ELSEVIER

What do we know about three-periodic nets?

Olaf Delgado-Friedrichs[a], Martin D. Foster[b], Michael O'Keeffe[a],*, Davide M. Proserpio[c], Michael M.J. Treacy[b], Omar M. Yaghi[d]

[a]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA*
[b]*Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287, USA*
[c]*Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy*
[d]*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA*

Abstract

An account is given of various classifications of three-periodic nets. It is convenient to classify nets according to the nature of their maximum-symmetry embeddings. Other classifications, particularly in terms of the tilings that carry the nets, are also discussed. Although there is an infinity of possible nets, for certain types the number of possibilities is limited—there are for example exactly five regular nets. An account is given of the enumerations of various types of special structures such as sphere packings, the nets of simple tilings and self-dual tilings. Some databases of relevant structures and computer programs are described.
© 2005 Elsevier Inc. All rights reserved.

For he that beats the bush the bird not gets,
But who sits still and holdeth fast the nets.
Edward de Vere [1]

1. Introduction

In an introductory article [2] to an earlier special issue of the *Journal of Solid State Chemistry* devoted to "The Design of Solids from Molecular Building Blocks" [3] an account was given of the more important periodic structures ("nets") for the design and synthesis of extended solid structures. It has been established [4] that these "default" structures are overwhelmingly preferred by nature in the construction of crystals. We revisit the question of why they are special here. But there are also outliers—less common topologies that

arise occasionally. What of them? What is their nature, and how many of them are there? How might they be classified? What is their relevance to crystal design and synthesis (reticular chemistry [5] and crystal engineering [6])? This article is an attempt to answer some of these questions also. The treatment is informal and is intended to serve as a tutorial for those interested in the design, synthesis and analysis of structures.

2. Basic ideas and definitions

Definitions of terms from graph theory and their application to nets are given in a companion contribution [7]. That paper might also be consulted for topics concerning how one specifies the topology of a net (*quotient graph* and *vector representation*) and determines intrinsic properties such as combinatorial symmetry. There also one will find definitions of terms such as *ring* and *vertex symbol* as used in the context of nets.

*Corresponding author.

E-mail address: mokeeffe@asu.edu (M. O'Keeffe).

Here we are more concerned with recognition of different types of net and their classification.

The term "net" as used in this article, and generally in crystal chemistry, refers to a periodic connected simple graph. Familiar examples are the nets of zeolite frameworks in which the tetrahedral (T) atoms are the vertices and –O– links act as the edges. These nets are examples of four-coordinated nets (each vertex is common to four edges, and thus has four neighbors in the graph-theory sense).

An *embedding* of a net is a realization in space in which coordinates can be assigned to each vertex and a metric to the lattice ("lattice parameters"). In a *faithful* embedding edges do not intersect or touch vertices, and the vertices are distinct points.

A *sphere packing* is a special kind of net that has an embedding in which all the edges are of equal length and correspond to the shortest distances between vertices. Note that we do not require the vertices to be equivalent (related by symmetry) in sphere packings in general, but, unless explicitly stated to the contrary, we assume all spheres to have the same diameter.

An *equilibrium placement* of a net assigns barycentric coordinates to the vertices. By this we mean that each vertex has coordinates that are the average of the coordinates of its neighbors. Once an origin is chosen, barycentric coordinates are unique for a given choice of basis vectors. Such a placement is valuable in determining properties such as combinatorial symmetry [8]. *Collisions* occur when two vertices have the same barycentric coordinates. Clearly this happens if, for example, two vertices have the same neighbors—for further discussion of collisions see [8].

In what follows, we consider only nets without collisions, as nets with collisions are so far very rare in crystal chemistry. An important result is that the combinatorial (topological) symmetry of a periodic net without collisions is isomorphic to a space group, and this space group is the symmetry of a maximum-symmetry embedding [9].

Nets are often identified by a symbol such as **dia** or **dia-a**. These are an attempt at providing universal identifiers for nets and are discussed further below. They should not be confused with the upper-case three letter codes assigned to zeolite framework types.

3. Embeddings

Usually in describing a net, parameters are given appropriate to a maximum-symmetry embedding. Ideally also the shortest distances are all equal (for convenience unity in the units of the lattice parameters) and correspond to the edges of the net. This ideal situation is not always possible however, as can be seen by considering a generic infinite net without symmetry.

