

Three-periodic nets and tilings: semiregular nets

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Three-periodic semiregular nets are defined as those with just one kind of vertex and one kind of edge, but excluding the five regular and one quasiregular nets described earlier. Fourteen of these and their natural tilings are described and their importance in crystal chemistry is indicated.

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1. Introduction

There is considerable interest in enumerating and characterizing the basic topologies that underlie crystal structures. In particular, it is desirable to assign some measure of 'regularity' to nets as it is the most regular that are the prime targets for synthesis of pre-designed structures (O'Keeffe *et al.*, 2000; Yaghi *et al.*, 2003). In the first paper of this series (Delgado Friedrichs *et al.* 2003a), we described five *regular* and one *quasiregular* three-periodic nets. The regular nets were those with one kind of vertex (vertex transitive) for which, in the maximum symmetry embedding in Euclidean space, the coordination figure is a regular polygon or polyhedron and the symmetry at the vertex site contains at least the rotational symmetries of that polygon or polyhedron. For the quasiregular net, the coordination figure is a quasiregular polyhedron (cuboctahedron).

In the same paper, we also introduced the concept of a *natural* tiling, which was defined to consist of the smallest possible tiles that preserve the symmetry, and in which all the faces of the tiles are strong rings. Strong rings are in turn defined as those that are not the ring sum of smaller rings (Goetzke & Klein, 1991). The faces of the tiles are the *essential* rings of the structure. We were not aware at the time that our natural tiles are essentially the same as the *interstitial domain* defined by Schoen (1970).

A structure with p kinds of vertex, q kinds of edge, r kinds of essential ring and s kinds of tile is said to have transitivity $pqrs$ (Delgado Friedrichs & Huson, 2000). The regular 3-periodic nets have transitivity 1111 referred to their natural tilings and the quasiregular net likewise has transitivity 1112. We conjecture that there are no other structures with these transivities *when referred to the natural tiling*. In this connection, we remark that, if any tiling at all can be found for a given net,¹ different tilings can be obtained, *e.g.* by

combining and/or dividing tiles to make new ones, but for the nets we have examined it appears that the natural tiling is unique. We gave an example of a non-natural tiling with transitivity 1111 for the quasiregular net in the earlier paper, and give another below (§2.7).

The transitivity $pqrs$ is an array of four numbers; however, from the point of view of a crystal designer, it is fruitful to consider this array as a single number and to suppose that the smaller this number the more regular the structure. Thus, in order with the most regular first, we have 1111 (regular), 1112 (quasiregular), 1121 (next) and so on. In this paper, we describe structures with transitivity 11rs (*i.e.* vertex and edge transitive) which we call *semiregular*. The regular, quasiregular and semiregular nets correspond to the symmetric 3-periodic graphs of Schoen (1970).

We require that all structures can be realized in an embedding in which each vertex is in the center of the coordination figure defined by the neighbors to which it is connected, and further that no two vertices are coincident in this embedding (we need this last condition to exclude certain pathological structures, *cf.* §7.1). Note that an N -coordinated structure might not be an N -coordinated sphere packing, as a given vertex may have vertices as close or closer to it than the vertices to which it is linked by edges. We limit our discussion of semiregular nets to those structures in which, in their maximum-symmetry embeddings, there are no intervertex distances less than the edge length. This last restriction is necessary to restrict the topic to a finite set of structures most likely to be of interest in crystal chemistry.

Every tiling has a *dual* obtained by placing a vertex in the center of each of the original tiles and connecting pairs of new vertices through the faces common to pairs of tiles to form new edges. The vertices of the faces of the dual tiling correspond to the centers of the original tiles meeting at an original edge, and each dual tile encloses one vertex of the original tiling.

The dual of the dual of a tiling must be the original tiling. As the vertices, edges, faces and tiles map onto the tiles, faces, edges and vertices of the dual, a tiling with transitivity $pqrs$ has a dual with transitivity $srqp$. All the dual tilings of the struc-

¹ There are nets in which some rings are catenated (linked) and hence cannot serve as faces of tiles and, as a consequence, a tiling may not exist. An example of such a net is the one identified as 12^3 (O'Keeffe *et al.*, 2000). In the Si net of the coesite form of SiO₂ (O'Keeffe & Hyde, 1996), the 8-rings are likewise catenated.

Table 1

Regular (1–5), quasiregular (6) and semiregular (7–20) nets.

l.c. = lattice complex, Fischer = Fischer symbol (see text), p.s. = point symmetry, s.g. = space group, trans. = transitivity, dual is the face symbol of the dual tiling (* denotes this is not a natural tiling). The origin is always taken at an inversion center when one is present [‘origin choice 2’ of *International Tables for Crystallography* (1983)].

No.	Z	Vertex figure	l.c.	Name	Fischer	p.s.	s.g.	<i>c/a</i>	<i>x, y, z</i>	Tiles	Trans	Dual
1	3	Triangle	<i>Y*</i>	srs	3/10/ <i>c1</i>	32	<i>I4₁32</i>		1/8, 1/8, 1/8	[10 ³]	1111	[10 ³]
2	4	Square	<i>J*</i>	nbo	4/6/ <i>c2</i>	4/ <i>mmm</i>	<i>Im3m</i>		0, 1/2, 1/2	[6 ⁸]	1111	[4 ⁴]
3	4	Tetrahedron	<i>D</i>	dia	4/6/ <i>c1</i>	43 <i>m</i>	<i>Fd3m</i>		1/8, 1/8, 1/8	[6 ⁴]	1111	[6 ⁴]
4	6	Octahedron	<i>cP</i>	pcu	6/4/ <i>c1</i>	63 <i>m</i>	<i>Pm3m</i>		0, 0, 0	[4 ⁶]	1111	[4 ⁶]
5	8	Cube	<i>cI</i>	bcu	8/4/ <i>c1</i>	83 <i>m</i>	<i>Im3m</i>		0, 0, 0	[4 ⁴]	1111	[6 ⁸]
6	12	Cuboctahedron	<i>cF</i>	fcu	12/3/ <i>c1</i>	63 <i>m</i>	<i>Fm3m</i>		0, 0, 0	[3 ⁸]+2[3 ⁴]	1112	[4 ¹²]
7	4	Rectangle	<i>^vT</i>	lvt	4/4/ <i>t1</i>	2/ <i>m</i>	<i>I4₁amd</i>	1.0	0, 0, 0	[4 ² . 8 ⁴]	1121	[5 ⁴ *]
8	4	Tetrahedron	<i>W*</i>	sod	4/4/ <i>c1</i>	42 <i>m</i>	<i>Im3m</i>		1/4, 0, 1/2	[4 ⁶ . 6 ⁸]	1121	[3 ⁴]
9	4	Tetrahedron	<i>S*</i>	lcs	4/6/ <i>c3</i>	4	<i>Ia3d</i>		3/8, 0, 1/4	[6 ² . 6 ³]	1121	[5 ⁴]
10	4	Tetrahedron	<i>V</i>	lcv	4/3/ <i>c1</i>	222	<i>I4₁32</i>		1/8, 0, 1/4	[3 ² . 10 ³]	1121	[6 ⁴]
11	4	Tetrahedron	<i>Q</i>	qtz	4/6/ <i>h1</i>	222	<i>P6₂22</i>	3/(2 × 2 ^{1/2})	1/2, 0, 0	[6 ² . 8 ²]	1121	[7 ⁴]
12	6	Hexagon	–	hxx	–	3 <i>m</i>	<i>Pn3m</i>		0, 0, 0	[4 ⁶ . 6 ⁴]	1121	[4 ⁶]
13	6	Metaprism	<i>Y</i>	lcy	6/3/ <i>c1</i>	32	<i>P4₁32</i>		3/8, 3/8, 3/8	[3. 5 ³]	1121	[6 ⁶ *]
14	6	Octahedron	<i>T</i>	crs	6/3/ <i>c2</i>	3 <i>m</i>	<i>Fd3m</i>		0, 0, 0	[3 ⁴]+[3 ⁴ . 6 ⁴]	1122	[4 ⁶]
15	6	Octahedron	–	bcs	–	3	<i>Ia3d</i>		0, 0, 0	[6 ²]+[4 ² . 6 ²]	1122	[8 ⁶]
16	6	Trigonal prism	<i>E</i>	acs	6/4/ <i>h2</i>	6 <i>m2</i>	<i>P6₃/mmc</i>	3 ^{1/2} /2	1/3, 2/3, 1/4	2[4 ³]+[4 ³ . 6 ²]	1122	[6 ⁶ *]
17	8	Trigonal prism	<i>J</i>	reo	8/3/ <i>c2</i>	4/ <i>mmm</i>	<i>Pn3m</i>		1/2, 0, 0	[3 ⁸]+[3 ⁸ . 4 ⁶]	1122	[3 ⁸]
18	8	Bisdisphenoid	<i>S</i>	thp	8/3/ <i>c1</i>	4	<i>I43d</i>		3/8, 0, 1/4	[4 ³]+[3 ² . 4 ³]	1122	[5 ⁸]
19	4	Rectangle	–	rhr	4/4/ <i>c3</i>	2 <i>m2</i>	<i>Im3m</i>		0.3333, <i>x</i> , 0	3[4 ⁴ . 8 ²]+[6 ⁸ . 8 ⁶]	1132	[4 ⁴]
20	4	Tetrahedron	–	ana	4/4/ <i>c5</i>	2	<i>Ia3d</i>		1/8, 0.3333, 1/4- <i>y</i>	3[4 ² . 8 ²]+2[6 ² . 8 ³]	1132	[5 ⁴]

