TECHNISCHE UNIVERSITÄT DRESDEN

A group-theoretical approach to interpenetrated networks

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Outline

- Symmetry properties of interpenetrating nets
- Generation of interpenetrating nets using group–supergroup relations: fundamentals
- Working examples to derive new interpenetration patterns
- Maximal isometry groups of interpenetrating networks
- Interpenetrated 2-periodic nets (layers), polycatenanes *etc*.

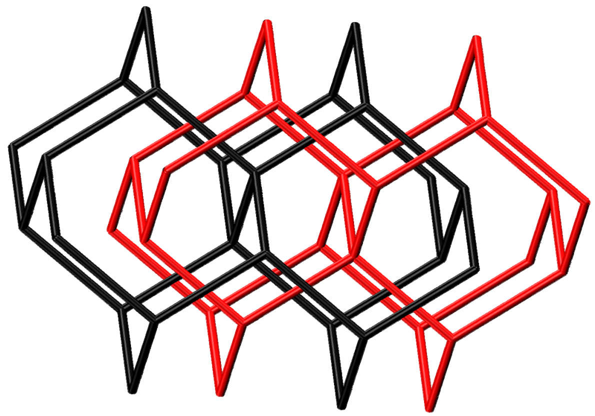
What is a *net* (network)?

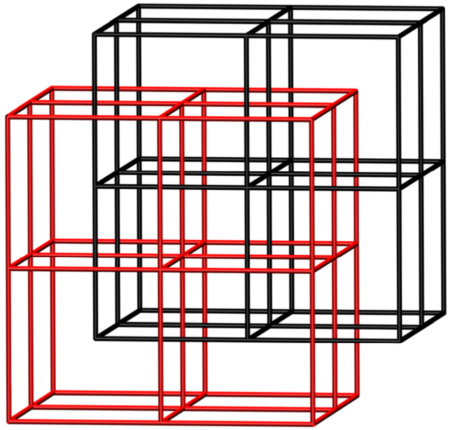
- A net Γ is a graph that is connected, simple, locally finite
- A net Γ is called ***periodic*** if its automorphism group Aut(Γ) contains Z^n (n≥1) as a subgroup (usually of finite index)
  → ***n-periodic*** nets (graphs); we will focus on ***n* = 2, 3**
- Aut(Γ) (all its 'symmetries') is considered (as usual) as a group of adjacency-preserving permutations on the vertex set of Γ
- In most cases of interest Aut(Γ) is isomorphic to a ***crystallographic group***, and there exists an ***embedding*** of Γ in R^3 where *all* automorphisms can be realized as ***isometries*** → *we mostly work with embeddings in* R^3

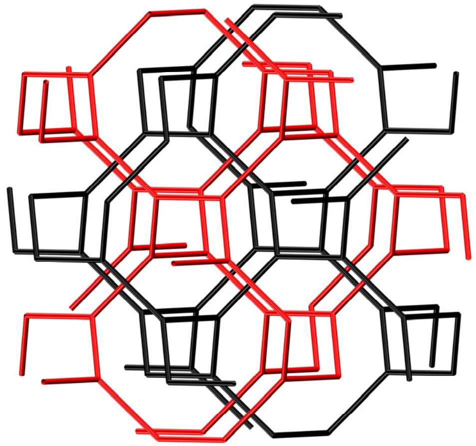
Cf. Delgado-Friedrichs & O'Keeffe, J. Solid State Chem., ***2005****, 178, 2480-2485*

Interpenetration of 3-periodic nets

Common interpenetrating 3-periodic nets

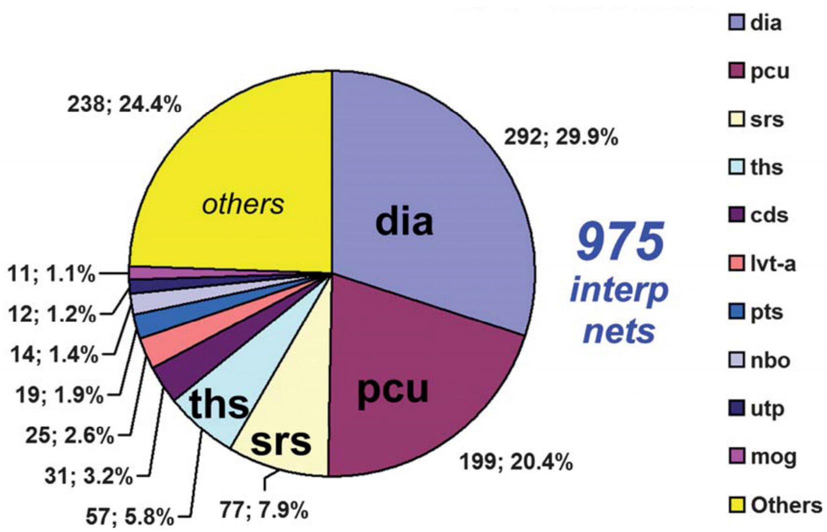


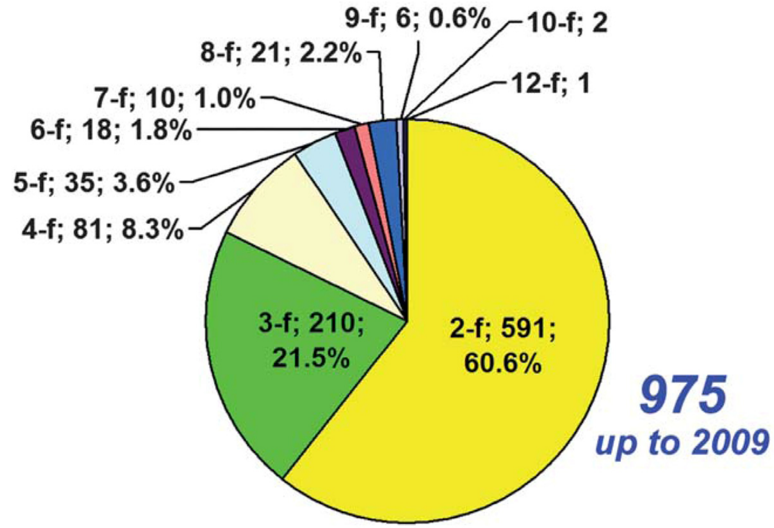




dia-c **pcu-c** **srs-c**

Occurrence of nets in 3D interpenetrated coordination polymers





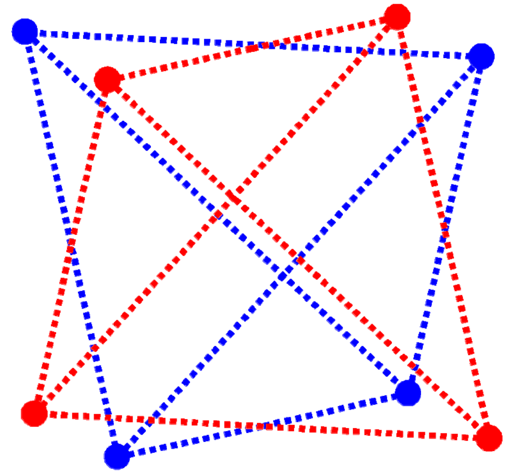
Blatov, Proserpio et al., CrystEngComm ***2011****, 13, 3947*

Properties of symmetry-related interpenetrating nets

- A symmetry group ***G*** acts transitively on a set of nets $\{\Gamma_i\}$, $i = 1,..n$;
- A group ***H*** maps an arbitrarily chosen net Γ_i onto itself; the index $|\boldsymbol{G} : \boldsymbol{H}| = n$

Finite example:

Cube as two *tetrahedra*: $m\bar{3}m$ - $\bar{4}3m$



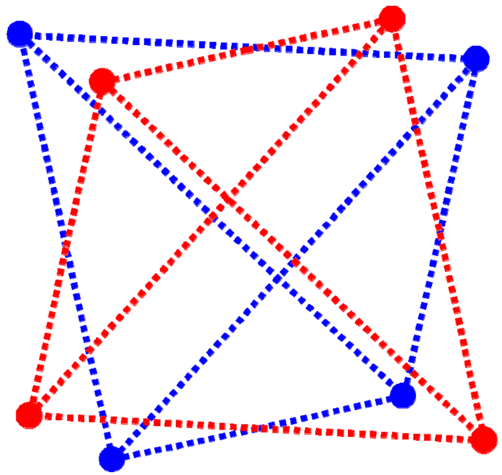
- It is therefore convenient to use a ***group–subgroup pair G – H*** to characterize the symmetry of interpenetrating nets.

Baburin, Acta Cryst. Sect. A ***2016****, 72, 366-375;*

Koch et al., Acta Cryst. Sect. A ***2006****, 62, 152-167*

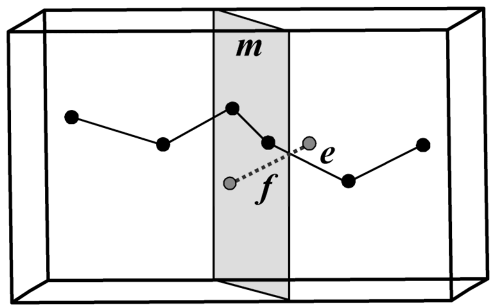
Properties of symmetry-related interpenetrating nets

Lemma*.** Let $\{\Gamma_i\}$ be a set of n nets Γ_i (i = 1, 2. . .n) which form an orbit with respect to a symmetry group ***G of the whole set. The elements of G which map a net Γ_i onto itself form a group H. Then ***stabilizers of vertices and edges*** of Γ_i in ***H*** are ***isomorphic*** to those in the group ***G***.



Stabilizers are the same in a group and a subgroup:

$$\left.\begin{matrix} m\bar{3}m \\ \bar{4}3m \end{matrix}\right\} \text{vertex: } .3m\ (C_{3v}),\ \text{edge: } 2.mm\ (C_{2v})$$



***Theorem*.** The cosets of H in G do not contain *mirror* reflections (non-intersection requirement)

***Remark*.** The cosets of H in G do not contain any rotation or roto-inversion axes which intersect vertices and/or edges of the nets.