Let the average coordination number be Z, then there are $Z/2$ edges per vertex. Each vertex has three coordinates (x, y, z), so if $Z > 6$ there are more constraints (edge lengths) than degrees of freedom (coordinates) and there is no solution for equal edges possible. In fact, as the equations for edge lengths are non-linear in coordinates, there is no guarantee that there is a solution even for $Z \leqslant 6$. Of course we are not dealing with generic structures, but rather with translational and, usually, other symmetries, so the problem is quite complicated. There are several cases to consider which we list first, then give examples:

1. For the simple nets most common in crystal chemistry the maximum-symmetry embedding is a sphere packing. There are three cases:
   a. The coordinates and unit cell shape are fixed by symmetry in the maximum-symmetry embedding.
   b. In other cases there are still degrees of freedom remaining. It is common [10,11] in this case to report a structure that is a minimum of density (maximum cell volume) subject to the constraint of equal edge lengths which can be taken as unity.
   c. Again there are free parameters, but the minimum density configuration corresponds to a structure with more contacts. See e.g. [11] where many examples are given. Structures of this type have been of less importance in crystal chemistry in the past.
2. The maximum-symmetry embedding corresponds to a sphere packing with more contacts than the coordination number, n, but n of those contacts correspond to edges; there are two cases:
   a. There is an embedding as an n-coordinated sphere packing of lower symmetry in which the n edges correspond to edges. Structures of this type are so far rather rare.
   b. There is not an embedding as above (strictly we should say that such an embedding cannot be found, *proving* one does not exist might be difficult). This case is more common than might be supposed.
3. The maximum-symmetry embedding is a sphere packing with fewer contacts than the coordination number, n; but the n shortest distances correspond to the edges of the n-coordinated net; there are three cases:
   a. There is a lower-symmetry embedding with equal edge lengths and edges still corresponding to shortest distances between vertices.
   b. There is no embedding with equal edge lengths.
   c. There is an embedding with shortest distances equal to edges, but they cannot all be made equal and remain shortest distances.
4. There may be no embedding with shortest distances corresponding to edges. This is in fact the case for the

vast majority of nets (see below). Until recently, they were not recognized in crystal chemistry, as normally bonds (corresponding to edges of nets) are formed to nearest neighbors, but, with flexible linkers instead of bonds as the edges of nets, they are beginning to appear.

5. There may be no faithful embedding in the maximum-symmetry conformation because the symmetry will require edges to intersect [8]. There is always a lower-symmetry embedding—all graphs have a faithful embedding in three-dimensional Euclidean space. These lower-symmetry embeddings may be any one of types described above in 1–4 (but of course not of maximum symmetry) and there may be several equally "good".

4. Example of embeddings

1. Maximum-symmetry sphere packings:
   a. *With fixed coordinates*. In the cubic diamond net (**dia**) the atoms are on fixed positions ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, etc.). There is one edge length which determines the unit cell parameter. In the cubic net (**fau**) of the zeolite faujasite the atoms are in general positions (x, y, z), but now four independent edge lengths which determine the coordinates and unit cell parameter.
   b. *Sphere packings at minimum density*. The familiar net (**crb**) of the B atoms in CrB_4 is an example [12]. It has symmetry $I4/mmm$ with vertices in positions x, x, 0, etc. There are three parameters: x and the unit cell edges a and c but only two independent edge lengths, so one degree of freedom after fixing the edge lengths, but before minimizing the density.
   c. *Sphere packings without minimum density*. An example from Ref. [11] is the cubic sphere packing

$3/8/c3$. This has symmetry $Im\bar{3}m$ and one kind of vertex in general positions (say) 0.3500, 0.1768, 0.0732, etc. and three edges, so one degree of freedom remaining after fixing the edge lengths. The minimum density conformation (0.4268, 0.1768, 0.0732) corresponds to a four-coordinated structure $4/4/c18$ (**wse**).

2. Maximum symmetry is a sphere packing of too high coordination number:
   a. *There is a lower-symmetry sphere packing of the right coordination number*. An important example is the structure (**cds**) named for the 4-coordinated net of $CdSO_4$ [13]. The maximum-symmetry form has symmetry $P4_2/mmc$ and in this configuration each vertex has six equidistant neighbors. However, there are lower-symmetry forms [12] with only four geometric neighbors, the simplest of which [14] has symmetry $P4_2/mbc$ with $a' = 2a$, $c' = c$ as shown in Fig. 1.
   b. *There is not a lower-symmetry sphere packing of the right coordination number*. In Fig. 2 we give two examples of six-coordinated structures in which the vertices occupy the points of a bcc lattice of edge a. The first net (**bcs**) has symmetry $Ia\bar{3}d$ with $a' = 2a$ and the vertices are on fixed positions (0, 0, 0, etc.) It is an important example of a semiregular net (see below) [15]. The second, **rob**, is derived from the topology of a crystal structure [16]. The symmetry is $Cccm$ with $a' = a$, $b' = c' = \sqrt{2}a$. In deriving these nets $\frac{1}{4}$ of the edges of body-centered cubic (**bcu**) are eliminated. In **bcs** these lie along all four $\langle 1\,1\,1 \rangle$ directions, in **rob** they lie along just two such directions.