tures described here have transitivity *sr*11, and hence consist of one kind of tile with one kind of face. Schoen (1970) calls the dual tile the *symmetry domain* of the vertex of the original net as it has of necessity the point symmetry of that vertex.

If the tiling and its dual are both natural tilings of nets, the essential rings of each net are penetrated by edges of the other and we say the nets are *fully catenated*. We have called these ‘dual nets’ [Delgado Friedrichs *et al.* (2003*a,b*), *cf.* ‘dual graphs’ (Schoen, 1970)] but, as the tiling of a net is not unique, the term is imprecise; we propose instead to refer to the nets of a pair of dual natural tilings as ‘natural duals’. However, it may be (and sometimes is, we give examples below) the case that the dual tiling is not a natural tiling. In this case, the nets of the pair are not fully catenated and at least one of the pair has no natural dual. To avoid these difficulties, we refer to the net of the dual of a natural tiling as ‘optimally interpenetrating’ the first.

We identify 14 examples of structures with transitivity 11*r*s and *r* ≥ 2. Accordingly, together with the regular and quasiregular structures, we have a total of 20 edge- and vertex-transitive 3-periodic structures. We believe that, with the restrictions noted above, the list is fairly complete, but we do not claim completeness.

Some structures correspond to invariant lattice complexes and we give the symbols previously assigned to them (Fischer & Koch, 1983). Most correspond to homogeneous sphere packings (Fischer, 1971, 1973, 1974, 1993; Koch & Fischer, 1995; Sowa *et al.*, 2003) and in Tables 1, 2 and 3 these are identified by the Fischer symbol *zlr/sn*, where *z* is the coordination number, *r* is the size of the smallest ring in the structure, *s* is a symbol denoting the crystal system (*c* = cubic,

h = hexagonal and *t* = tetragonal) and *n* is a serial number for given *z*, *r* and *s*.

As in the earlier paper (Delgado Friedrichs *et al.*, 2003*a*), we assign a three-letter code to each structure, as some structures have a multitude of names and others have none that are known to us. This name refers to the underlying topology of the net, not only to the maximum-symmetry embedding that is described here. Tiles are characterized by a face symbol [*M^m.Nⁿ...*], which signifies that there are *m* faces that are *M*-rings, *n* that are *N*-rings *etc.* Names and some data for the 20 nets are listed in Table 1.

The semiregular nets fall into three groups with transivities 1121, 1122 and 1132, respectively, and we consider them in that order. They are generally illustrated in *augmented* form (O’Keeffe *et al.*, 2000), in which a polygon or polyhedron corresponding to the coordination figure replaces the original vertex. This is the form in which the nets often appear in *e.g.* metal–organic frameworks (MOFs) in which we are particularly interested (Yaghi *et al.*, 2003) – the polygons or polyhedra representing the secondary building units (SBUs) of the framework.

2. Structures with transitivity 1121

2.1. Lattice complex ^vT, symbol lvt

Although not very well known in crystal chemistry, this tetragonal structure with *c/a* = 1 and square coordination (Fig. 1) is of some interest and should be better known. It has been found as a partially catenated interpenetrating pair in a hydrogen-bonded framework (Hawkins *et al.*, 1993, *cf.* Batten

& Robson, 1998) and also in a Cu^{II} -bipyridine metal–organic framework (Carlucci *et al.*, 2002). If the symmetry is lowered to $\bar{1}42d$, the structure can serve as the T net of a TX_2 framework of corner-connected regular TX_4 tetrahedra with $T-X-T \approx 115^\circ$, and it occurs in this way in a supertetrahedral sulfide framework (Wang *et al.*, 2001). The vertex symbol (O’Keeffe & Hyde, 1996, 1997) of the net is $4\cdot4\cdot8_4\cdot8_4\cdot8_8\cdot8_8$.

If c/a is increased from 1.0 to $2^{1/2}$, each vertex has six nearest neighbors arranged as in the T lattice complex (**crs**) described in §3.1 below. The relationship to this structure (*q.v.*), and hence to the self-dual diamond structure (**dia**), explains the propensity for intergrowth. Two intergrown nets optimally avoiding collisions are displaced from each other by 0, 0, $1/2$.

The natural tiles are cages $[4^2\cdot8^4]$ (Fig. 1). The dual structure with transitivity 1211 is carried by a tiling $[5^4]$ (Fig. 1) and is the 6-coordinated β -Sn structure (O’Keeffe & Hyde, 1996). However, the dual tiling is not a natural tiling as the tile has a smaller ring (a 4-ring) around the perimeter, and the natural tiling for the β -Sn structure is $[4\cdot5^2]$ so the transitivity for the natural tiling of that net is 1221 and its dual structure is a 3-coordinated net corresponding to sphere packing $3/8/t1$ of Koch & Fischer (1995).²

2.2. Sodalite, lattice complex W^* , symbol sod

The four-coordinated sodalite net (zeolite code SOD; Baerlocher *et al.*, 2001) is very well known in crystal chemistry and elsewhere and we briefly recapitulate some of its more important properties. The net is carried by a tiling by truncated octahedra (Fig. 2). It is an example of a *simple* tiling, which is one in which the tiles are simple polyhedra (*i.e.* polyhedra in which three edges meet at every vertex) and in which two tiles meet at each face, three at each edge and four at each vertex; as such it acts as an ideal model for the structure of monodisperse cellular materials such as foams (Weaire & Hutzler, 1999) and the universe (Hamilton *et al.*, 1986).

The **sod** net can be derived from the regular net **nbo** by placing vertices in the middle of the edges of that net, discarding the original vertices and joining the new vertices to the nearest neighbors by new edges to form what we have called an edge net (Delgado Friedrichs *et al.*, 2003*b*). We show (Fig. 2) the augmented **sod** net; if the edge lengths of this structure are all equal, the vertices are at the positions of what is believed to be the least-dense stable homogeneous sphere packing (O’Keeffe, 1991; Aste & Weaire, 2000).

The dual structure with transitivity 1211 is 14-coordinated and is carried by an isohedral tiling by tetrahedra, which is the

² It might be noted that O’Keeffe & Sullivan (1998) considered the structure derived by a tiling of Voronoi domains of the β -Sn structure. This is a simple tiling by polyhedra with 18 faces and corresponds to a point of view in which the β -Sn structure is 18-coordinated (*cf.* the sodalite structure discussed below, which is the dual of a body-centered cubic considered as 14-coordinated) and has transitivity 1442. Thus, we see that, for a given array of points of space, there is always some arbitrariness about what we call edges, faces (rings) and tiles. However, once we have decided on the edges, we believe that the natural tiling is unique (provided that it exists) and thus a single transitivity referred to that tiling.

only vertex-transitive such tiling (Delgado Friedrichs & Huson, 1999). It corresponds to the net obtained by linking each vertex of the body-centered cubic lattice to its nearest and next-nearest geometrical neighbors. Clearly, this cannot be realized in a form in which all 14 edges have equal length (this would correspond to a tiling by regular tetrahedra, which is readily shown to be impossible). It might be noted that 24 of the dual tetrahedra combine to form a rhombic dodecahedron (Fig. 2); the centers of these tetrahedra are, of course, the vertices of a truncated octahedron.