*Baburin, Acta Cryst. Sect. A **2016**, 72, 366-375*

Generation of interpenetrating nets: the *supergroup* method

- Fix an embedding of a 3-periodic net Γ_1 in R^3, let H be its symmetry group

- Replicate Γ_1 by a supergroup G_k of H with index n ($g_n \in G_k$):
  $G_k \cdot \Gamma_1 = (H \cup g_2 \cdot H \cup \cdots \cup g_n \cdot H) \cdot \Gamma_1 = \Gamma_1 \cup \Gamma_2 \cup \cdots \cup \Gamma_n$

- Characterize interpenetrating nets which arise for different supergroups G_k (k = 1,..m) with respect to *isotopy classes* and *maximal (intrinsic)* symmetry groups

How to determine supergroups? How to find H?

*Baburin, Acta Cryst. Sect. A **2016**, 72, 366-375*

Group–subgroup vs. group–supergroup relations

- Let $H < G$, $n = [G : H]$ is finite
- How to find *all* supergroups of H isomorphic to G?

- Take a list of subgroups of G with index n. Filter out subgroups isomorphic to H.
- For each subgroup determine affine normalizers $N(H)$.
  Consider $M = N(H) \cap N(G)$.
- In each case the number of supergroups isomorphic to H is given by the index $[N(H) : M]$ – it can be infinite!
- Generate the orbit of supergroups by applying the elements of $N(H)$.

Aroyo et al. Phys. Rev. B., 1996, 54, pp. 12744-12752

Which groups *H* to take?

- *H* is a symmetry group of a net embedding
- *H* ≤ Aut(net); Aut(net) = the automorphism group of a net

- Aut(net) is usually isomorphic to a crystallographic group, and can be found using the method of Olaf Delgado
- *H* is a subgroup of Aut(net) with a finite index
- Restrict the number of vertex orbits: consider ***minimal groups*** with a specified number of vertex orbits

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- *H*'s are subgroups of Aut(net) with the desired number of vertex orbits

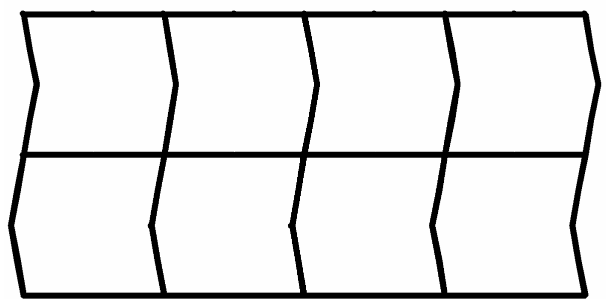
- Vertex-transitive nets: ***minimal vertex-transitive groups*** (vertex stabilizers are either trivial or have order 2 in R^3)

Groups *H*'s are fixed – what else?

- Complication: the symmetry group *H* usually does not fix the embedding of a net up to similarity (or even up to isotopy)
- A net can undergo deformations allowed by *H:* *subgroup-allowed deformations*

- The shape of ***edges***: ***straight lines*** or arbitrary ***curved*** segments?

- A solution for practice: keep the embedding in *H* as in the full automorphism group
- Edges are either straight-line segments or V-shaped, ***as allowed by edge stabilizers***

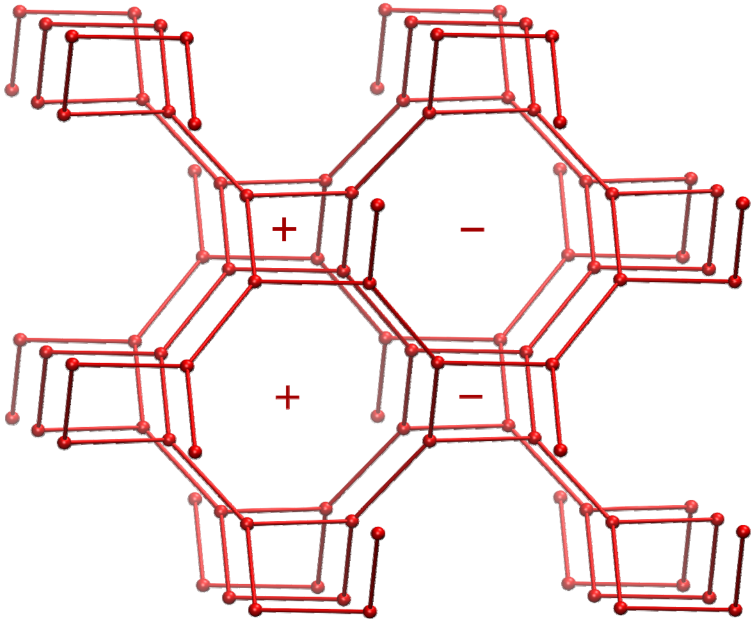


Towards an algorithm

- Find *H*'s up to conjugacy in Aut(net) – GAP (Cryst, Polycyclic)
- For each group *H* list all supergroups G_k (k = 1,..m) with index *n* (*m* can be infinite for fixed *n – so be careful*) – GAP (Cryst, Carat)
- Take advantage of the restrictions: additional mirrors or other rotation or roto-inversion axes which intersect vertices or edges of the net(s) must ***not*** belong to the supergroups G_k
- Transform the coordinates of vertices and edges from a basis of a group to that of a supergroup (take care that ***stabilizers*** of ***vertices and edges*** should be the ***same*** in both *H* and G_k)
- Classify into patterns (Hopf ring nets, TOPOS)

*Baburin, Acta Cryst. Sect. A **2016**, 72, 366-375*

Example: the (10,3)-*d* net (**utp**) and its 2-fold intergrowths: only *three* possibilities



Space group: ***Pnna*** [=Aut(**utp**)]

Vertex Stabilizer: trivial

Admissible supergroups of index 2:

Ccce, Pcca, Pban

cf. International Tables for Crystallography, Volume A1

Minimal non-isomorphic *klassengleiche* supergroups

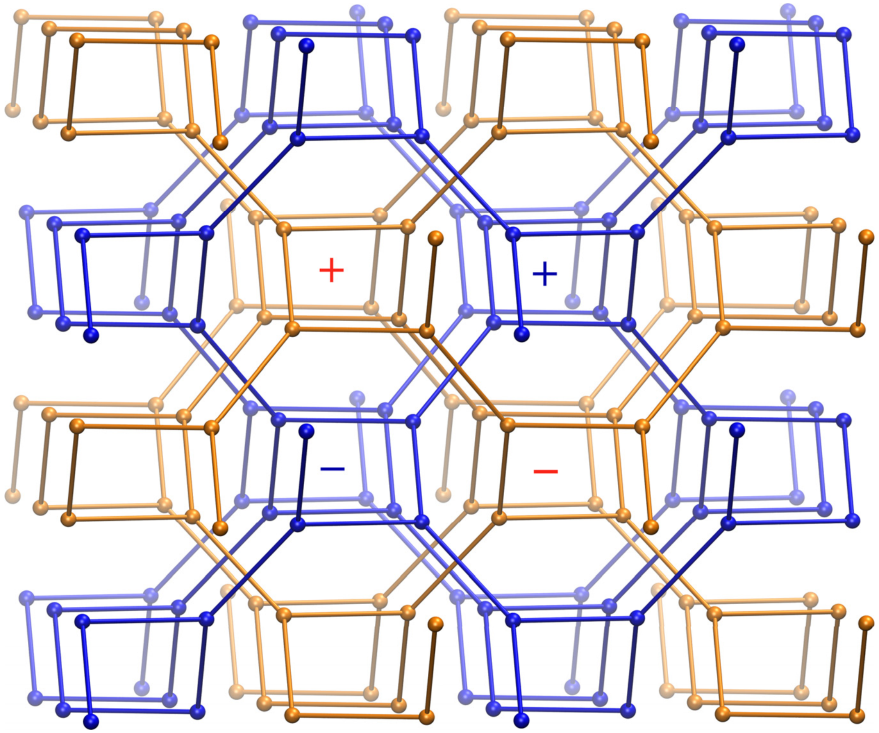
- **Additional centring translations**

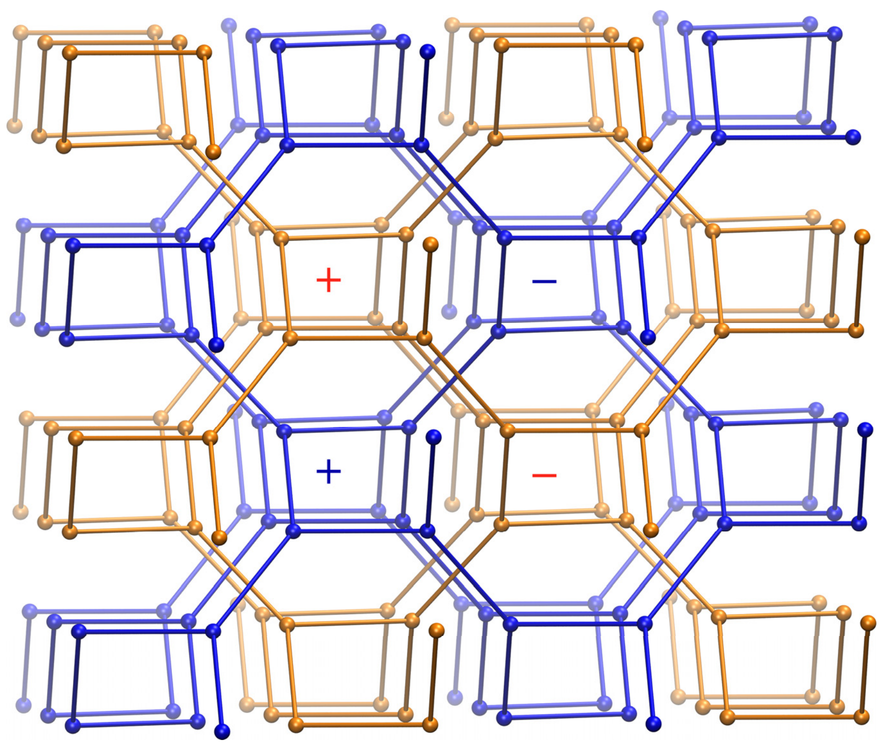
[2] ~~*Bbmm* (63, *Cmcm*)~~; [2] ~~*Amaa* (66, *Cccm*)~~; [2] *Ccce* (68); [2] ~~*Imma* (74)~~