   Another important example is the "quartz dual" structure **qzd** discussed elsewhere [13]. In

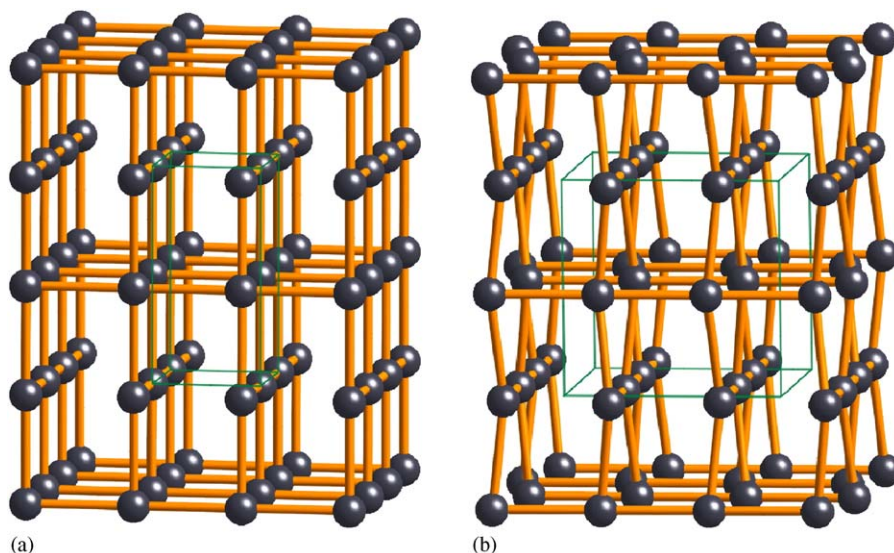(a)   (b)

Fig. 1. Two embeddings of the **cds** net: (a) maximum symmetry $P4_2/mmc$, (b) $P4_2/mbc$.
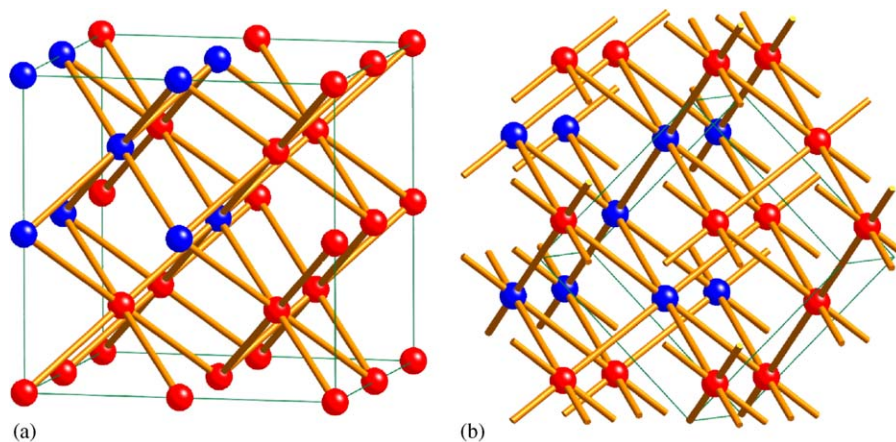
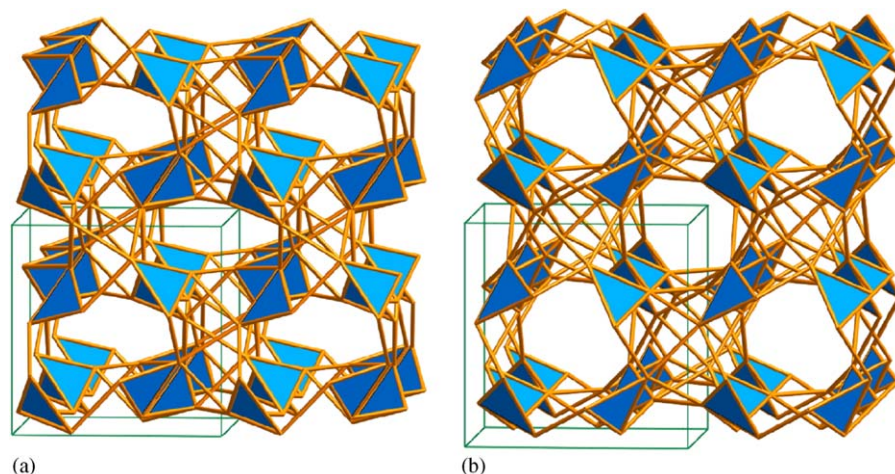Fig. 2. (a) The net **bcs**, (b) the net **rob**. Blue spheres outline a unit of the *bcc* lattice (net **bcu**).