2.3. Lattice complex S^* , symbol lcs

This is another 4-coordinated net, of lesser importance in crystal chemistry. Although all the faces of the natural tiles are hexagons (Fig. 3), they are of two topological types and we write the symbol for the tile as $[6^2\cdot6^3]$. A (not-natural!) tiling by infinite tiles can be constructed by fusing rods of tiles that

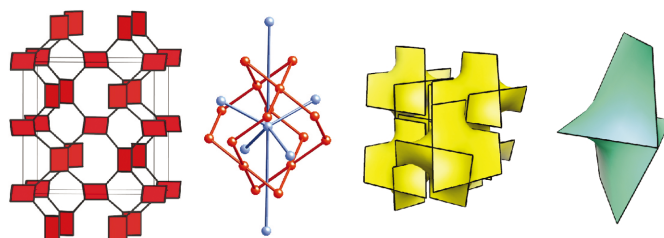


Figure 1

From the left: the augmented **lvt** net, the outline of one $[4^2\cdot8^4]$ tile (red) with a fragment of the dual structure (blue), a packing of the tiles (yellow) and, right, one dual tile $[5^4]$. Note that the dual tile has a 4-ring around the middle and hence is not a natural tile.

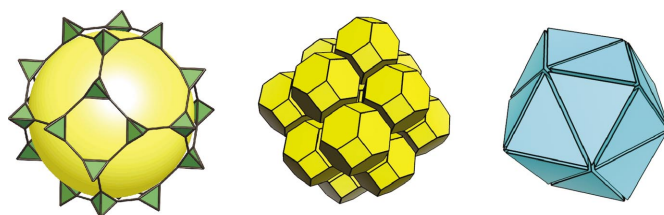


Figure 2

Left: a fragment of the augmented **sod** net. Center: the **sod** net as a tiling of truncated octahedra. Right: 24 dual $[3^4]$ tiles forming a rhombic dodecahedron.

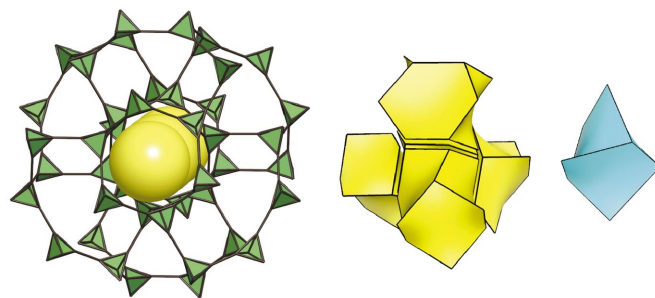


Figure 3

Left: the augmented **lcs** net. The view is almost down $[111]$ and the centers of the yellow balls are on this direction. Center: the **lcs** net as a tiling by pentahedra $[6^2\cdot6^3]$. Right: a dual $[5^4]$ tile.

run along $\langle 111 \rangle$. This structure now has transitivity 1111 (Delgado Friedrichs *et al.*, 2002). The dual tiling is by cages $[5^4]$ (Fig. 3). See also Hyde *et al.* (2003).

2.4. Lattice complex V, symbol lcv

The **lcv** net is another 4-coordinated net, again of lesser importance in crystal chemistry. It is the edge net of the regular net **srs**. The tiles are cages $[3^2.10^3]$ illustrated in Fig. 4. The augmented structure is particularly open with channels running along $\langle 111 \rangle$ and $\langle 100 \rangle$. The dual tile is $[6^4]$.

2.5. Quartz net, lattice complex Q, symbol qtz

This 4-coordinated net is familiar as the net of the Si atoms in the quartz form of SiO_2 (the $-\text{O}-$ links in quartz correspond to the edges of the net). The tile (Fig. 5) is a tetrahedron with two hexagonal and two octagonal faces. The 4-coordinated dual net ('quartz dual', symbol **qzd**) cannot be realized as a 4-coordinated sphere packing, but is nevertheless of considerable interest in crystal chemistry, as is the quartz net itself. We have discussed some properties of these nets and their intergrowths elsewhere (Delgado Friedrichs *et al.*, 2003b).

2.6. Net hxg and polybenzene

The 6-coordinated **hxg** net is the only structure with transitivity 1121 that we have identified in which the edges are not the shortest distances between vertices that correspond to an invariant lattice complex. The arrangement of vertices in the most symmetrical embedding is in fact the same as the points of the face-centered cubic lattice. However, only one half of the edges of that structure are retained so that the topological neighbors of a vertex form a regular hexagon. The symmetry is $Pn\bar{3}m$ with vertices in $4(b)$ $(0, 0, 0 \text{ etc.})$; the midpoints of the edges are in $12(f)$ $(1/2, 1/4, 3/4 \text{ etc.})$.

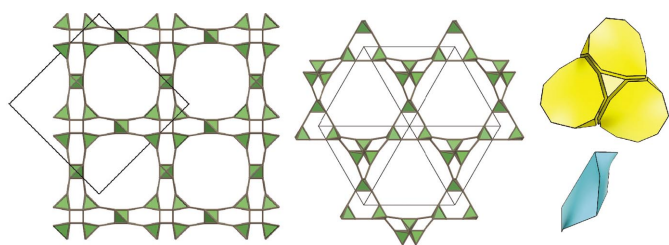


Figure 4
Left and center: the **lcv** net viewed down $[100]$ and $[111]$, respectively. On the right, a group of natural tiles are shown in yellow, and one dual $[6^4]$ tile is shown in blue.

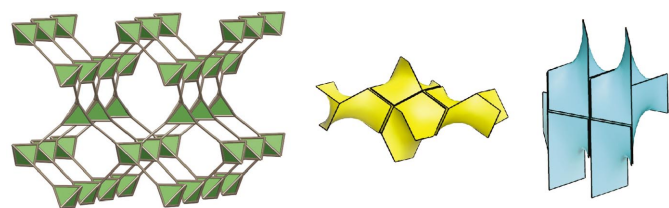


Figure 5
Left: the augmented **qtz** net. Center: the natural tiling of the **qtz** net. Right: the dual tiling.

In Fig. 6, we show the augmented net. This latter structure has been called polybenzene to reflect its calculated stability and electronic properties as a form of elemental carbon (O'Keeffe *et al.*, 1992); it is also known as 'cubic graphite' (Shen *et al.*, 2003).

The natural tile (Fig. 6) has ten faces: $[4^6.6^4]$ (so the dual structure is 10-coordinated) and is the 'tetrahedral decahedron' of Pearce (1978). The vertices of the tetragonal faces are at the corners of a regular tetrahedron and the vertices of the hexagonal faces are at the corners of a regular octahedron. Schoen (1970) remarks that, if the **hxg** net is constructed using straight edges, it can be embedded in both the P and the D minimal surfaces. Indeed, if the tiles are assembled sharing only the tetragonal faces, the hexagonal faces form the P minimal surface; if they are assembled sharing only the hexagonal faces, the tetragonal faces form the D minimal surface as shown in Fig. 7.

2.7. Lattice complex Y, symbol lcy

This 6-coordinated net, although also of lesser importance in crystal chemistry, illustrates some important points about dual nets and interpenetration. The coordination figure is a triangular metaprism [intermediate between a prism and an antiprism (O'Keeffe & Hyde, 1996)]. The tile (Fig. 8) is a tetrahedron with one triangular and three pentagonal faces, $[3.5^3]$; accordingly, the dual net is four-coordinated and is in fact the diamond (**dia**) net (coordinates $0, 0, 0 \text{ etc.}$ or

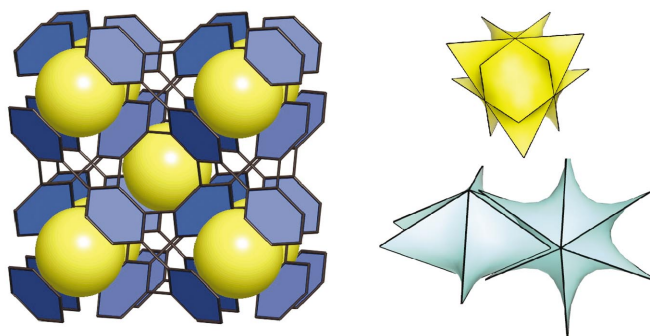


Figure 6
Left: the augmented **hxg** net ('polybenzene'). The yellow spheres are in the centers of cavities with tetrahedral symmetry and form a body-centered cubic array. Right: The natural tile ($[4^6.6^4]$, yellow) and two dual tiles (blue).