- **Decreased unit cell**

[2] ~~$\mathbf{a}' = \frac{1}{2}\mathbf{a}$ *Pncm* (53, *Pmna*)~~; [2] $\mathbf{b}' = \frac{1}{2}\mathbf{b}$ *Pcna* (50, *Pban*); [2] $\mathbf{c}' = \frac{1}{2}\mathbf{c}$ *Pbaa* (54, *Pcca*)

Example: the **utp** net and its intergrowths





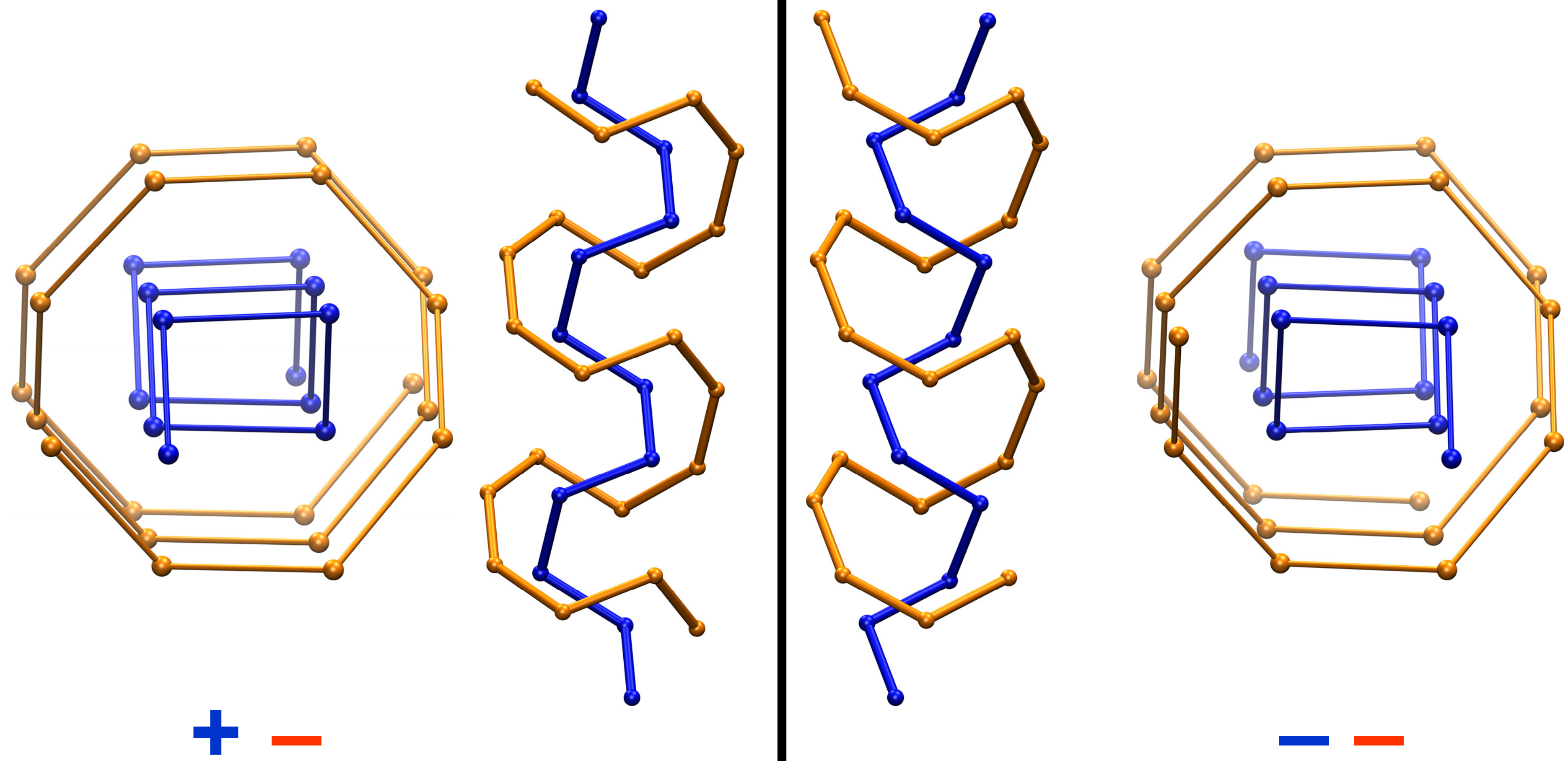
+ −	+ −
+ −	− +

Ccce* – *Pnna

+ +	− −
+ +	− −

***Pcca* – *Pncn* (2b)**

Example: the **utp** net and its intergrowths



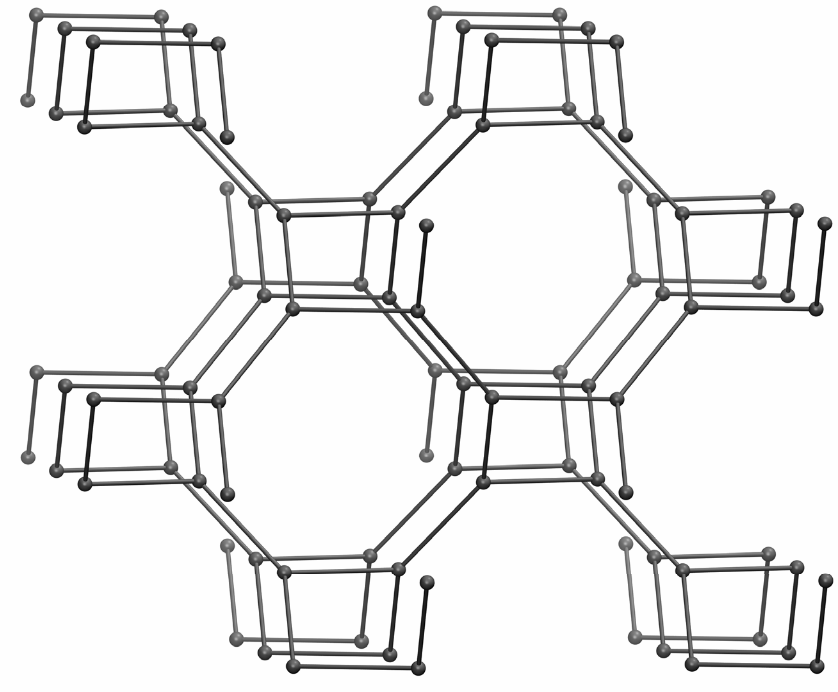
Ccce ***Pcca***

different handedness

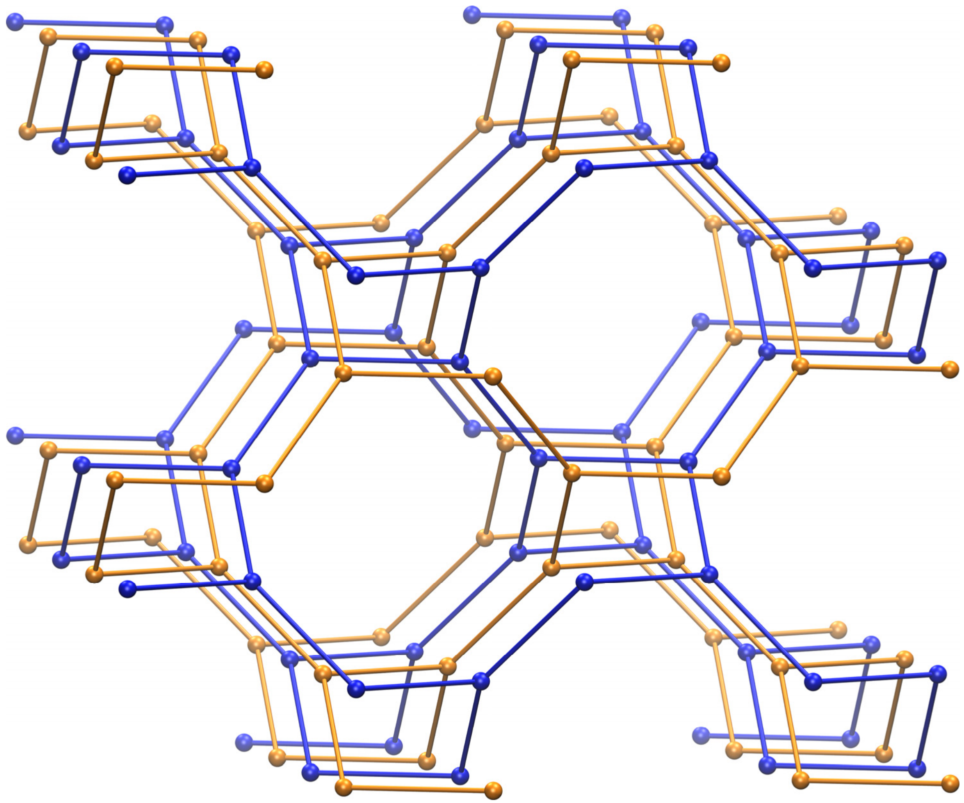
~10 (isostructural) examples in CSD

1 related structure in CSD

Example: the **utp** net and its intergrowths



Pnna



***Pban – Pnan* (2c)**

1 related structure in CSD

Classifying and characterizing interpenetrating nets

- Now we can generate embeddings of interpenetrating nets

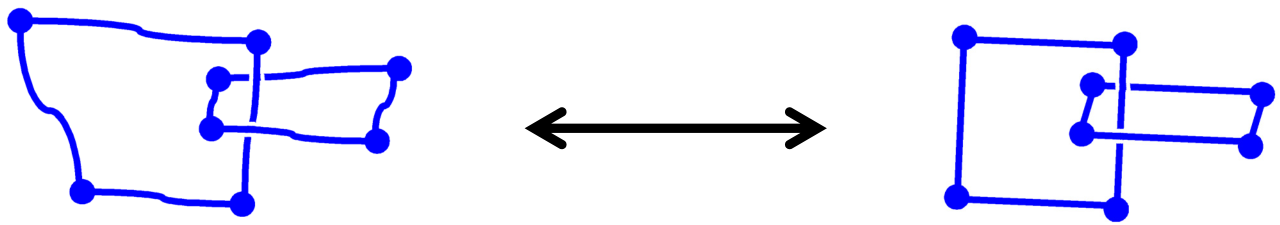
- Every embedding is characterized by a group–subgroup pair G – H *(and it is known by construction)*

- How to recognize *isotopy classes* of interpenetrating nets?