Fig. 3. The net **fcb**: (a) as a sphere packing with symmetry *I*23, (b) in a maximum-symmetry embedding *I*432.

this four-coordinated net the vertices are at the positions of the nodes of a hexagonal lattice.

3. Maximum symmetry is a sphere packing of too-low coordination number:

   a. *There is a lower-symmetry embedding as a sphere packing.* An example (Fig. 3) is the five-coordinated net **fcb** which has symmetry *I*432 with vertices in positions $x, \frac{1}{4}, \frac{1}{2} + x$, etc. and thus two parameters (a and x), but three independent edge lengths which cannot be made all equal. However in an embedding in *I*23 the vertices are in general positions x, y, z and again three independent edge lengths, and an embedding is possible with all edges equal. The *I*23 structure is the sphere packing $5/3/c13$ of Fischer [11]. A second example (**fnm**, Fig. 4) is also a five-coordinated sphere packing $5/5/c1$. As a sphere packing the symmetry is $I\bar{4}3d$ with vertices in positions x, x, x and two kinds of edge; there are two parameters (a and x), In the maximum symmetry ($Ia\bar{3}d$) the vertices are

in special positions $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$, etc. but still two edge lengths which cannot be made equal. This net is an example of what we call a "rod net" [17] as there are straight non-intersecting rods of edges. It is also a rare example of a net with only five-rings; the vertex symbol is $5.5.5.5_2.5_2.5_2.5_2.5_2.5_2.$*.

   b. *There is not a lower-symmetry embedding as a sphere packing.* A simple example is the case of the body-centered cubic lattice considered as a 14-coordinated structure (**bcu**) as shown in Fig. 5. There are of course no sphere packings for $n > 12$. For lower-coordination numbers the absence of an embedding as a sphere packing will be difficult to prove in general. An interesting case is the six-coordinated net (**mep-e**) of the O atoms in the mineral melanophlogite. This is a form of silica (with organic inclusions) so the O atoms form a framework of tetrahedra linked by corners. The maximum-symmetry form is cubic, $Pm\bar{3}n$, and there are seven parameters (including the cell edge)
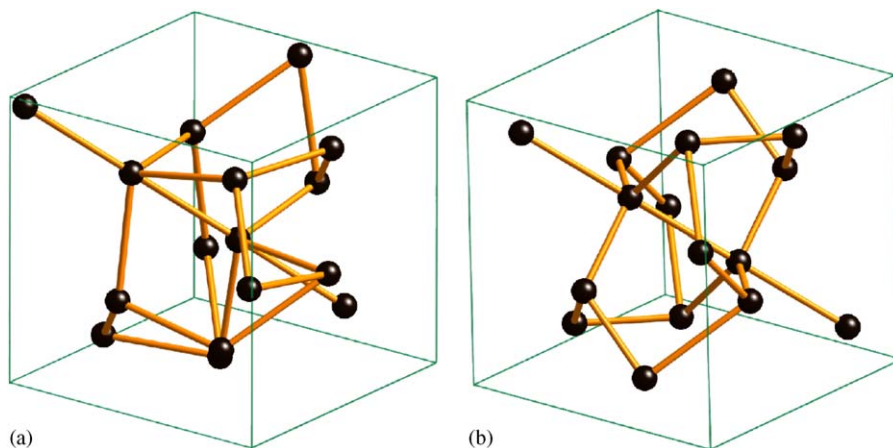
Fig. 4. The net **fnm** (a) as a five-coordinated sphere packing with symmetry $I\bar{4}3d$ and (b) with maximum symmetry, $Ia\bar{3}d$.
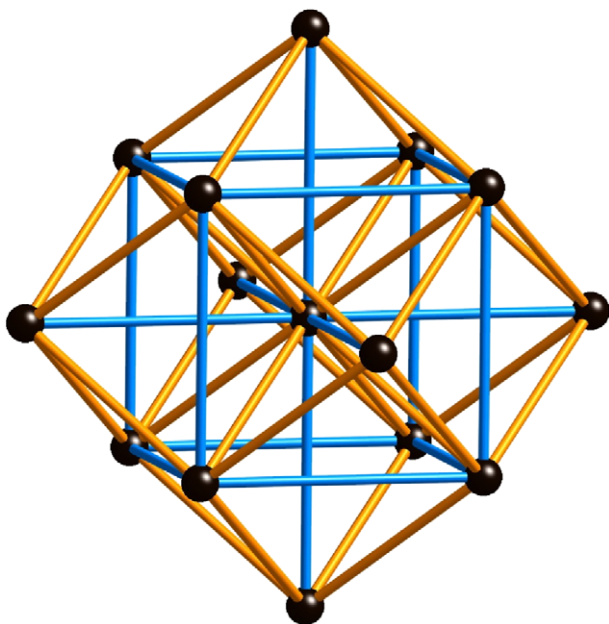