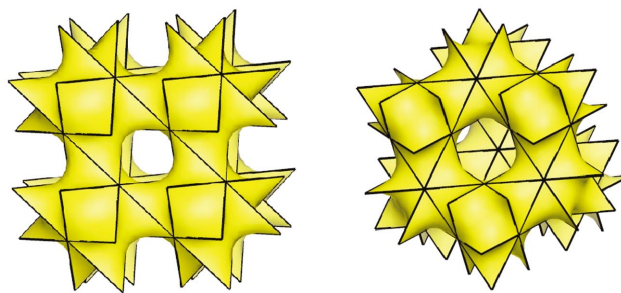


Figure 7
Groups of fused **hxg** tiles forming a fragment of the P surface (left) and the D surface (right).

$1/2, 1/2, 1/2$ etc. in $P4_132$ correspond to vertices of diamond nets). However, to recover the **lcy** net as the dual of **dia** we must use a non-natural tiling of the latter in which pairs of tetrahedral normal tiles (adamantane units) are fused together to form a hexahedral tile (see Fig. 8).

On the other hand, if we start with a non-natural tiling [5⁶] for **lcy** in which pairs of natural tiles are fused at a common triangular face, the net of the dual structure is again **lcy** so pairs of **lcy** nets can interpenetrate with all pentagonal rings catenated, and in fact these are the labyrinth graphs of the Y minimal balance surface (Fischer & Koch, 1989). The tiling (not natural!) ignoring the 3-rings has transitivity 1111.

We do not know of an extended structure with a net based on **lcy** but the above discussion suggests that it would be an interesting challenge to attempt the design and synthesis of one.

3. Structures with transitivity 1122

3.1. Lattice complex T , symbol **crs**

This structure is of course very familiar in crystal chemistry. The positions of the vertices are the middles of the edges in the regular 4-coordinated **dia** net. In the cristobalite form of silica, the Si atoms are on a **dia** net and the links of the net are $-O-$. Accordingly, in the idealized form of cristobalite with symmetry $Fd\bar{3}m$, the O atoms are in the positions of lattice complex T , hence the symbol **crs**. There are now two kinds of tile: tetrahedra and truncated tetrahedra (Fig. 9). The reciprocal tiles are oblate rhombohedra with $\alpha = \cos^{-1}(1/3)$ (the same shape as the primitive unit cell of the body-centered

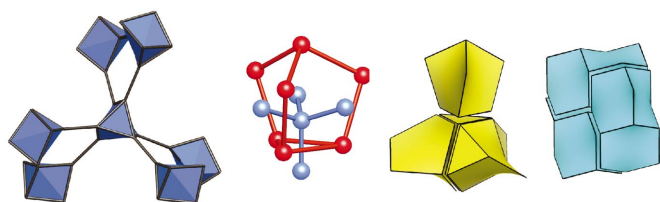


Figure 8

Left: a fragment of the augmented **lcy** net. Next on the right is the outline of one tile (red) with an element of the dual structure (blue). Next is a group of five natural tiles [3.5³], yellow). Right: a group of dual tiles [6⁶] each consisting of a pair of natural **dia** tiles (adamantane units).

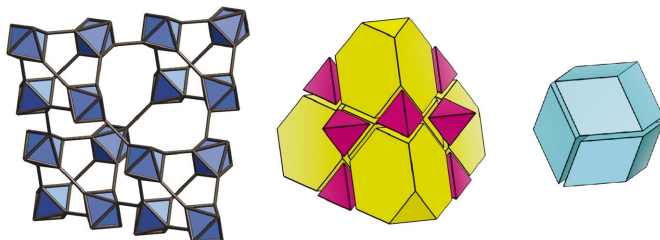


Figure 9

Left: a fragment of the augmented **crs** net. Middle: the **crs** net as a tiling by regular truncated tetrahedra [3⁴.6⁶], yellow) and tetrahedra [3⁴], magenta). Right: three of the dual rhombohedral [4⁶] tiles forming a rhombic dodecahedron.

cubic lattice); four of them fit together to form a rhombic dodecahedron (Fig. 9, cf. Fig. 3).

The augmented structure corresponds to a linkage of octahedra by equal links. The vertices form a 5-coordinated net; for all equal edge lengths the coordinates are $1/28, 23/28, 23/28$ etc.

The vertices of two **crs** nets (A and B say) displaced by $1/2, 1/2, 1/2$ combine to form a face-centered cubic lattice (**fcc**). The links $A-B$ alone form an **hcg** net (§2.6, see also §5).

3.2. A six-coordinated structure **bcs**

In this structure, there are eight neighbors equidistant to each vertex but edges to only six of them. A way to generate the structure is as follows. Start with a body-centered cubic lattice and connect each vertex to its eight neighbors. This will generate a set of lines with four meeting at each lattice point. Now embed this pattern in a doubled cell with symmetry $Ia\bar{3}d$ and delete the lines along the (non-intersecting) threefold rotation axes of that group. Each point will have three lines intersecting in the pattern shown in Fig. 10. The middles of the edges have coordinates $1/8, y, 1/4 - y$ etc., with $y = 3/8$. The site symmetry at each vertex is $\bar{3}$ and the coordination is a flattened octahedron with vertices at six of the eight corners of a cube. There are two kinds of tile that are very concave and thus rather hard to visualize (Fig. 10).

3.3. Lattice complex E as 6-coordinated. Structure **acs**

This is a hexagonal structure so the ratio of cell edges c/a is a free parameter. If $c/a = (8/3)^{1/2} = 1.63\dots$, the arrangement of vertices is as in hexagonal closest packing. If $c/a > (8/3)^{1/2}$, each vertex has six neighbors in a plane and the structure is a sequence of parallel 3⁶ nets. If $2/3 < c/a < (8/3)^{1/2}$, each vertex has six nearest-neighbor vertices at the corner of a trigonal prism and has maximum volume for a given edge length when $c/a = (2/3)^{1/2} = 0.816\dots$. This six-coordinated structure we refer to as **acs**.

The structure ('squashed' hexagonal closest packing) has 3⁶ layers packed in an $AB\dots$ sequence. The primitive cubic structure (**pcu**) has the same layers packed with the same spacing but in the sequence $ABC\dots$. Just as there is an infinite family of closest packings (Barlow packings), there is an infinite family of 'squashed' 6-coordinated structures. The next member, with sequence $ABAC\dots$ (hc), is the NiAs structure, which we will discuss in the next paper in this series. Notice

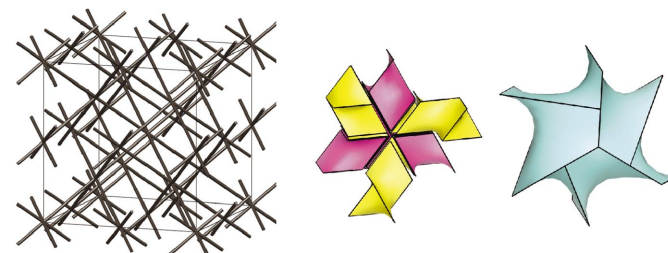


Figure 10

Left: a stick model of the **bcs** net. Center: the natural tiling of [6³] and [4².6²] (yellow). Right: the dual tile [8⁶].

that, if $c/a = 2/3$, the structure is 8-coordinated with two kinds of edge and, for $c/a < 2/3$, there are just two nearest neighbors.

The augmented **acs** structure (Fig. 11) represents the only way of linking trigonal prism units with symmetry $\bar{6}m2$ with equal linkers.

The natural tiling involves two tiles with three and five vertices as shown in the figure. Accordingly, the dual structure has two kinds of vertex, one 3- and one 5-coordinated. This structure is the hexagonal graphite structure with the spacing between the 6^3 graphite layers equal to the nearest-neighbor distance in the layers, so half the vertices become 5-coordinated. The $[6^6]$ dual tiles have 6-rings around the perimeter so they are not the natural tiles of the hexagonal graphite structure.

We digress briefly to describe two related structures with similar tilings. The natural tiling of the hexagonal graphite structure is instead tetrahedra $[6.6^3]$ and the dual of this structure is the lonsdaleite structure (so, pleasingly, the

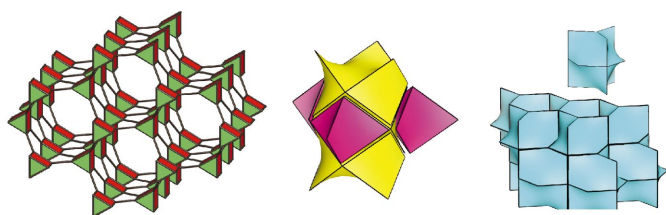


Figure 11
Left: the augmented **acs** net shown as linked trigonal prisms. Center: the natural tiling by trihedra $[4^3]$, (magenta) and pentahedra $[4^2.6^2]$, (yellow). Right: the dual tiling by hexahedra $[6^6]$. Note that the dual tiles have a hexagon around the perimeter so they are not natural tiles.