- How to find a maximal isometry group for each isotopy class? $G - H \rightarrow G_{max} - H_{max}$

Catenation patterns (= *isotopy classes*)

- Two sets of interpenetrating nets are said to show the same ***catenation*** (or ***interpenetration***) ***pattern*** (= belong to the same ***isotopy class***) if they can be deformed into each other without edge crossings (more precisely, in this case knot theorists speak of ***ambient isotopy****)



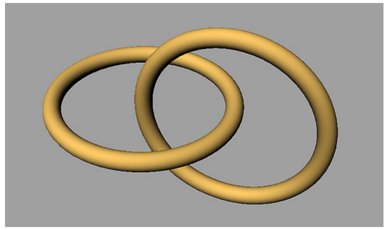
- This may be difficult to check by 'inspection' →

  look at *local* properties of catenation ("knotting"), *i.e*. how cycles (= *rings*) of nets are catenated. If cycles are catenated differently, then the patterns are distinct.

** Cromwell, Knots and Links, Cambridge University Press, 2004*

Hopf ring net (HRN): a tool to classify catenation patterns

- ***Vertices***: barycenters of catenated rings
- ***Edges***: stand for Hopf links between the rings



- Describes the catenation pattern if all links are of Hopf type:

if HRNs are not isomorphic, then the patterns are different

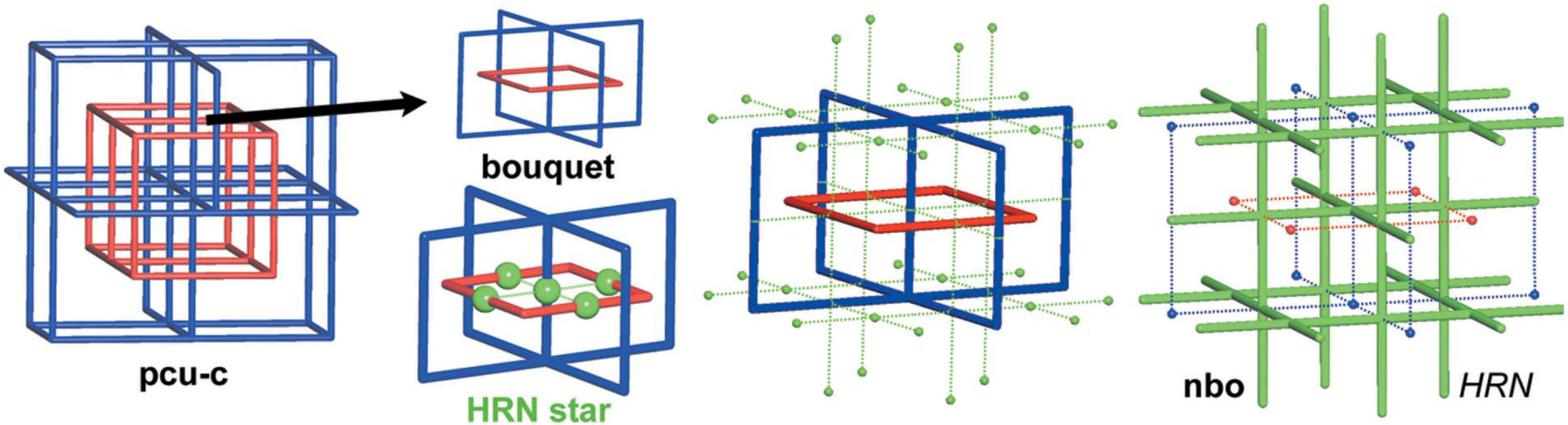


*Fig. 2 from Alexandrov, Blatov, Proserpio, Acta Cryst. Sect. A **2012**, 68, p. 485*

Hopf ring net (HRN)

- The valencies of vertices describe the “density of catenation”
- Given isomorphism type of a network, does there exist an upper bound for the valencies of vertices in the respective HRN if the number of networks in the set is fixed? (In other words: are there any combinatorial restrictions on the “density of catenation”?)
- The answer is no

Infinite series of non-isotopic patterns

pcu in monoclinic symmetry: $P2/m$, x=0, y=0, z=0; $a = b = c$; $\beta = 90^\circ$

(vertex-transitive, edge 3-transitive)

- Basis transformation: –n 0 –1 / 0 1 0 / 1 0 0

  $\beta = \mathrm{acos}(-n/\mathrm{sqrt}(n^2 + 1))$

- Deform the net by setting $\beta = 90^\circ$ again (a series of deformations)
- Apply supergroup operations (*e*.*g*. a 2-fold screw parallel to [100], *i*.*e*., original [-n 0 -1] direction)

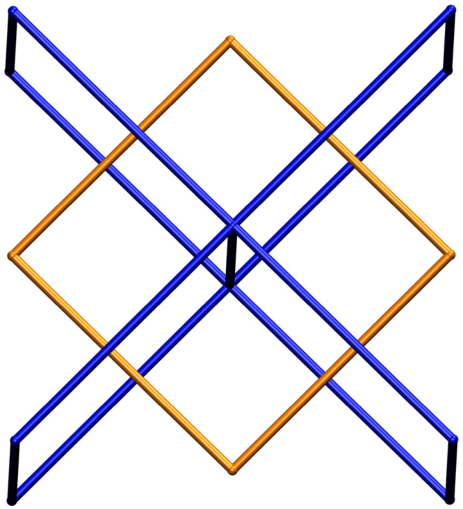
n = 0 -> $P\,2_1/n\;2/m\;2_1/n$ – $P2/m$ (**pcu-c** pattern)

n = 1 -> $P\,2_1/b\;2/m\;2/n$ – $P2/m$ (more ‘knotted’ pattern)

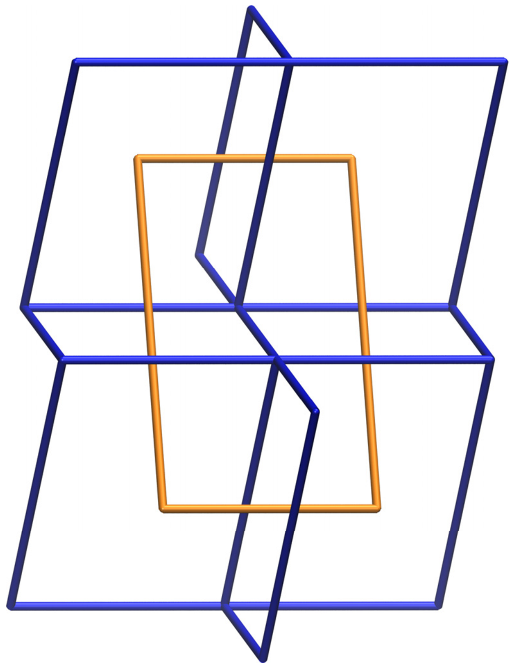
n = 2 -> $Pnmn$ – $P2/m$

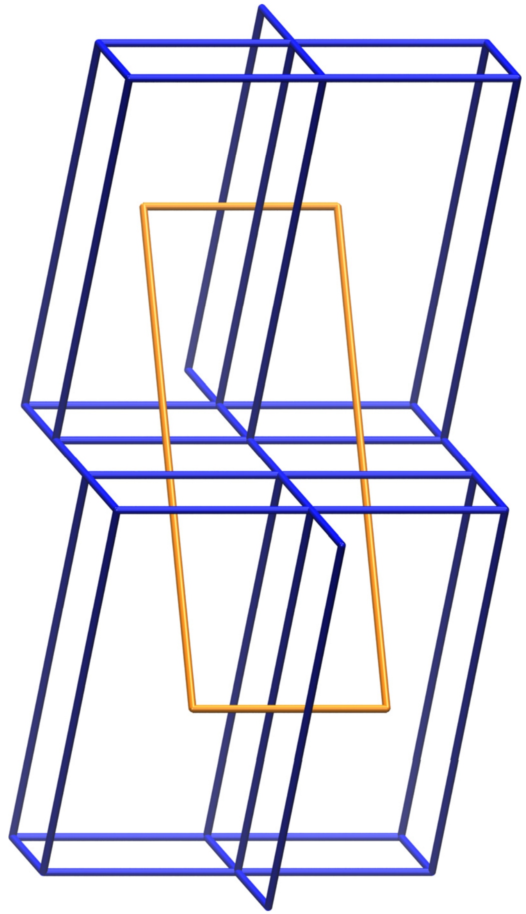
n = 3 -> $Pbmn$ – $P2/m$, ……….