Fig. 5. The 14-coordinated net **bcu-x**. The blue and yellow edges are necessarily of different length.

and eight edges. There is no solution for equal edges, but one can make the edges "almost" equal (spread of less than 1%). We do not know if there is a lower-symmetry embedding with all edges equal. The net **mep** of the linked Si atoms (centers of the tetrahedra) is discussed as a tiling below:

c. *There is not a lower-symmetry embedding as a sphere packing, but edges can be made equal.* An example is provided by the seven-coordinated net (**gar-e**) of the anions in the cubic garnet structure. Here there are four parameters (x, y, z, and a) and four independent edges. If the edges are made all equal it is found that there is one shorter intervertex distance (0.92 times the edge length), however configurations can be found with the

seven shortest intervertex distances corresponding to edges; those coordinates are given in the RCSR database described below. (The coordinates for all equal edges are 0.9578, 0.0589, 0.1488.) The structure is shown as corner-sharing octahedra and tetrahedra in Fig. 6. The net of the centers of the linked polyhedra is a (4,6)-coordinated net (**gar**).

4. No embedding with shortest distances corresponding to edges.

As a first example we illustrate in Fig. 7 the net **tcb** which was found recently by three independent groups [18–20] in metal-organic frameworks (MOFs). The symmetry is *Pnna* and the vertices of the net are in positions 4 a: 0, 0, 0, etc. To complete the specification of the net we have to specify the two independent bonds which are from 0, 0, 0 to 0, $\frac{1}{2}$, $-\frac{1}{2}$ and to $\frac{1}{2}$, 1, 0. All the shortest ring at each angle in this net are eight-rings—the vertex symbol is $8_2 \cdot 8_2 \cdot 8_5 \cdot 8_5 \cdot 8_5 \cdot 8_5$.

A second net (**ten**) was found (by MDF and MMJT) in a search for possible zeolite nets (see below). It has symmetry *I*23 and is also illustrated in Fig. 7. The vertices are in general position positions x, y, z and the edges are from x, y, z to $-x$, $1-y$, z; $-x$, $-y$, z; and $\frac{1}{2} - z$, $x - \frac{1}{2}$, $\frac{1}{2} - y$. All the shortest rings at each angle in this net are 10-rings—the vertex symbol is $10_7 \cdot 10_7 \cdot 10_9 \cdot 10_{13} \cdot 10_{12} \cdot 10_{12}$.

A 4-coordinated net (**elv**) with vertex symbol $11 \cdot 11_2 \cdot 11 \cdot 11_2 \cdot 11_2 \cdot 11_3$ was found in the same search. The symmetry is again *I*23 and edges are from x, y, z to $-\frac{1}{2} - y$, $1\frac{1}{2} - z$, $\frac{1}{2} + x$; x, $-y$, $1-z$; and $1-x$, $1-y$, z. In its minimum density conformation each vertex has 88 vertices closer than the ones to which it is linked.

