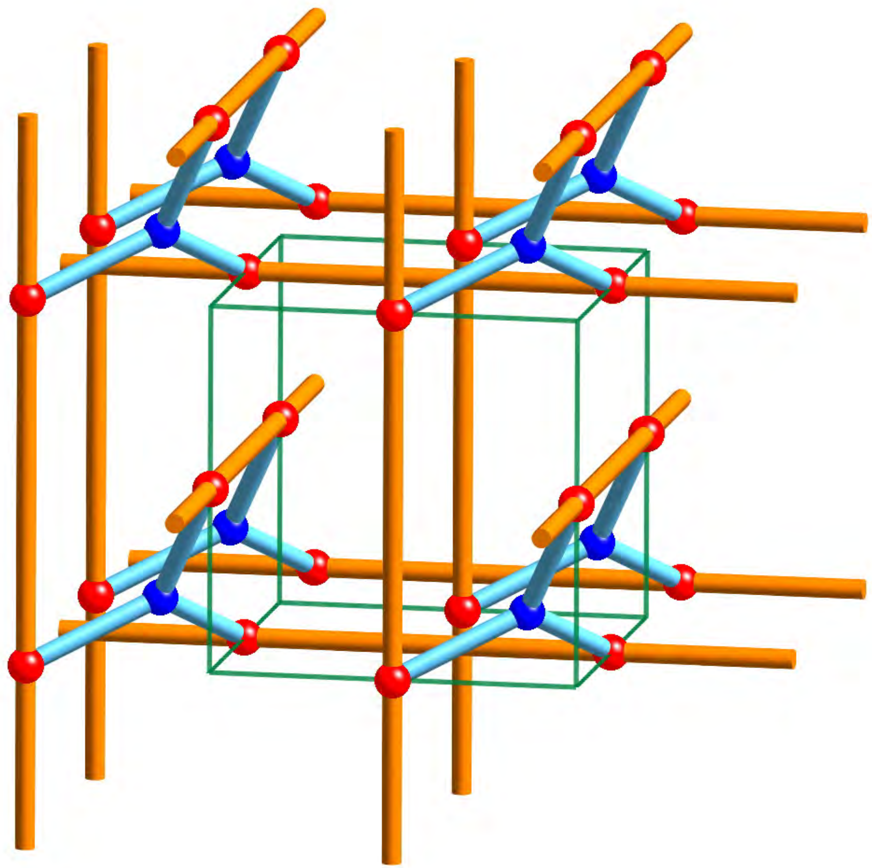


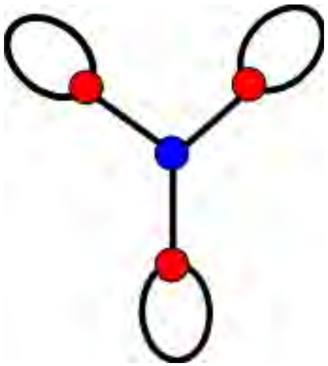
example of a ladder. Note uninodal 4-c net



example of an “anti-ladder”

a minimal net with collisions.