Infinite series: local catenation



pcu-c





4 rings catenate the central

8 rings catenate the central

12 rings catenate the central

and so on…

More on Hopf ring nets (HRN)

- If HRN net is connected and Aut(HRN) is isomorphic to a crystallographic group, it is easy to show that the maximal symmetry G_{max} for a set Γ of interpenetrating nets Γ_i (i = 1,..n) is a subgroup of Aut(HRN): $G_{max} \leq$ Aut(HRN)

  This holds for ***any*** patterns (*i*.*e*., transitive or not)

- For transitive patterns: the index $|G_{max} : H_{max}| = n$

- For transitive patterns: G_{max} is determined based on subgroup relations between Aut(HRN) and Aut(Γ_i)

Baburin, Acta Cryst. Sect. A ***2016****, 72, 366-375*

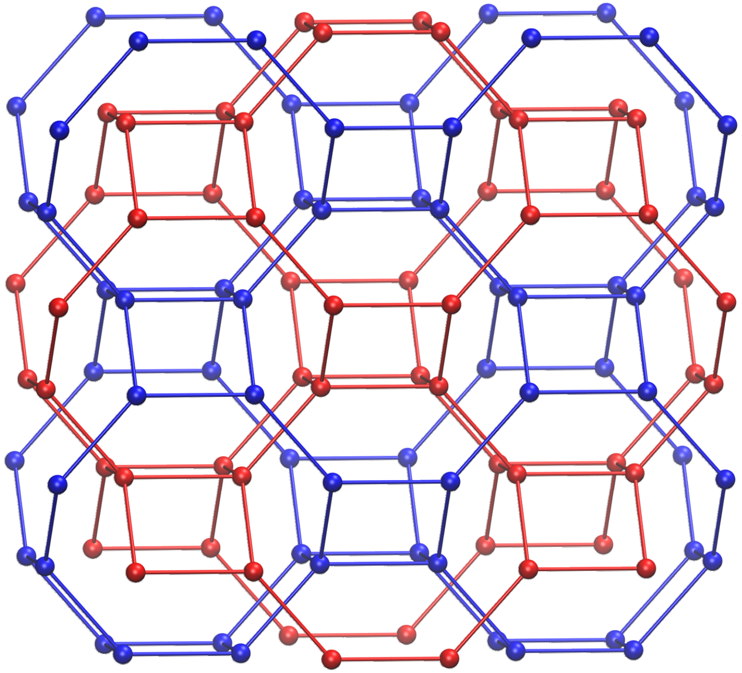
On the maximal symmetry of a set of interpenetrating nets $G_{max} – H_{max}$

- In general: $G_{max} \leq$ Aut(HRN); $H_{max} \leq$ Aut(Γ_i)
- Look for the intersection group(s) K = Aut(Γ_i) ∩ Aut(HRN)
- If the index |Aut(HRN) : K| = n (the number of connected components), then G_{max} is found: G_{max} = Aut(HRN); $K = H_{max}$

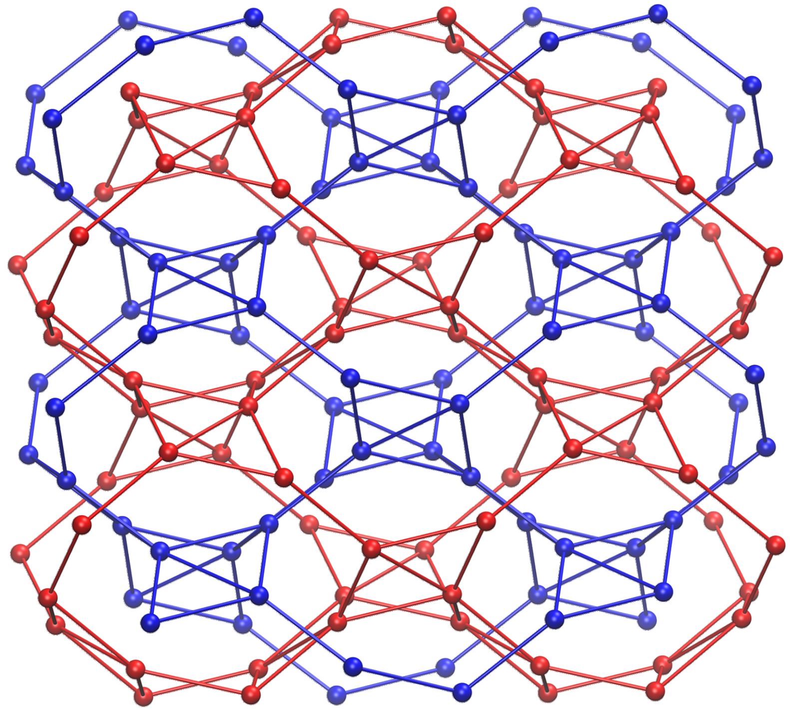
- If not, then suppose H_{max} = Aut(Γ_i). To find G_{max}, look for supergroups of Aut(Γ_i) with index n which have a subgroup relation to Aut(HRN)
- If supergroup search for Aut(Γ_i) is not successful [or does not make sense if Aut(HRN) ≤ Aut(Γ_i)], it has to be performed for subgroups of Aut(Γ_i)

*Baburin, Acta Cryst. Sect. A **2016**, 72, 366-375*

Example: a pair of gismondine (**gis**) networks



$P4_2/nnm - I4_1/amd$



$I4_1/acd - I4_1/a$

Aut(**gis**) = $I4_1/amd$; Aut(HRN) = $Pn3m$; Aut(HRN) ∩ Aut(**gis**) = $I4_1/amd$.

|Aut(HRN) : Aut(**gis**)| = 6 → G_{max} ≠ Aut(HRN).

The only supergroup of Aut(**gis**) = $I4_1/amd$ with index 2 is $P4_2/nnm$ (that is in turn a subgroup of Aut(HRN) = $Pn3m$ with index 3).

*Baburin, Acta Cryst. Sect. A **2016**, 72, 366-375*

2-fold vertex-transitive **dia** nets

Assumptions:

(i) vertex stabilizer has order ≥ 2

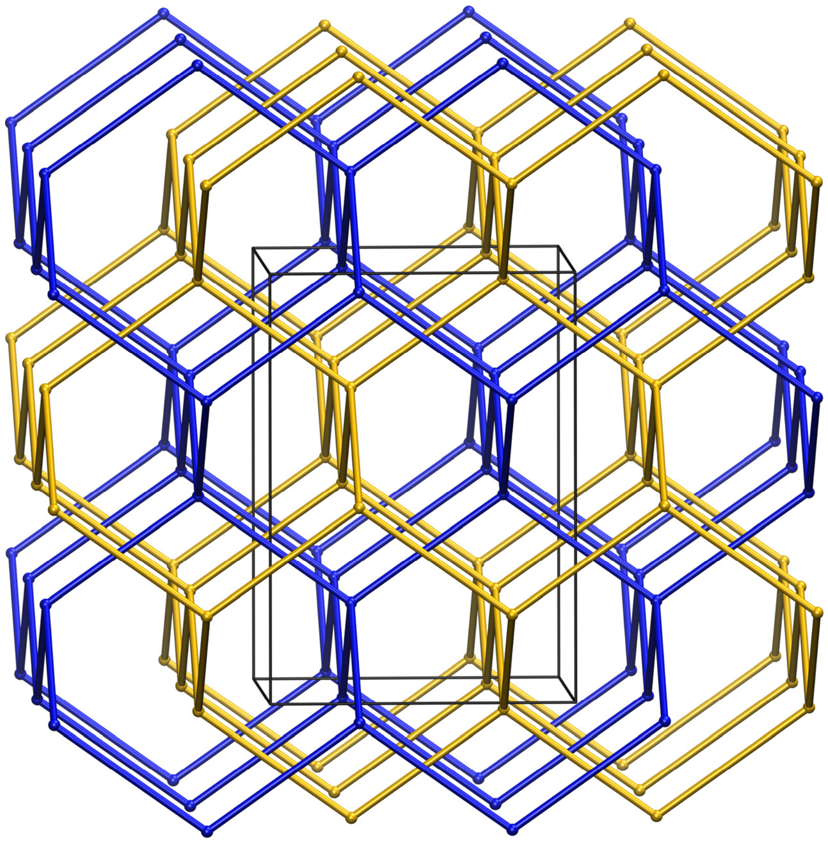
(ii) vertices can be displaced from their ideal positions as allowed by stabilizers, V-shaped edges and lattice mismatch are allowed

There are 8 patterns + 2 infinite series

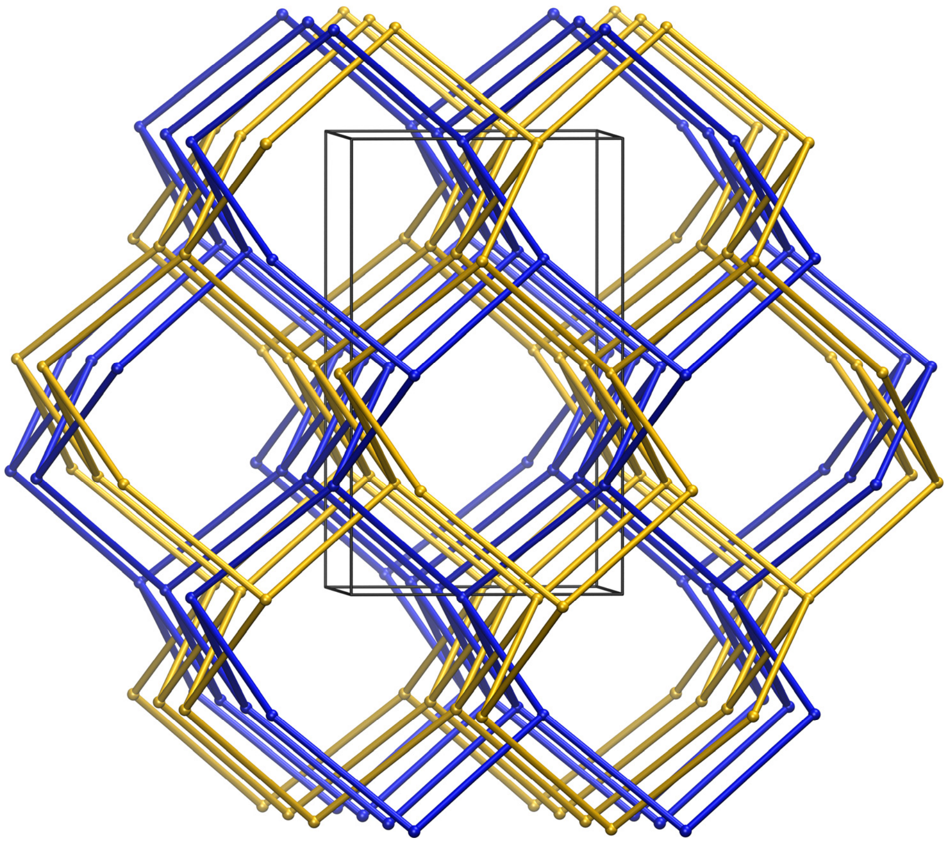
Max. symmetry	Max. vertex stabilizer	Transitivity	HRN	TD10 for HRN
$Pn\bar{3}m - Fd\bar{3}m$	T_d	111	**hxg**	3359
$I4_122 - P4_12_12$	C_2	111	N/A	N/A
$I\bar{4}2d - I2_12_12_1$	C_2	122	6,8-coor	3966
$I4_122 - P4_122$	C_2	122	6,10-coor	6090
$Ccca - C2/c$*	C_2	122	6,10-coor	6660
$Pban - Pnan$	C_2	122	6,10-coor	7755
$C222 - I2_12_12_1$	C_2	122	6,12-coor	5752
$I4_122 - I2_12_12_1$	C_2	122	8,12-coor	5679
$Cccm - Pcnm$	C_s	133	6,6,10-coor	5183
$Ccma - C2/m$*	C_s	133	6,6,10-coor	5752