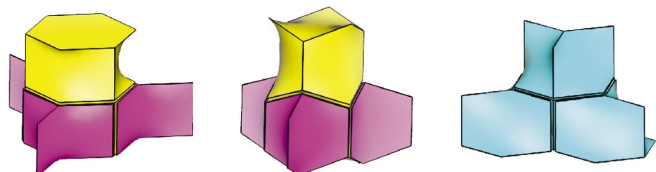


Figure 12
Left: a self-dual tiling by $[6^3]$ (magenta) and $[6^2.6^3]$ (yellow) tiles. Middle: the lonsdaleite structure as a tiling by $[6^3]$ and $[6^2.6^3]$ tiles. Right: the dual of the lonsdaleite structure. The net dual structure is the same as that of the dual of the **acs** net (Fig. 11) but now the tiles are $[6.6^3]$.

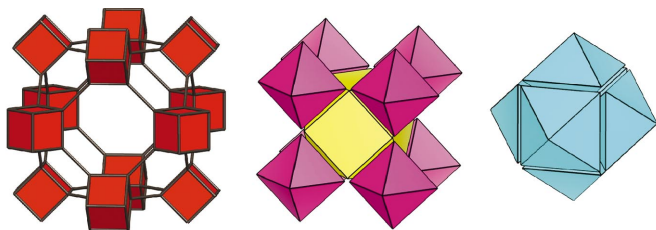


Figure 13
Left: the augmented **reo** structure shown as linked cubes. Center: the **reo** structure shown as a tiling by regular octahedra and cuboctahedra. Right: The dual octahedral tiles shown combining to form a rhombic dodecahedron.

graphite and lonsdaleite structures are natural duals of each other). The lonsdaleite structure is also a tiling by trihedra ($[6^3]$) and pentahedra ($[6^2.6^3]$), as shown in Fig. 12. We also show in Fig. 12 another (3, 5)-coordinated structure that is a tiling by topologically equivalent trihedra and pentahedra. This structure is naturally self dual, and in fact the net corresponds to the labyrinth graph of the H minimal surface (Schoen, 1970).

3.4. The **ReO₃** structure net, symbol **reo**

The **reo** structure (Fig. 13) is familiar as the net of a tiling by regular octahedra and cuboctahedra and corresponds to the O positions in crystalline ReO_3 . The augmented net consists of linked cubes and this second net is the same as that of the zeolite LTA (Baerlocher *et al.*, 2001). The dual tiles are octahedra; six of these combine to form a rhombic dodecahedron (Fig. 13, *cf.* Figs. 2 and 9).

3.5. The **thp** net

The **thp** net corresponds to the Th array in the Th_3P_4 structure and also occurs in a number of related crystal structures. It is often described as 12-coordinated by counting nearest- and next-nearest-neighbor distances as edges. In this description (O'Keeffe & Andersson, 1977; O'Keeffe & Hyde, 1996), it is generated by a tiling of twisted octahedra (trigonal metaprisms) and tetrahedra (Fig. 14), and has transitivity 1232. Here we prefer to count just the nearest-neighbor links as edges, so the structure is 8-coordinated and the transitivity is 1122. The coordination figure is a bisdisphenoid and the

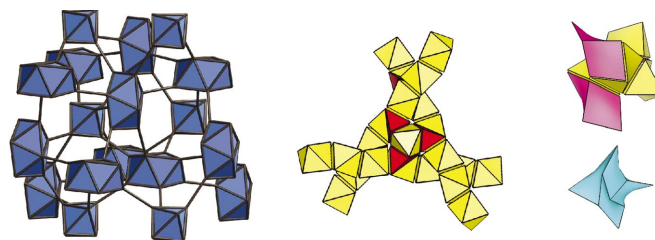


Figure 14
Left: the augmented **thp** net shown as linked bisdisphenoids. Center: the 12-coordinated structure as a tiling by tetrahedra and octahedra (see text). Right: the natural tiles for the **thp** net ($[3^2.4^3]$, yellow and $[4^3]$, magenta) and a dual tile ($[5^8]$, blue).

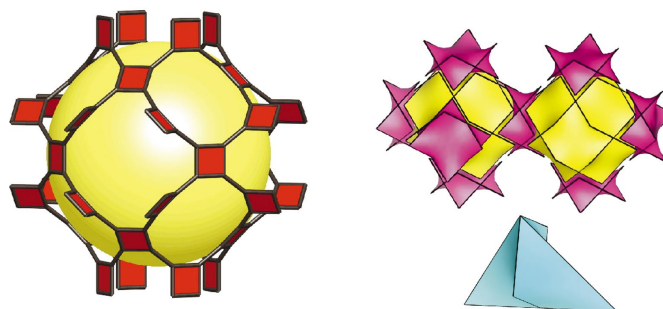


Figure 15
Left: the augmented **rhr** net. Right top: the normal tiles of the **rhr** net ($[6^8.8^6]$, yellow and $[4^4.8^2]$, magenta). Below is one dual tile ($[4^4]$, blue)

Table 2

The edge nets of regular (1–5), quasiregular (6) and semiregular nets (7–20).

Fischer = Fischer symbol (see text), c.n. = coordination number, s.g. = space group, p.g. = point group. The origin is always taken at an inversion center when one is present [‘origin choice 2’ of *International Tables for Crystallography* (1983)].

No.	Net	Edge net	c.n.	Fischer	s.g.	p.g.	<i>a</i>	<i>c</i>	<i>x</i>	<i>y</i>	<i>z</i>
1	srs	lcv	4	4/3/c1	$I4_132$	222	3.2660		1/8	0	1/4
2	nbo	sod	4	4/4/c1	$Im\bar{3}m$	$4m2$	2.8284		1/4	0	1/2
3	dia	crs	6	6/3/c2	$Fd\bar{3}m$	$\bar{3}m$	2.8284		0	0	0
4	pcu	reo	8	8/3/c2	$Pm\bar{3}m$	$4/mmm$	1.4142		1/2	0	0
5	bcu	pcu (×8)	6	6/4/c1	$Pm\bar{3}m\ddagger$	$m\bar{3}m$	1.0		0	0	0
6	fcu	reo (×8)	8	8/3/c2	$Pm\bar{3}m\ddagger$	$4/mmm$	1.4142		1/2	0	0
7	lvt	gis	4	4/4/t3	$I4_1/amd$	2	3.3337	2.9815	0.6500	1/4+x	7/8
8	sod	sod-e	6	6/3/c6	$Im\bar{3}m$	$mm2$	3.4142		0	0.3536	<i>y</i>
9	lcs	lcs-e	6	6/3/c7	$Ia\bar{3}d$	2	3.8637		1/8	0.2835	1/4– <i>y</i>
10	lcv	lcv-e ‡	6	–	$I4_132$	2	3.9681		1/8	0.2341	1/4– <i>y</i>
11	qtz	qtz-e	6	6/3/h3	$P6_222$	1	1.9319	2.1213	0.7887	2 <i>x</i>	1/2
12	hgx	sod	4	4/4/c1	$Im\bar{3}m\ddagger$	$4m2$	2.8284		1/4	0	1/2
13	lcy	lcy-e	6	6/3/c17	$P4_132$	2	2.3800		1/8	0.2035	1/4+y
14	crs	pyc	8	8/3/c2	$Fd\bar{3}m$	<i>m</i>	3.7712		0.9375	1/8	1/8
15	bcs	bcs-e §	8	–	$Ia\bar{3}d$	2	3.0938		1/8	0.4268	1/4– <i>y</i>
16	acs	kag (×2)	6	6/3/h13	$P6/mmm\ddagger$	<i>mmm</i>	2.0	1.0	1/2	0	0
17	reo	reo-e	6	6/3/c3	$Pm\bar{3}m$	<i>mm2</i>	2.4142		0	0.2929	<i>y</i>
18	thp	thp-e ‡	9	–	$I4_13d$	1	3.3779		0.0791	0.1420	0.6164
19	rhr	rho	4	4/4/c4	$Im\bar{3}m$	2	4.8284		1/4	0.1035	1/2+y
20	ana	ana-e	6	6/3/c36	$Ia\bar{3}d$	1	5.1615		0.2216	0.3917	0.8681

† True symmetry (and coordinates) of edge net. ‡ **lcv-e** and **thp-e** have unequal edges. § **bcs-e** has distances shorter than edges.

augmented net shown as linked bisdisphenoid in the figure, which also shows the tiles and dual tiles.