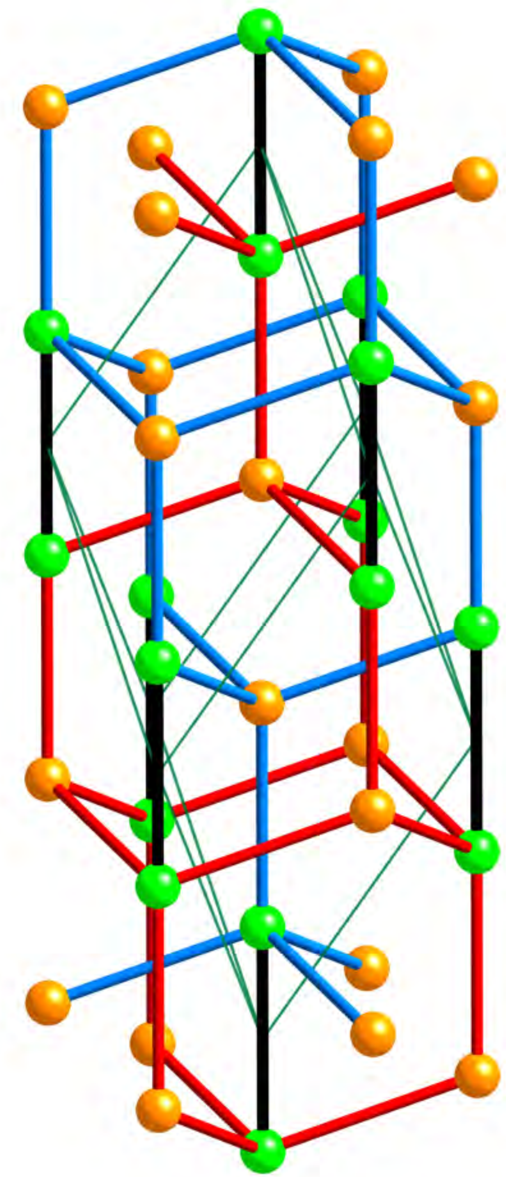




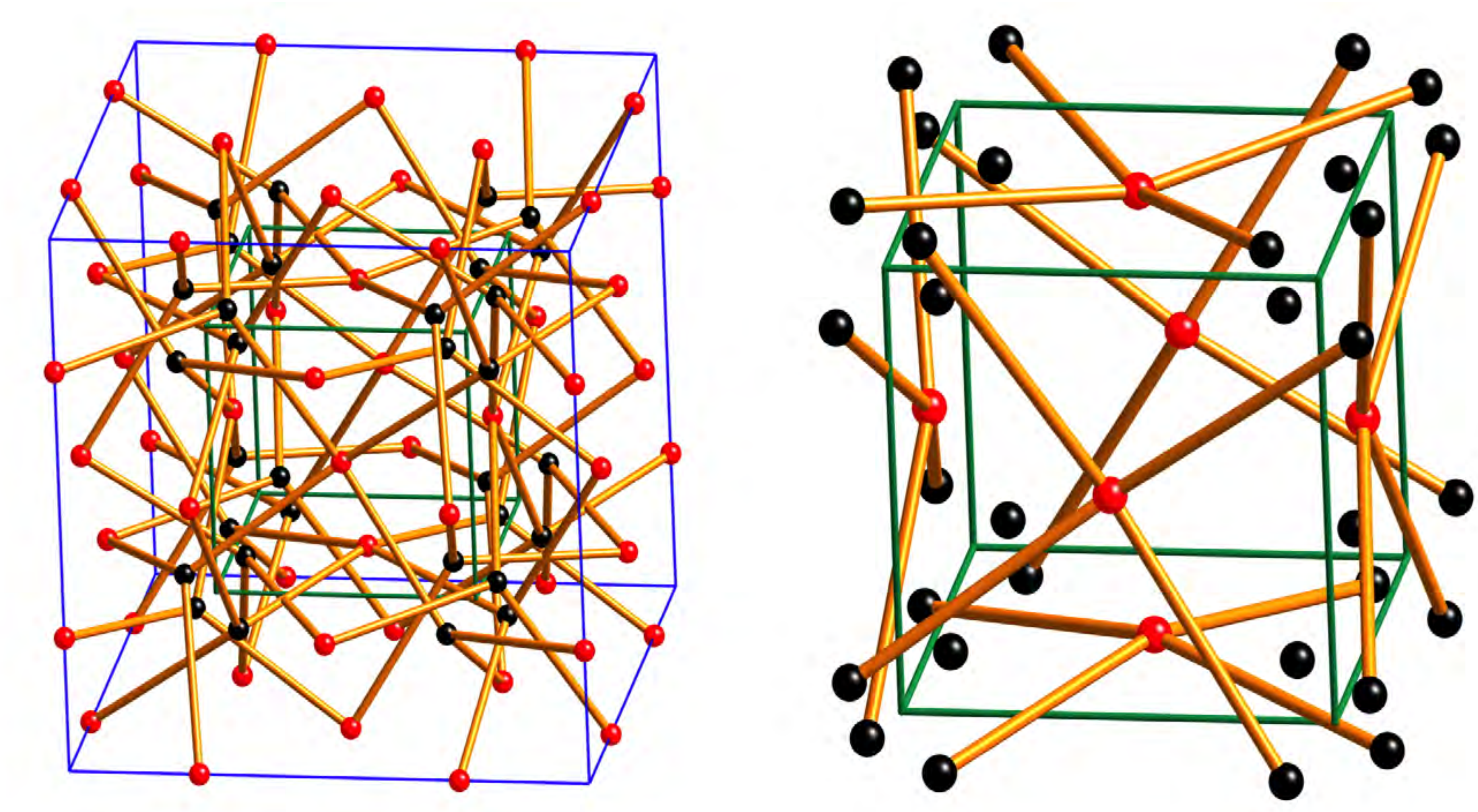
quotient graph

two intwrpwnwtrating diamonds linked.