* - first members of infinite series

2-fold dia nets with transitivity 111

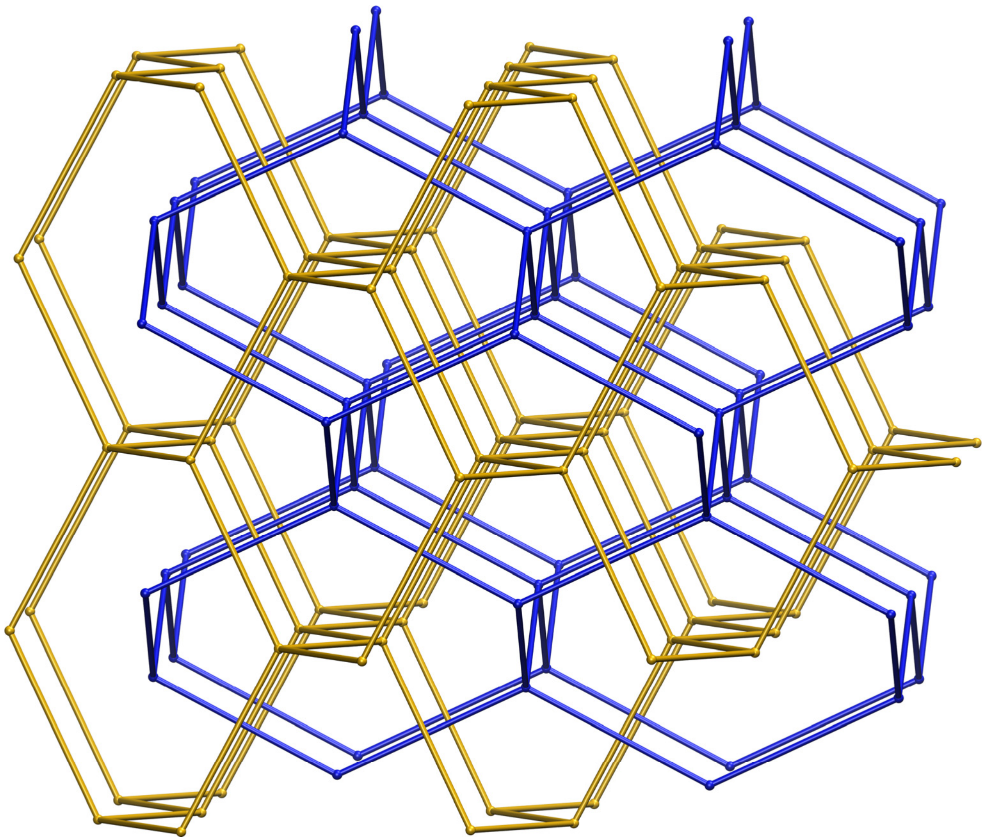


$Pn3m$ – $Fd3m$ ($-43m$)

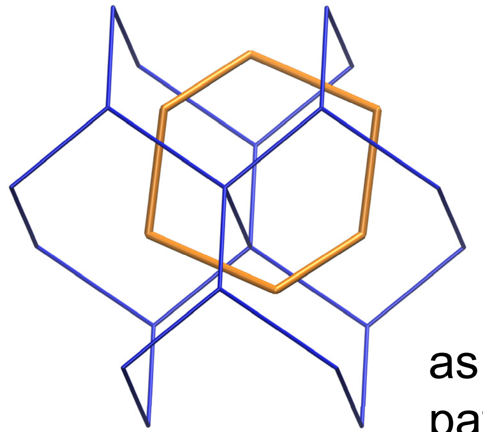


$I4_122$ – $P4_12_12$ (..2)

2-fold dia with transitivity 122

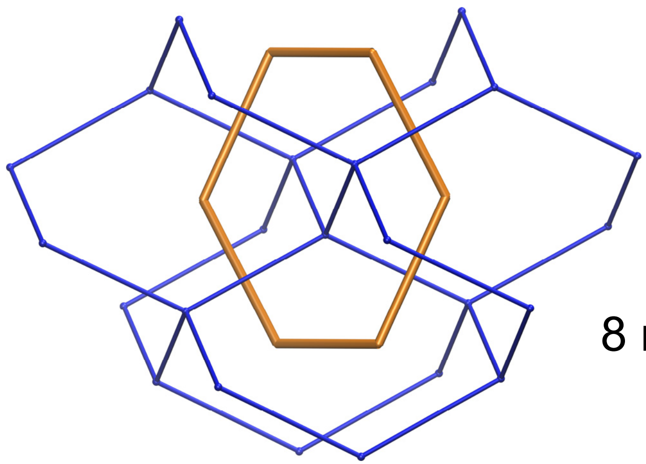


$I\text{-}42d - I2_12_12_1$



6 rings

as in the cubic pattern



8 rings

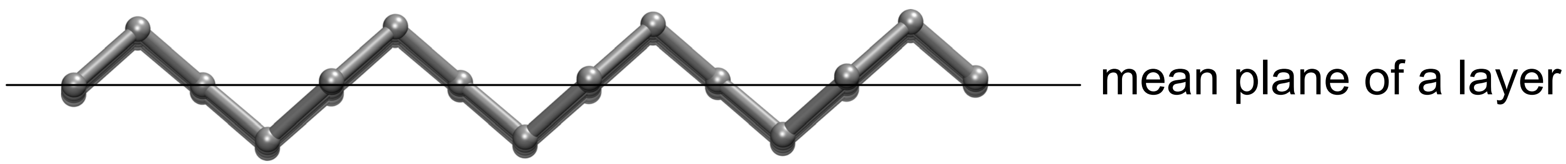
Interpenetration of 2-periodic layers

What is special compared to 3-periodic nets?

- The *reference* embedding of a layer is more uncertain because we need a corrugated, wavy layer – its symmetry is described by a ***layer group*** (2-periodic isometry group in R^3)

- All symmetry groups of corrugated vertex-transitive 2-periodic nets where all edges incident with the vertices retain equal lengths were listed in 1978 by Koch and Fischer (“sphere packings in layer groups”)

- A practical way is to keep the vertices in their max. symmetry positions in the plane, and consider V-shaped edges running out of plane, as allowed by edge stabilizers



What is special compared to 3-periodic nets?

- Not all group-supergroup pairs yield entangled layers (one layer can just lie on top of another)

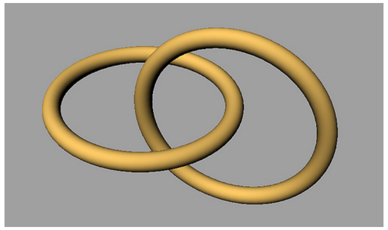
- This property is net-specific (unfortunately not group-specific!):

  if *G* – *H* is a group-subgroup pair of the interpenetration pattern, then the symmetry elements from the coset(s) of *H* in *G* must penetrate the ring to generate a symmetry-related ring that is interlaced with it – this is especially relevant for ring-transitive embeddings of layers

- What are the symmetry conditions for (Hopf) links?

Symmetry conditions for (Hopf) links

Which symmetry operations can map
<u>two interlocked rings</u> onto each other?