It might be noted that in this structure the edges are polar so in the augmented net the vertices at each end of a link are different (they are respectively 5- and 6-coordinated).

4. Structures with transitivity 1132

4.1. The rhr net

The **rhr** net has square-planar coordination and is shown in Fig. 15 in its augmented form as linked squares. The natural tiles are $[4^4.8^2]$ and $[6^8.8^6]$; if they are joined by sharing only the octagonal [tetragonal] faces, the remaining faces combine to produce the $P[C(P)]$ minimal surface (Fig. 15). The dual tile $[4^4]$ has the same topology as the natural tile for body-centered cubic (**bcu**).

4.2. The ana net

The **ana** net is the net of the tetrahedral atoms in the zeolite analcime (zeolite framework code ANA, Baerlocher *et al.*, 2001). The vertices have the lowest possible symmetry (2) for an edge-transitive net and although analcime-related materials are common zeolites, the net does not appear to have arisen elsewhere in crystal chemistry. A TX_2 structure with the ANA topology made from corner-linked regular TX_4 tetrahedra has a $T-X-T$ angle of 147.7° , which makes it particularly favorable for aluminosilicates. The edges necessarily are polar as they have symmetry 1. Aspects of the net are illustrated in Fig. 16.

5. Edge nets and augmented nets

An edge net is obtained by placing new vertices in the middle of edges of a parent net and discarding the old vertices. The new vertices are then joined by edges to echo the coordination figures of the old vertices (*e.g.* a square or tetrahedron for originally square or tetrahedral coordination) – note that in general it is not the same as an edge graph of graph theory in which vertices in edges common to a given original vertex are joined to form a complete graph. As all the semiregular nets are edge transitive, the edge nets are vertex transitive. We list these derived nets in Table 2. Notice that two distinct nets may have the same edge net. Thus, **sod** is the edge net of both **nbo** and **hgx**. The edge net of **lvt** is the net of the zeolite GIS, which we symbolize **gis** and that of **rhr** is the net of zeolite RHO, symbol **rho** (*cf.* Hyde *et al.*, 2003). The edge net of **crs** is the 8-coordinated packing **pyc** named for the pyrochlore structure (O’Keeffe & Hyde, 1996). Notice that the coordinates are for homogeneous sphere packings (*i.e.* all edges equal) when possible, so the vertices in the derived net are not necessarily in the geometric center of the original edge.

For convenience, we also give the coordinates of the vertices of the augmented nets in Table 3.

6. Derived two-colored nets

Some of the nets we have described are bipartite – *i.e.* they can serve as structures AB in which A is connected only to B and *vice versa*. This is of interest as one may want to link different SBUs with the same shape and symmetry; a simple example is afforded by the structure of berlinite $AlPO_4$ in which AlO_4 tetrahedra alternate with PO_4 tetrahedra to form a superstructure of the quartz form of SiO_2 . The groups may be of

Table 3

Coordinates for augmented regular (1–5), quasiregular (6) and semiregular nets with non-polar bonds (7–17, 19).

c.n. = coordination number, Fischer = Fischer symbol (see text), s.g. = space group, p.g. = point group, unit-cell parameters for unit edge. The origin is always taken at an inversion center when one is present ['origin choice 2' of *International Tables for Crystallography* (1983)].

No.	Net	Aug. net	c.n.	Fischer	s.g.	p.g.	<i>a</i>	<i>c</i>	<i>x</i>	<i>y</i>	<i>z</i>
1	srs	srs-a	3	3/3/c1	$I4_132$	2	6.0948		1/8	0.0580	1/4– <i>y</i>
2	nbo	nbo-a	3	3/4/c1	$Im\bar{3}m$	<i>mm2</i>	4.8284		0.1464	0	1/2
3	dia	dia-a	4	4/3/c6	$Fd\bar{3}m$	<i>3m</i>	5.1374		0.0562	<i>x</i>	<i>x</i>
4	pcu	cab	5	5/3/c3	$Pm\bar{3}m$	<i>4mm</i>	2.4142		0.2929	0	0
5	bcu	pcb	4	4/4/c2	$Im\bar{3}m$	<i>3m</i>	3.1457		0.1585	<i>x</i>	<i>x</i>
6	fcu	ubt	5	5/3/c4	$Fm\bar{3}m$	<i>mm2</i>	4.2426		1/2	0.3333	<i>y</i>
7	lvt	lvt-a	3	3/4/ <i>t</i> 3	$I4_1/amd$	1	5.6334	5.3139	0.0887	0.0609	0.9315
8	sod	sod-a	4	4/3/c10	$Im\bar{3}m$	<i>m</i>	6.2426		0	0.3066	0.4199
9	lcs	lcs-a	4	4/3/c32	$Ia\bar{3}d$	1	7.1678		0.0647	0.2238	0.4243
10	lcv	lev-a	4	4/3/c27	$I4_132$	1	6.8284		0.1768	0.1768	0.0000
11	qtz	qtz-a	4	–	$P6_222$	1	3.5718	3.8390	0.4582	0.1144	0.0921
12	hxx	pbz	3	3/6/c2	$Pn\bar{3}m$	2	4.2426		1/2	0.3333	– <i>y</i>
13	lcy	lcy-a	4	4/3/c17	$P4_132$	1	4.0358		0.0325	0.4675	0.8341
14	crs	crs-a	5	5/3/c10	$Fd\bar{3}m$	<i>m</i>	6.6001		0.3214	<i>x</i>	0.0357
15	bcs	bcs-a	5	5/3/c43	$Ia\bar{3}d$	1	5.4297		0.0935	0.0797	0.9569
16	acs	acs-a	4	–	$P6_3/mmc$	<i>m</i>	3.4545	3.0865	0.4298	2 <i>x</i>	0.0880
17	reo	lta	4	4/4/c6	$Pm\bar{3}m$	2	3.8284		0	0.1847	0.3694
19	rhr	rhr-a	3	3/4/c9	$Im\bar{3}m$	1	8.2930		0.3701	0.2848	0.0603

Table 4

Two-colored derivatives of the regular and semiregular nets.

s.g. refers to space group, under cell the entry 'same' means that the conventional cell is unchanged, **2a** means that the cell edges are all doubled and **2c** means that just the *c* axis is doubled in the binary derivative. The origin is always taken at a center of symmetry when there is one ['origin choice 2' of *International Tables for Crystallography* (1983)]. Array refers to the pattern of points in one of the sets of points in the binary structure (see text). **lcw** refers to the 2-coordinated invariant lattice complex *W* (Fischer & Koch, 1983).

No.	Name	Unary s.g.	Binary s.g.	Cell	<i>x, y, z</i>	<i>x, y, z</i>	Array
1	srs	$I4_132$	$P4_132$	Same	1/8, 1/8, 1/8	5/8, 5/8, 5/8	13 lcy
2	nbo	$Im\bar{3}m$	$Pm\bar{3}m$	Same	0, 1/2, 1/2	1/2, 0, 0	17 reo
3	dia	$Fd\bar{3}m$	$F4\bar{3}m$	Same	0, 0, 0	1/4, 1/4, 1/4	6 fcu
4	pcu	$Pm\bar{3}m$	$Fm\bar{3}m$	2a	0, 0, 0	1/2, 0, 0	6 fcu
5	bcu	$Im\bar{3}m$	$Pm\bar{3}m$	Same	0, 0, 0	1/2, 1/2, 1/2	4 pcu
7	lvt	$I4_1/amd$	$Imma$	Same	0, 0, 0	1/4, 1/4, 1/4	
8	sod	$Im\bar{3}m$	$Pm\bar{3}n$	Same	1/4, 0, 1/2	1/4, 1/2, 0	lcw
9	lcs	$Ia\bar{3}d$	$I4_13d$	Same	3/8, 0, 1/4	7/8, 0, 1/4	18 thp
11	qtz	$P6_222$	$P6_222$	2c	1/2, 0, 0	1/2, 0, 1/2	
12	hxx	$Pn\bar{3}m$	$Fd\bar{3}m$	2a	0, 0, 0	1/2, 1/2, 1/2	14 crs
15	bcs	$Ia\bar{3}d$	$Ia\bar{3}$	Same	0, 0, 0	1/4, 1/4, 1/4	4 pcu
16	acs	$P6_3/mmc$	$P6m2$	Same	1/3, 2/3, 0	2/3, 1/3, 1/2	
19	rhr	$Im\bar{3}m$	$Pm\bar{3}m$	Same	0.3333, <i>x</i> , 0	0.8333, <i>x</i> , 1/2	

different size and stoichiometry: in the $MnGe_4S_{10}$ framework, tetrahedral MnS_4 groups and tetrahedral Ge_4S_{10} groups are linked to form a network of the diamond (**dia**) topology (Yaghi *et al.*, 1994). The maximum symmetry is lowered to $F4\bar{3}m$ and the *AB* structure is that of the sphalerite form of ZnS . Other familiar binary structures derived from regular nets are those of NbO , $NaCl$ and $CsCl$.