5. *No embedding in maximum symmetry.* Fig. 8 gives two examples (**ulk** and **fcw** with symmetry $Im\bar{3}m$ and $Pn\bar{3}m$, respectively) in which edges of necessity intersect in maximum-symmetry configurations, but
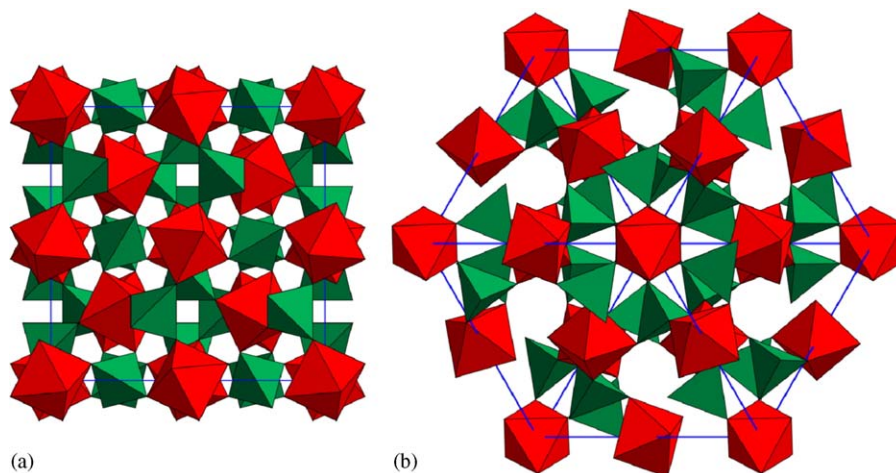
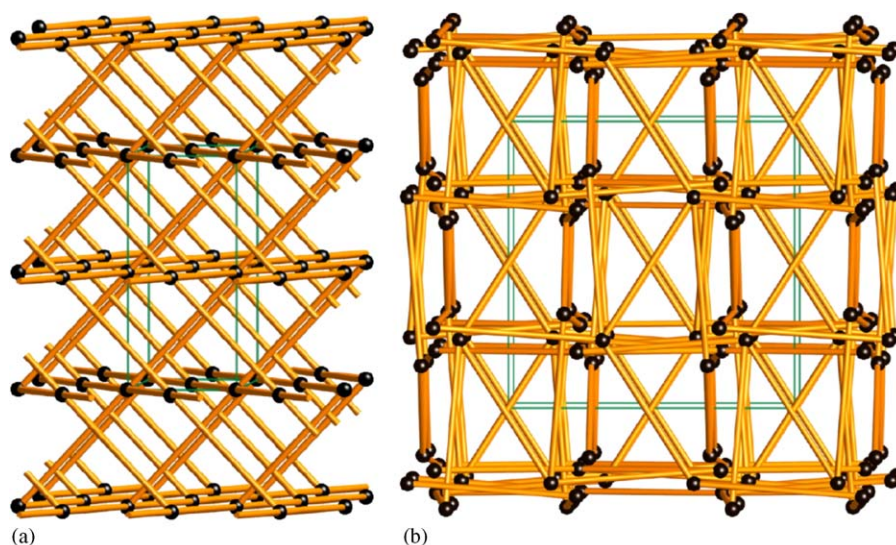Fig. 6. The garnet anion net **gar-e** projected (a) on (1 0 0) and (b) on (1 1 1).

Fig. 7. (a) The net **tcb**, (b) **ten**.

that are uninodal sphere packings ($4/3/c13$ and $5/3/c39$ [11]) in lower-symmetry ($Fd\bar{3}c$ in both cases) embeddings. A related example, Fig. 9, is provided by the anion net (**mog-e**) of the moganite form of silica. With symmetry *Ibam* this can be made with regular SiO_4 tetrahedra. However, the combinatorial symmetry is *Cmmm* with a unit cell half the size ($c' = c/2$), and with this symmetry the "tetrahedra" are forced to be planar.

For convenience the nets mentioned in this article are listed by embeddability type in Table 1. Most are types **1a** or **1b** as these are generally the most interesting in crystal chemistry, but in the grand scheme of things type **4** must predominate.

5. Nets and tilings

Covering the plane with equal squares as in Fig. 10 is an example of a tiling in which the tiles are *edge to edge*. The edges and vertices of the tiling form a two-periodic net, familiar as the square lattice 4^4. We say that this net is *carried* by the tiling. Note that the tiling corresponding to the face of a brick wall is really a 6^3 tiling by hexagons if we require each edge to be common to exactly two tiles (Fig. 10).

In three dimensions the tiles become generalized polyhedra or *cages*. A familiar example is filling space by cubes sharing faces. Another example (Fig. 11) is provided by the subdivision of the diamond structure into adamantine units; in this case some of the vertices of the cage are divalent (belong to only two edges).
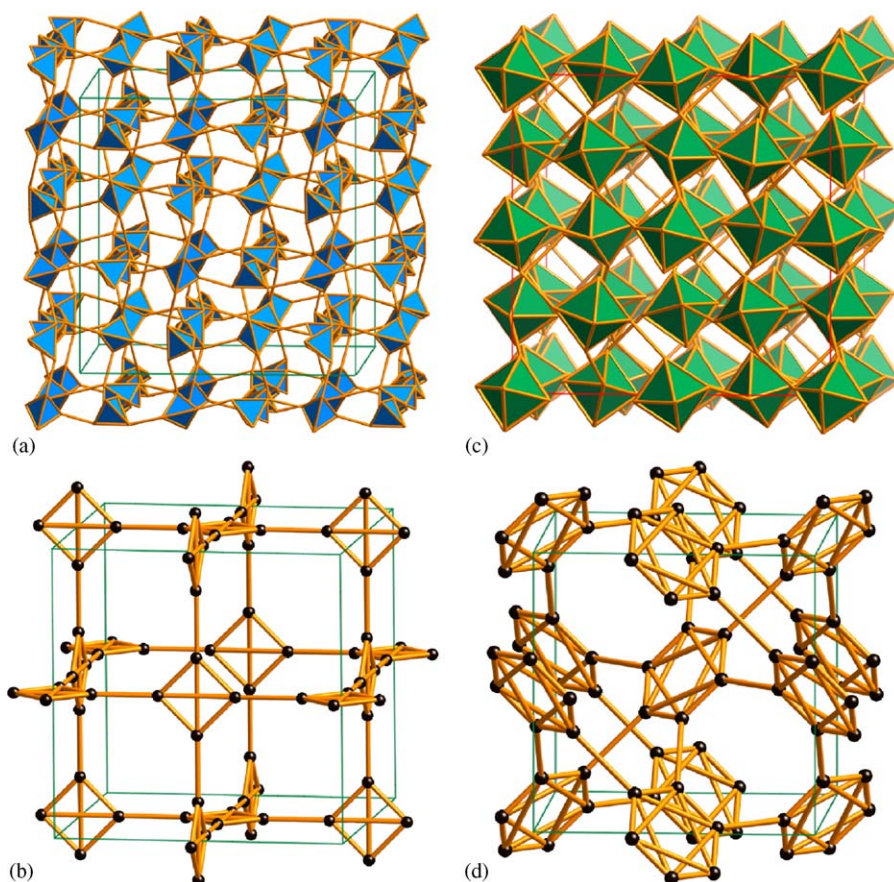
Fig. 8. (a) The net **ulk** as a sphere packing and (b) in a maximum-symmetry embedding. (c) The net **fcw** as a sphere packing and (d) in a maximum-symmetry embedding. Note that the edges that lie inside a square in (b) or a planar hexagon in (d) intersect—their apparent non-intersection is an artifact of the drawing program.