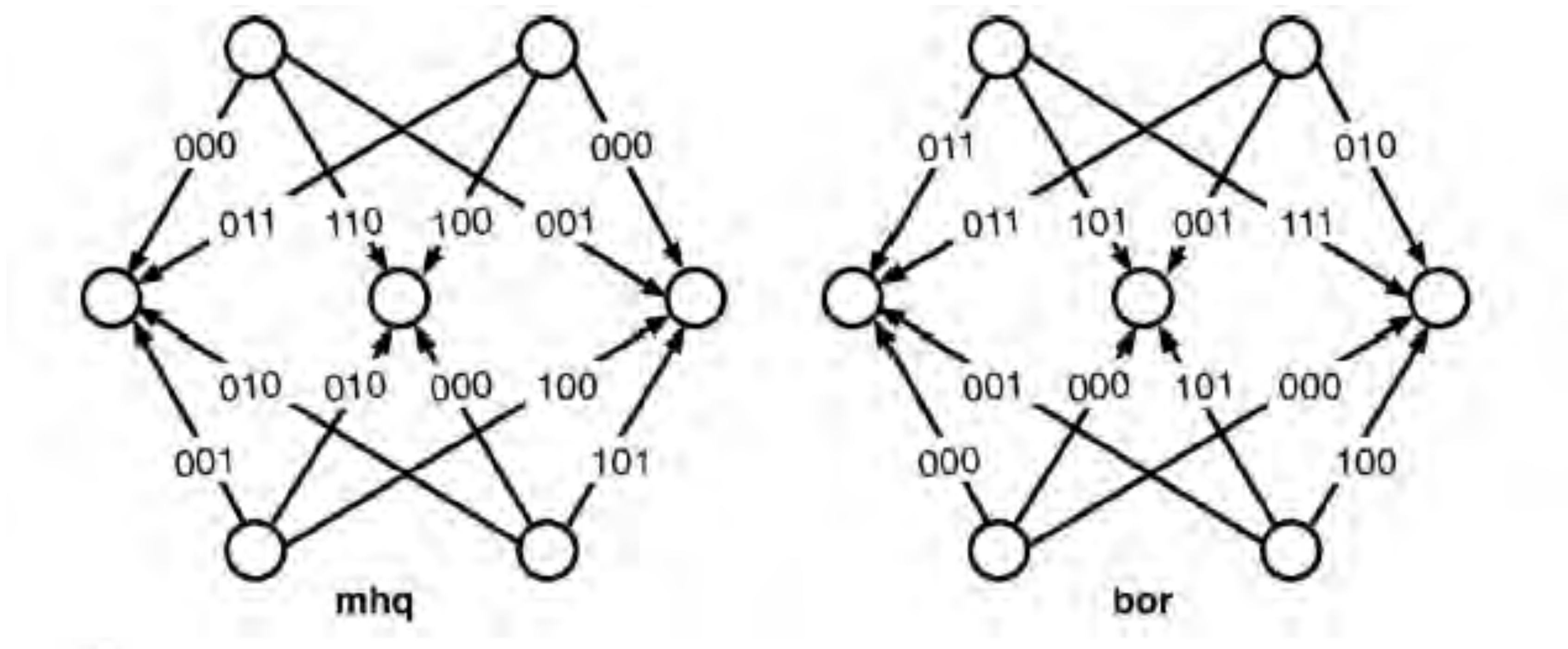
If the blak links go to zero length, vertices collide, symmetry is higher arrangement of points same as in CaF_2 (**flu**)



net **mhq**



A (3-4)-c edge-transitive net (Blatov, Sun et al.).
Embeddin in *F*432. In P432 **a’** – **a**/2) vertices collide



Two quotient graphs that are labelled $K_{3,4}$.
Graphs are edge-transitive

end