In order to have a binary derived structure with one kind of edge, the edges of the original structure must be non-polar and all rings must be even. Thirteen of the twenty vertex-and-edge-transitive structures meet these criteria. Data for the derived structures are listed in Table 4. In every case but that of the binary **bcs** net, the shortest *A*···*B* distances uniquely define the edges. For the binary **bcs** net, the centers of the edges remain in positions 1/8, 3/8, 7/8 *etc.* The pattern of points of *A* or *B* alone is often that of one of the structures we

have described. For example, in the binary **srs** net each set of points is that of **lcy** (see Table 2).

7. Linked polygons and polyhedra

A major motivation for this work is the desire to enumerate ways in which geometric figures (polygons and polyhedra) corresponding to clusters of atoms can be linked by one kind of linker to form extended crystal structures (Yaghi *et al.*, 2003). The points of extension of the clusters correspond to the vertices of these figures which are often referred to as secondary building units (SBUs). The augmented forms of the nets we have described provide examples.

Unfortunately, the augmented forms of the nets do not provide a complete enumeration. For example, the augmented tetrahedral structures could be modified by systematically

removing pairs of opposite edges of the tetrahedra to leave a pattern of linked quadrilaterals (which, in some instances at least, may be squares). Similarly, prisms and antiprisms may be interconverted by adding or removing edges as appropriate and many polyhedra with N vertices may be converted into N -gons. Nets that are amplified by replacing each vertex by a cluster of vertices are referred to as *decorated* (O’Keeffe *et al.*, 2000). Any such net of equal figures connected by equal links would correspond to a decoration of one of the nets enumerated above if our enumeration is complete. We consider some special cases below.

7.1. Linked squares

In Fig. 17, we show a net of linked squares derived from the augmented diamond net. This net was discussed at length by Wells (1977) and has recently been found in a metal–organic framework (MOF) (Carlucci *et al.*, 2001). In the augmented **qtz** (quartz) and **lcv** structures, the tetrahedra have symmetry 222 (D_2) and three different structures with the same symmetry as the parent structure are derived according to which pairs of opposite edges of the tetrahedra are removed.

Such nets are 3-coordinated, so they and others might be expected to be found in the list of vertex-transitive 3-coordinated sphere packings of Koch & Fischer (1995) in which there is a single 4-ring at each vertex. There are 16 such structures; 15 of these are either augmented (*a*) or otherwise decorated (*d*) versions of the nets in this paper. We list these 16 structures here:

$3/4/c1$ (*a-nbo*); $3/4/c2$ (*d-sod*); $3/4/c3$ (see below); $3/4/c4$ (*d-sod*); $3/4/c5$ (*d-lcv*); $3/4/c6$ (*d-lcv*); $3/4/c7$ (*d-lcv*); $3/4/c8$ (*d-sod*); $3/4/c9$ (*a-rhr*); $3/4/c10$ (*d-lcs*); $3/4/t1$ (*d-dia*); $3/4/t2$ (*d-dia*); $3/4/t3$ (*a-lcv*); $3/4/h1$ (*d-qtz*); $3/4/h2$ (*d-qtz*); $3/4/h3$ (*d-qtz*).

The case of $3/4/c3$ is instructive. The underlying net (decorated in $3/4/c3$) is shown in Fig. 18. The symmetry is $I432$ and vertices are in $12(e)$, x , 0 , 0 *etc.* with $x \neq 0$ or $1/2$ (actually the symmetry of just the vertices is $Im\bar{3}m$). The vertices have one or two (for $x = 1/4$) nearest neighbors but in fact edges link four of eight equidistant further neighbors to make the 4-coordinated net shown. The centers of the edges are in $24(i)$, $1/4$, y , $1/2 - y$ with $y = x/2$. It should be clear from the figure that if the vertices are at the center of mass of their neighbors

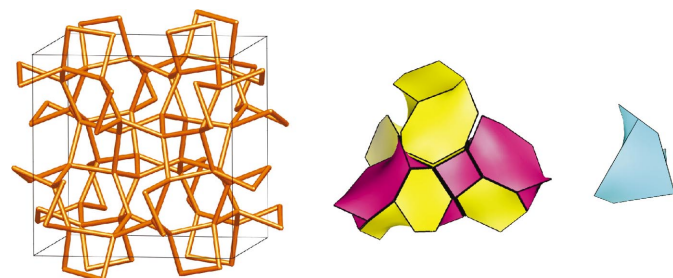


Figure 16

Left: the **ana** net as a stick model. Center: natural tiles ($[4^2.8^2]$, magenta and $[6^2.8^3]$, yellow) for the **ana** net. Right: a dual tile ($[5^4]$).

they will come together in pairs ($x = 0$) so we excluded such a net from consideration at the outset. The figure also shows the augmented net (sphere packing $3/4/c3$) as a linkage of squares.

The only 4-coordinated net in our list that does not appear decorated in the Koch–Fischer list of vertex-transitive 3-coordinated sphere packings is **ana**. This is because the bonds in **ana** are polar and as a consequence the augmented net has two kinds of vertex.

7.2. Linked hexagons, octahedra and trigonal prisms

Fig. 17 shows a net formed by linking planar hexagons with a decorated **pcu** (primitive cubic) topology. This net was discussed by Wells (1977) who remarked on its occurrence in the hydrogen-bonded structure of β -quinol clathrates (Palin & Powell, 1947).

The Koch & Fischer (1995) compilation of 3-coordinated sphere packings contains nine structures containing 6-rings. In the first of these ($3/6/c1$), the 6-rings share edges, but in the rest they are linked by single edges so they are decorations of our 6-coordinated edge-transitive structure. The identification, made in the same way as in §7.1, is:

$3/6/c2$ (*a-hxg*); $3/6/c3$ (*d-crs*); $3/6/c4$ (*d-pcu*); $3/6/c5$ (*d-pcu*); $3/6/c6$ (*d-bcs*); $3/6/h1$ (*d-pcu*); $3/6/h2$ (*d-acs*); $3/6/h3$ (*d-acs*).

The net of Fig. 17 is that of $3/6/h1$. The cubic minimal surfaces of genus 3, the D , P and G surfaces can be tiled with hexagons and octagons in such a way that two octagons and one hexagon meet at each vertex. These structures, labeled $6.8^2 D$, $6.8^2 P$ and $6.8^2 G$ (O’Keeffe & Hyde, 1996) are those of $3/6/c2$, $3/6/c4$ and $3/6/c6$, respectively. $6.8^2 D$ is the polybenzene structure of §2.6.

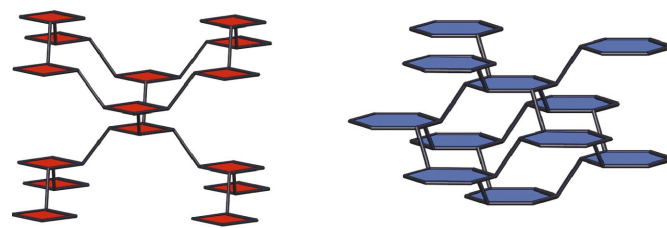


Figure 17

Two nets described by Wells (1977). Left: linked squares with a decorated **dia** topology. Right: linked hexagons with a decorated **pcu** topology.

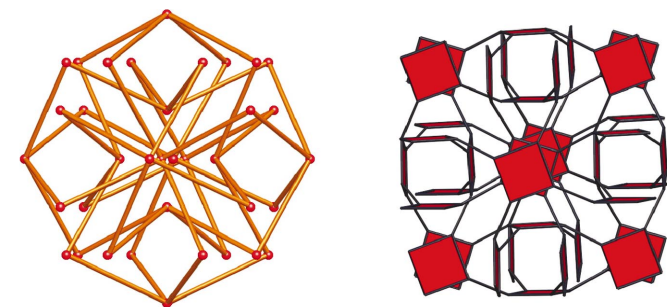


Figure 18

Left: a vertex and edge-transitive 4-coordinated net with symmetry $I432$. Right: the augmented net shown as linked squares. This is the net of the sphere packing $3/4/c3$ of Koch & Fischer (1995).