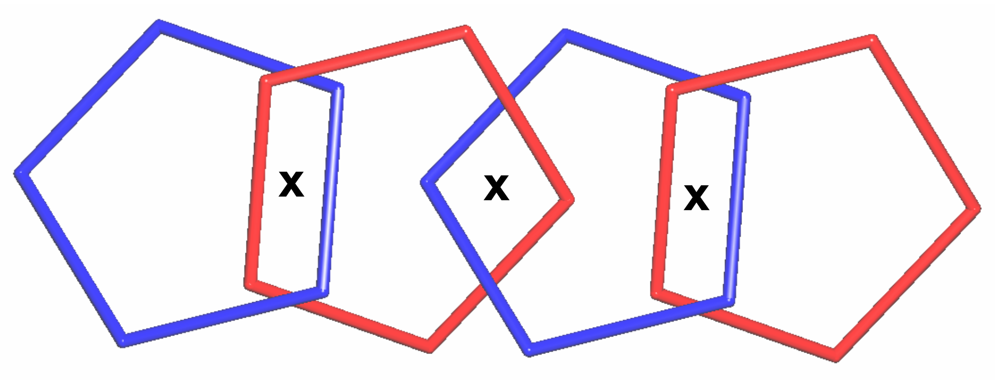
- ***inversion*** does not generate any link (apart from trivial)
- a ***mirror*** does not generate a link (apart from trivial) or induces crossings

- **2-fold axis** generates a Hopf link if the axis intersects a ring (but none of its edges)

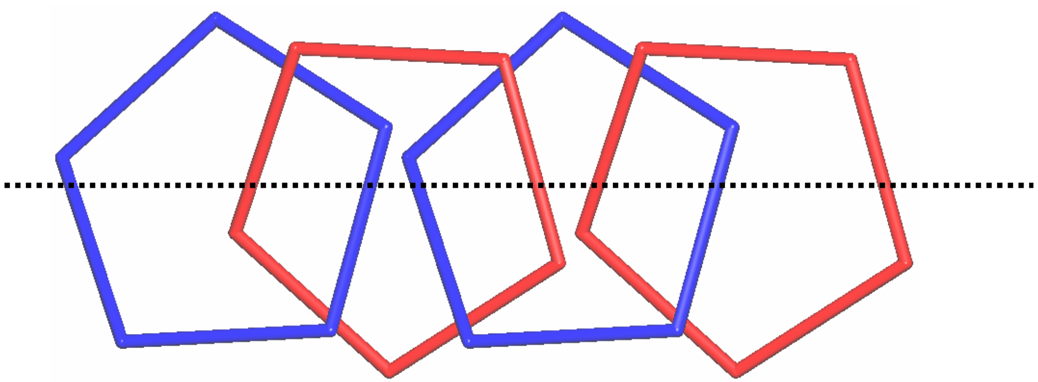
- ***translations, screw rotations, glide reflections*** can generate Hopf links if respective symmetry elements intersect a ring and their translation component is comparable to the (maximal) lateral dimension of a ring

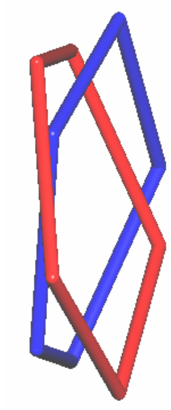
- any rotation axis, -3 and -4 rotoinversion axes (-6 contains a mirror so it is forbidden) can generate either Hopf or multiple links (Solomon or more complicated)

Symmetry conditions for (Hopf) links



2-fold axis



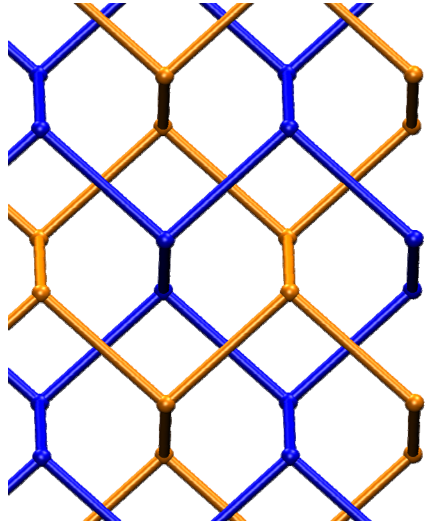


glide plane

Vertex- and edge-transitive honeycomb layers

- 2-fold interpenetrated honeycomb layers in 2D MOFs *etc*.:

  following the *minimal transitivity principle**,
  what are the most symmetric patterns
  i.*e*., those with <u>*one kind*</u> of node and
  <u>*one kind*</u> of link (edge)?



- Never observed**… do they exist?

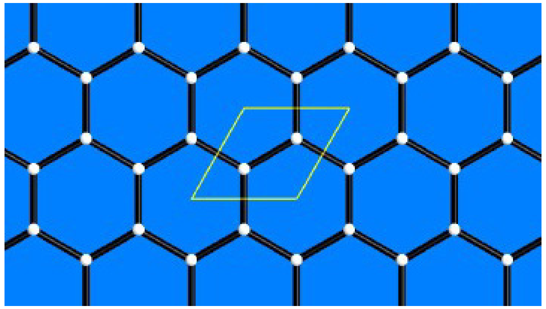
- If they do exist, why aren't they observed?

* M. O'Keeffe *et al*., C*hem*. *Rev*., **2014**, 114, 1343
** Blatov, Proserpio *et al*., *CrystEngComm* ***2017***, 19, 1993

Honeycomb layers: both vertex- and edge-transitive groups

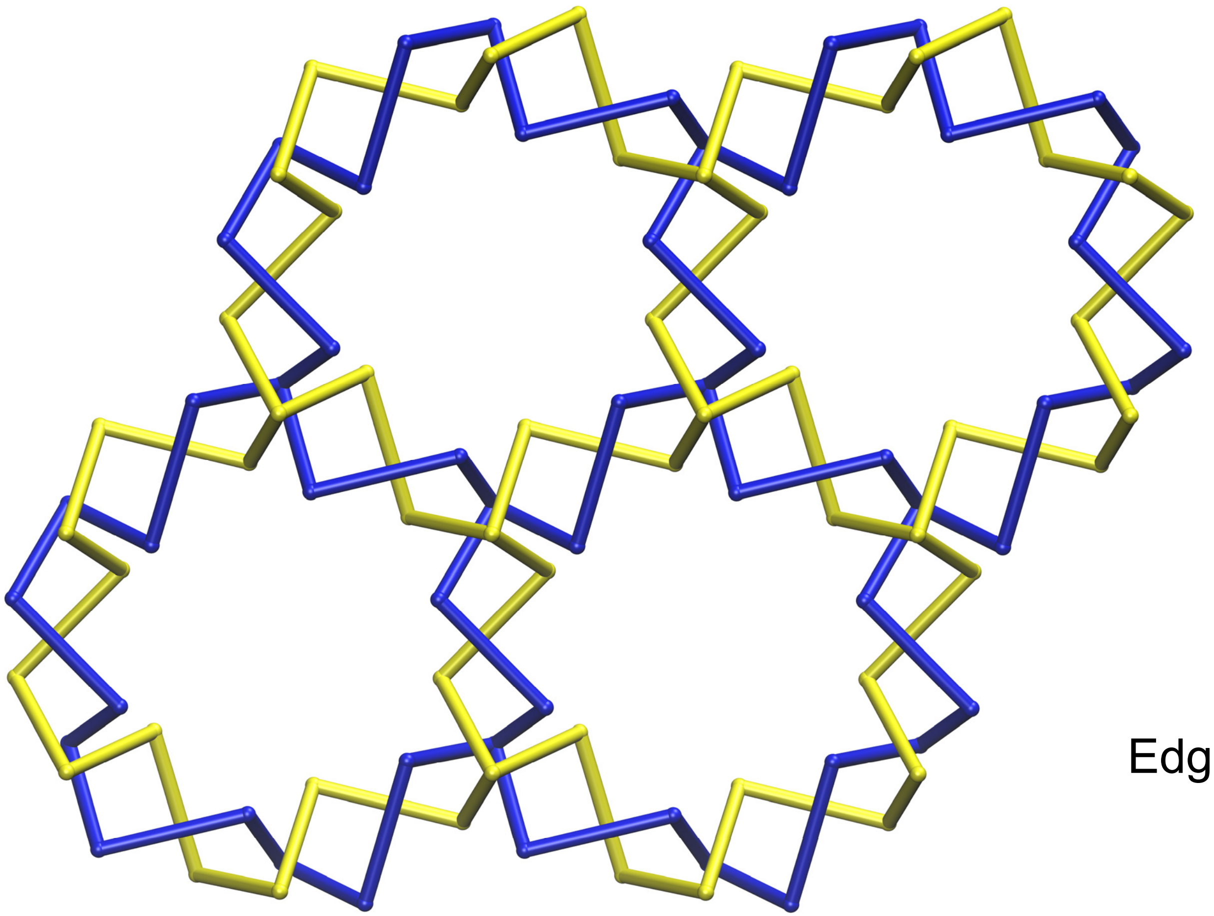
- Vertex stabilizer must have order 3 to exchange the edges incident with a vertex (edges could be nonplanar arcs)

- Four groups (up to conjugacy) remain



Layer group	$p6$	$p321$	$p31m$	$p\bar{3}$
Edge stabilizer	2..	.2.	..m	$\bar{1}$
Supergroups of index 2 without additional mirrors	$p622$	$p622$	$p\bar{3}1m$	–