Note that, unless explicitly stated to the contrary, when we refer to a tiling it is always *face-to-face*, i.e. each face is common to exactly two tiles, and a pair of tiles have at most one face in common. Just as in two dimensions, a periodic three-dimensional tiling carries a net. A given tiling carries a unique net, but a net may have more than one (even an infinity) of tilings that carry it. However we have defined [7,21] a natural tiling that is generally (but not always!) unique.

Every tiling has a *dual* tiling derived in the following way. Put new vertices in the center of each old tile and connect them to new vertices with edges passing through the faces of the old tiles. Then complete the new tiling so that each new tile encloses one old vertex and the old tiling is the dual of the new one. Occasionally, the dual of a tiling is the same as the original and the tiling is said to be *self-dual*.[1] If a natural tiling is self-dual the tiling and the net are said to be *naturally self-dual*.

Why in an article on nets are we discussing tilings? One reason is that the theory of tilings has developed in some sophisticated ways and it is possible to systematically enumerate tilings of various types [22–25] and hence the nets carried by these tilings. We summarize some results below. The concept of duality also leads to insight into the tendency for certain nets to form interpenetrating pairs (or higher multiplicities).

A property of a tiling that we find very useful is the *transitivity*. This is a set of four integers *pqrs* that indicates that the tiling has p kinds of vertex, q kinds of edge, r kinds of face and s kinds of tile. Here only vertices, etc., that are related by symmetry are considered as one kind. The dual of a tiling with transitivity *pqrs* has transitivity *srqp*. Nets with one kind of vertex are sometimes called *uninodal* and tilings with one kind of tile are called *isohedral*.

---

[1]Recall that the concept of duality is familiar for polyhedra (which may be considered as tilings of the surface of a sphere). Now the new vertices are in the centers of the original faces (tiles). The cube, 4^3, and

(footnote continued)
octahedron, 3^4, are duals of each other and the tetrahedron 3^3 is self-dual, as are pyramids in general.
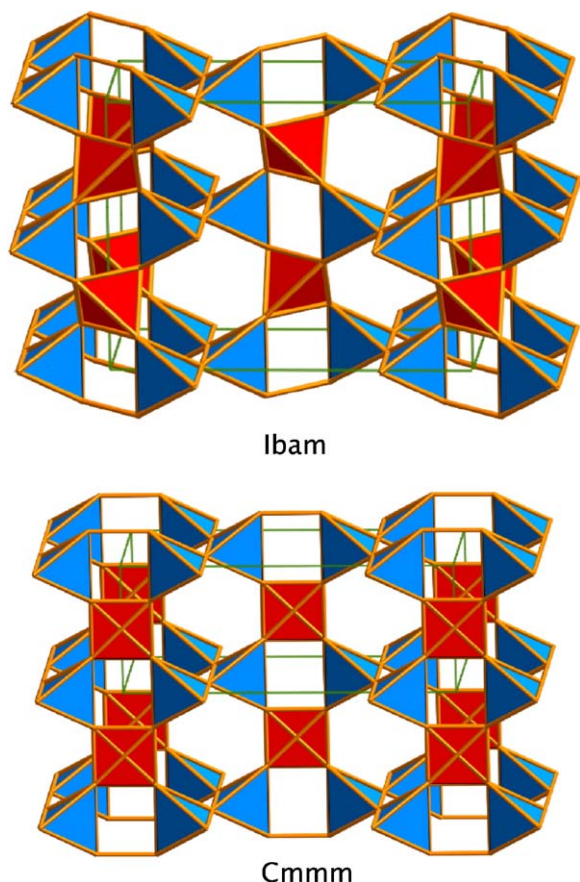
Fig. 9. The moganite anion net, **mog-e**, with regular tetrahedra (top) and in maximum-symmetry conformation (below). In the lower figure the edges that are diagonals of a red square intersect.