The augmented **acs** net is a linkage of trigonal prisms with symmetry $P6_3/mmc$. The trigonal prisms can be converted to trigonal antiprisms (octahedra) linked by equal links in two ways with symmetry $P\bar{3}1c$ and symmetry $P6_322$. These correspond to the sphere packings $3/6/h2$ and $3/6/h3$ with hexagon angles equal to 60° . Parameters a, c, x, y, z for all edges equal to unity are: $P\bar{3}1c$: 2.9134, 2.5308, 0.1352, 0.6667, 0.9113; $P6_322$: 3.1715, 2.7453, 0.1513, 0.4846, 0.3987.

7.3. Linked cubes, square antiprisms and octagons

MOFs based on nets with coordination numbers ≥ 8 are rare, indeed we know of only one 8-coordinated case (Long *et al.*, 2001), and in this case the structure is based on linked single atoms so the SBU is just a single vertex; the net is that of **bcu**. Accordingly, we do not expect structures built from SBUs with eight vertices to be very common and our analysis is rather cursory.

The Koch–Fischer list of sphere packings includes three ($3/8/t2$, $3/8/t3$ and $3/8/t4$) with 8-rings that do not have common edges. As expected, they are all decorated **bcu** nets and may be considered as derived from augmented **bcu** ('polycubane') by removing four edges per cube. The net of the packing $3/8/t1$ can also be considered as derived from octagons each linked to eight other octagons.

One can also derive two linkings of square antiprisms from augmented **bcu** by adding four edges per cube. Two ways that have all links between the polyhedra the same are obtained from $3/8/t2$ (symmetry $I422$) and $3/8/t3$ (symmetry $P4/nnc$) by making the octagon angles equal to 60° . Parameters a, c, x, y, z for all edges equal to unity are: $I422$: 2.9869, 2.8687, 0.0906, 0.2188, 0.1466; $P4/nnc$: 2.7934, 2.7015, 0.0161, 0.1532, 0.5944 (origin at $\bar{1}$).

8. Concluding remarks

It is simple to enumerate all vertex-and-edge-transitive structures with periodicity less than three. In tilings of the sphere (0-periodic), there are the five regular (platonic) polyhedra (3^3 , 3^4 , 3^5 , 4^3 , 5^3) and the two quasiregular polyhedra – the cuboctahedron (3.4.3.4) and the icosidodecahedron (3.5.3.5). For 1-periodic structures (tilings of a cylinder), there is only the infinite family of 4^4 tiles (Koch & Fischer, 1978; Eddaoudi *et al.*, 2002). For tilings of the plane (2-periodic), there are three regular tilings (3^6 , 4^4 , 6^3) and one quasiregular tiling (3.6.3.6). Advantage has been taken of these results to show that there are just nine basic ways of linking square SBUs by one kind of linker into structures of different dimensionality, and the successful synthesis of many of them has been demonstrated (Eddaoudi *et al.*, 2002).

The next step is to enumerate and describe structures with two kinds of vertex and one kind of edge, *i.e.* the remaining edge-transitive nets. This will be the subject of the next paper in this series.

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References

- Aste, T. & Weaire, D. (2000). *The Pursuit of Perfect Packing*. Bristol: Institute of Physics.
- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1461–1494.
- Baerlocher, Ch., Meier, W. M. & Olson, D. H. (2001). *Atlas of Zeolite Framework Types*. Amsterdam: Elsevier. <http://www.iza-structure.org/databases/>.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Rizzato, S. (2001). *Chem. Commun.* pp. 1198–1199.
- Carlucci, L., Cozzi, N., Ciani, G., Moret, M., Proserpio, D. M. & Rizzato, S. (2002). *Chem. Commun.* pp. 1354–1355.
- Delgado Friedrichs, O. & Huson, D. H. (1999). *Discrete Comput. Geom.* **21**, 299–315.
- Delgado Friedrichs, O. & Huson, D. H. (2000). *Discrete Comput. Geom.* **24**, 279–292.
- Delgado Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2003a). *Acta Cryst.* **A59**, 22–27.
- Delgado Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2003b). *Solid State Sci.* **5**, 73–78.
- Delgado Friedrichs, O., Plévert, J. & O'Keeffe, M. (2002). *Acta Cryst.* **A58**, 77–78.
- Eddaoudi, M., Kim, J., Vodak, D., Sudik, A., Wachter, J., O'Keeffe, M. & Yaghi, O. M. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4900–4904.
- Fischer, W. (1971). *Z. Kristallogr.* **133**, 18–42.
- Fischer, W. (1973). *Z. Kristallogr.* **138**, 129–146.
- Fischer, W. (1974). *Z. Kristallogr.* **140**, 50–74.
- Fischer, W. (1993). *Z. Kristallogr.* **205**, 9–26.
- Fischer, W. & Koch, E. (1983). *Lattice Complexes*. In *International Tables for Crystallography*, Vol. A, edited by Th. Hahn. Dordrecht: Kluwer Academic Publishers.
- Fischer, W. & Koch, E. (1989). *Acta Cryst.* **A45**, 726–732.
- Goetzke, K. & Klein, H.-J. (1991). *J. Non-Cryst. Solids*, **127**, 215–220.
- Hamilton, A. J. S., Gott, J. R. & Weinberg, D. (1986). *Astrophys. J.* **309**, 1–12.
- Hawkins, S. C., Bishop, R., Dance, I. G., Lipari, T., Craig, D. C. & Scudder, M. L. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 1729–1735.
- Hyde, S. T., Larsen, A.-K., Di Matteo, T. & Ramsden, S. (2003). *Aust. J. Chem.* **56**, 981–1000.
- International Tables for Crystallography* (1983). Vol. A, edited by Th. Hahn. Dordrecht: Kluwer Academic Publishers.
- Koch, E. & Fischer, W. (1978). *Z. Kristallogr.* **148**, 107–152.
- Koch, E. & Fischer, W. (1995). *Z. Kristallogr.* **210**, 407–414.
- Long, D.-L., Blake, A. J., Champness, N. R., Wilson, C., Schröder, M. (2001). *Angew. Chem. Int. Ed. Engl.* **40**, 2444–2447.
- O'Keeffe, M. (1991). *Z. Kristallogr.* **196**, 21–37.
- O'Keeffe, M., Adams, G. B. & Sankey, O. F. (1992). *Phys. Rev. Lett.* **68**, 2325–2328.
- O'Keeffe, M. & Andersson, S. (1977). *Acta Cryst.* **A33**, 914–923.
- O'Keeffe, M., Eddaoudi, M., Li, H., Reineke, T. & Yaghi, O. M. (2000). *J. Solid State Chem.* **152**, 3–20.
- O'Keeffe, M. & Hyde, B. G. (1996). *Crystal Structures I: Patterns and Symmetry*. Washington: Mineralogical Society of America.
- O'Keeffe, M. & Hyde, S. T. (1997). *Zeolites*, **19**, 370–374.
- O'Keeffe, M. & Sullivan, J. M. (1998). *Z. Kristallogr.* **213**, 374–376.
- Palin, D. E. & Powell, H. M. (1947). *J. Chem. Soc.* pp. 208–221.
- Pearce, P. (1978). *Structure in Nature is a Strategy for Design*. Cambridge: MIT Press.
- Schoen, A. H. (1970). *Infinite Periodic Minimal Surfaces without Self-intersections*. Technical Note D-5541. Washington: National Aeronautics and Space Administration.

- Shen, X., Ho, D. M. & Pascal, R. A. (2003). *Organic Lett.* **5**, 369–371.
- Sowa, H., Koch, E. & Fischer, W. (2003). *Acta Cryst.* **A59**, 317–326.
- Wang, C., Li, Y., Bu, X., Zheng, N., Zivcovic, O., Yang, C.-S. & Feng, P. (2001). *J. Am. Chem. Soc.* **123**, 11506–11507.
- Weaire, D. & Hutzler, S. (1999). *The Physics of Foams*. Oxford: Clarendon Press.
- Wells, A. F. (1977). *Three-Dimensional Nets and Polyhedra*. New York: Wiley.
- Yaghi, O. M., O’Keeffe, M., Eddaoudi, M., Chae, H. K., Kim, J. & Ockwig, N. W. (2003). *Nature (London)*, **423**, 705–714.
- Yaghi, O. M., Sun, Z., Richardson, D. A. & Groy, T. L. (1994). *J. Am. Chem. Soc.* **116**, 807–808.