2-fold interpenetrated **hcb**-layers



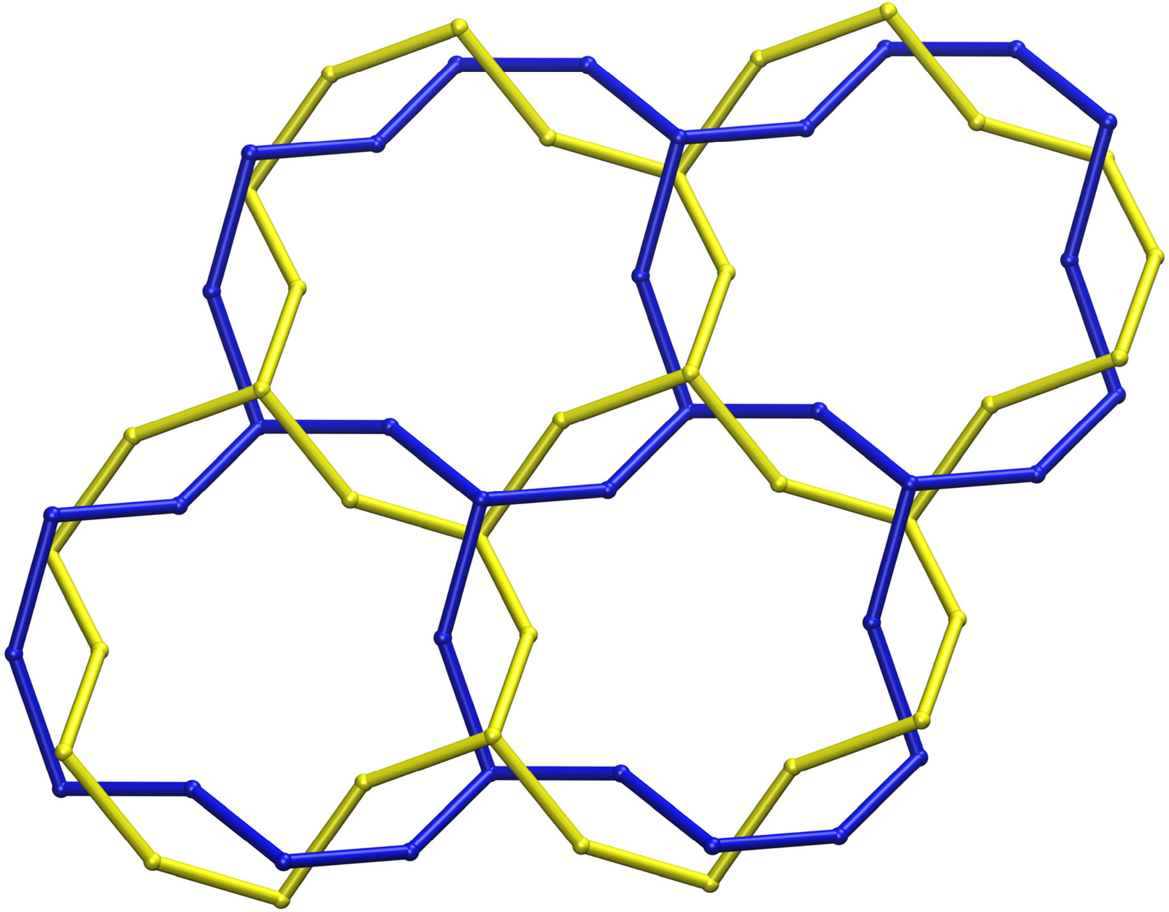
*p*622 – *p*6

Edges are nonplanar arcs

Multiple knot

Baburin (*2017*), available from chemrxiv.org

2-fold interpenetrated **hcb**-layers

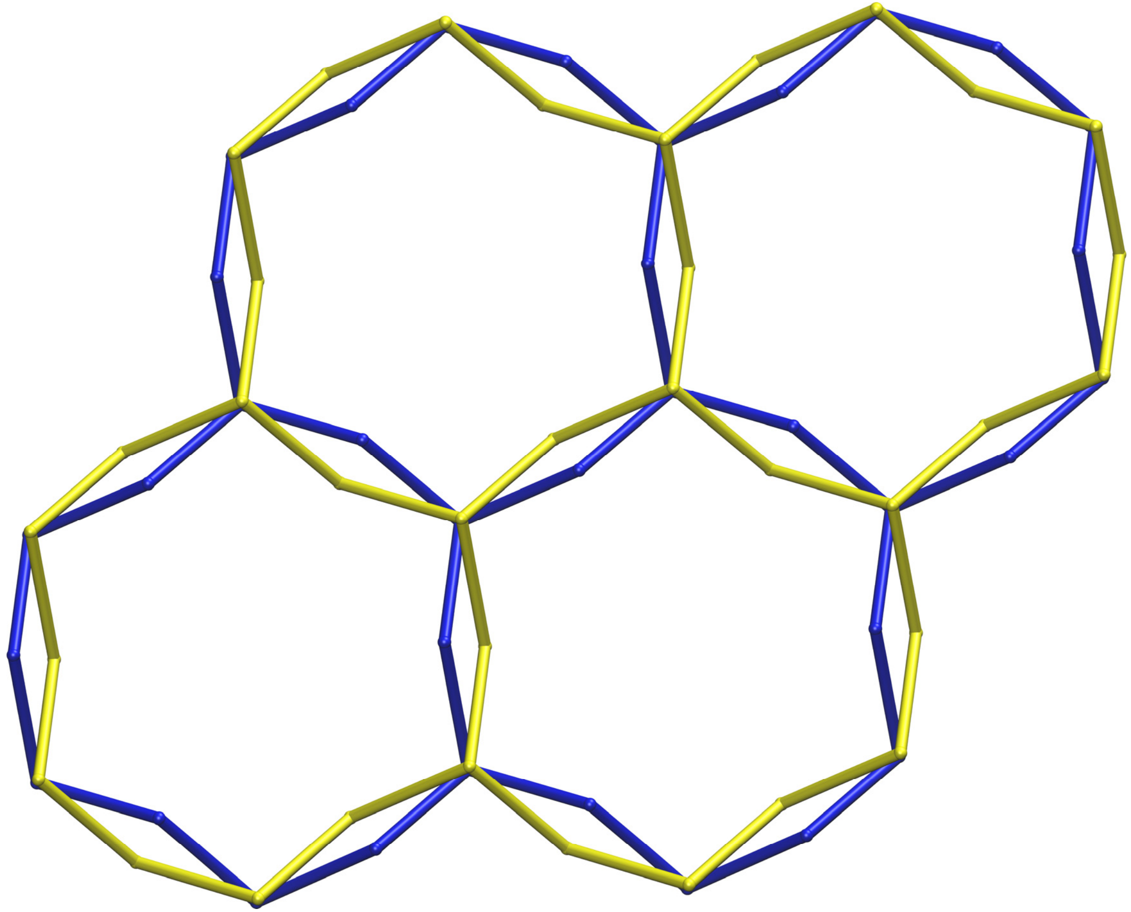


*p*622 – *p*321

Multiple knot

Baburin (*2017*), available from chemrxiv.org

2-fold “interpenetrated” **hcb**-layers

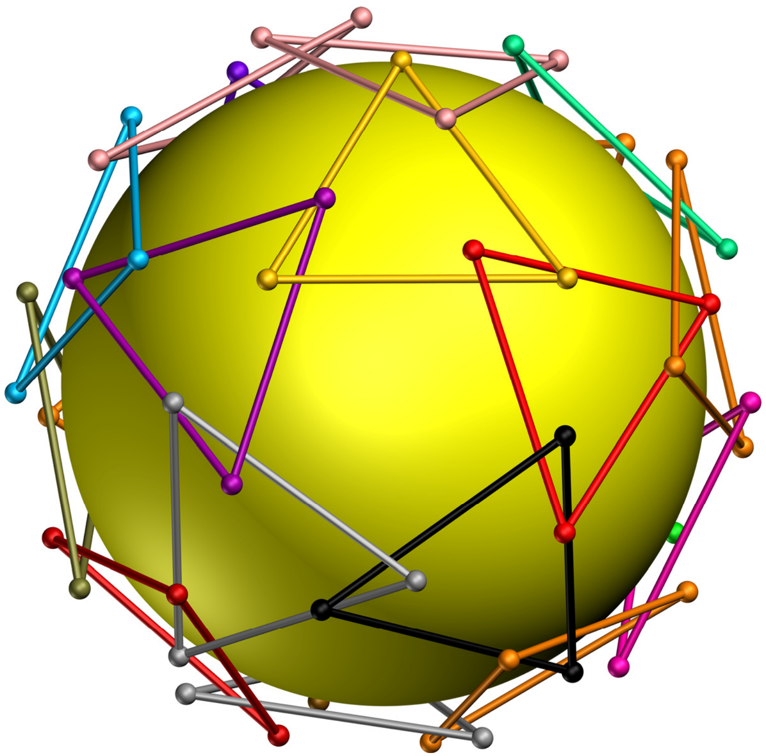


Trivial knot

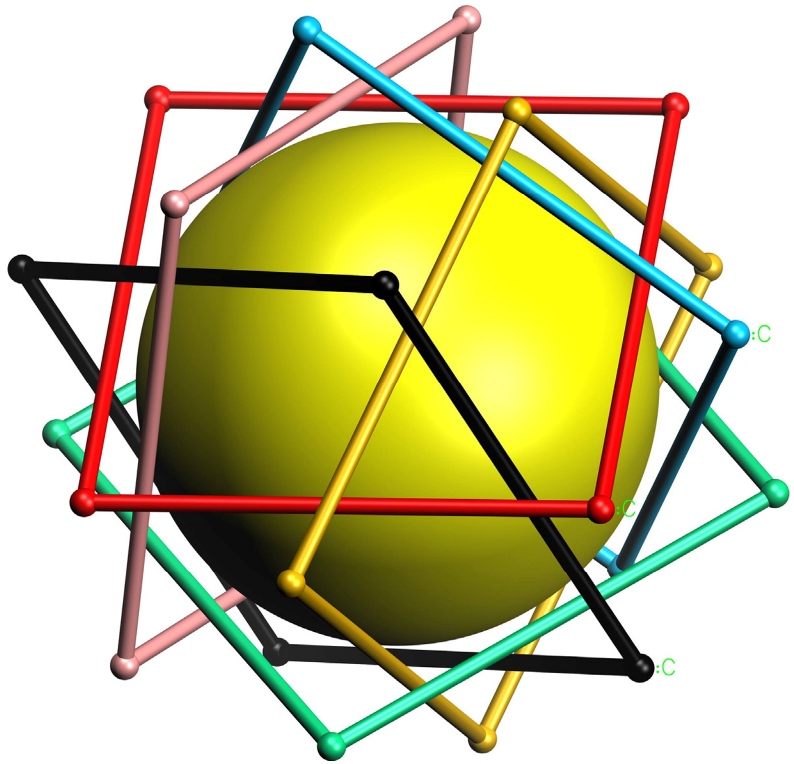
p-31*m* – *p*31*m*

individual layers are ***polar***

Polycatenanes



532



432

Mirrors/inversions can only stabilize vertices (edges) in catenanes

Cf. Liu, O'Keeffe, Treacy, Yaghi, *Chem. Soc. Rev.* 2018

Conclusions

- A universal recipe to derive interpenetrating nets is developed based on group–supergroup relations for crystallographic groups
- Towards rationalization of observed *vs*. possible patterns
- Deformation equivalence classes of connected components?
- Any relation to physical properties?

Thank you