Table 1
The nets of this paper listed by embeddability type

1	1a	**bct bcu dia fau fcu flu gar lcv mep mtn nbo pcu rho sod srs srs-a wse**
	1b	**crb coe fcy fcz gie nia pts qtz rtl sra ths uks**
	1c	3/8/*c*3
2	2a	**cds**
	2b	**bcs fnu hms msw qzd rob**
3	3a	**fnm fcb**
	3b	**bcu-x mep-e**
	3c	**gar-e**
4	4	**elv tcb ten**
5	5	**fcw mog-e ulk**

6. Polyhedra and cages

We will use the term polyhedron in the restricted sense of a convex three-dimensional figure bounded by planar faces. This means that a line joining two points on the same face lies entirely in that face, and a line joining points on two different faces lies entirely, except for the end points, in the interior of the polyhedron. Polyhedra

commonly encountered in chemistry, such as most fullerenes, or the "supercage" of the zeolite faujasite, are not convex as they occur, but they are topologically equivalent to convex polyhedra of the sort described above. An important theorem (Steinitz's theorem) states that a simple graph is the graph (Schlegel diagram) of a convex polyhedron if, and only if, it is (a) planar and (b) three-connected. By this we mean (a) that the graph can be drawn on a plane without edges intersecting and (b) there is no pair of vertices whose deletion (together with their incident edges) would separate the graph into disjoint parts.

Many of the tiles (cages) that are encountered in tilings of nets have planar graphs but are not three-connected. Clearly, no tile with a divalent vertex (as in Fig. 11) is three-connected; a less obvious example is shown in Fig. 12.

A convex polyhedron with all trivalent vertices is *simple*, and its dual, with all triangular faces, is *simplicial*. The tile shown in Fig. 12(a) is topologically equivalent to a simple convex polyhedron, but that shown in (b) is not a simple polyhedron sensu stricto as its graph is not three-connected even though all vertices are trivalent (three-coordinated).

7. Numbers of nets

Clearly, the numbers of nets is infinite as there is no limit to the number of kinds of vertex one can have. But what of nets with a finite number of kinds of vertex, e.g. uninodal? We can easily show by example that there are infinite families of uninodal nets. Thus consider the eight-coordinated two-periodic net with just one vertex per unit cell with edges going to vertices in unit cells $\pm u$, $\pm v$ and $\pm v$, $\pm u$; where u and v are integers of opposite parity and co-prime. Fig. 13 shows the structure for $u = 1$, $v = 2$. One can easily convert these to three-periodic structures by linking vertices in a third non-coplanar direction. These nets clearly have embeddings of type 4.

It seems likely however that the number of nets with embeddings of types 1–3 for a given number of kinds of vertex, p, is finite though increasing exponentially with p (see below). About the only firm results we have available are the enumeration of uninodal sphere packings with connected graphs (i.e. those for which there is a path of edges between any pair of vertices) carried out over the years by Fischer, Koch and Sowa. From their results (for references see [14,26–29]), which do not extend yet to the monoclinic and orthorhombic systems, we can estimate that the number of such structures is at most a few thousand. A nice result is that there is exactly one intrinsically triclinic sphere packing [26].
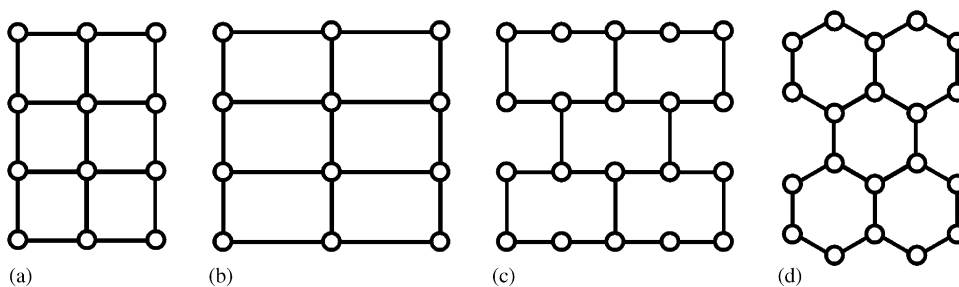
Fig. 10. (a) and (b) Two 4^4 tilings with different shaped tiles. (c) and (d) Two 6^3 tilings with different shaped tiles.
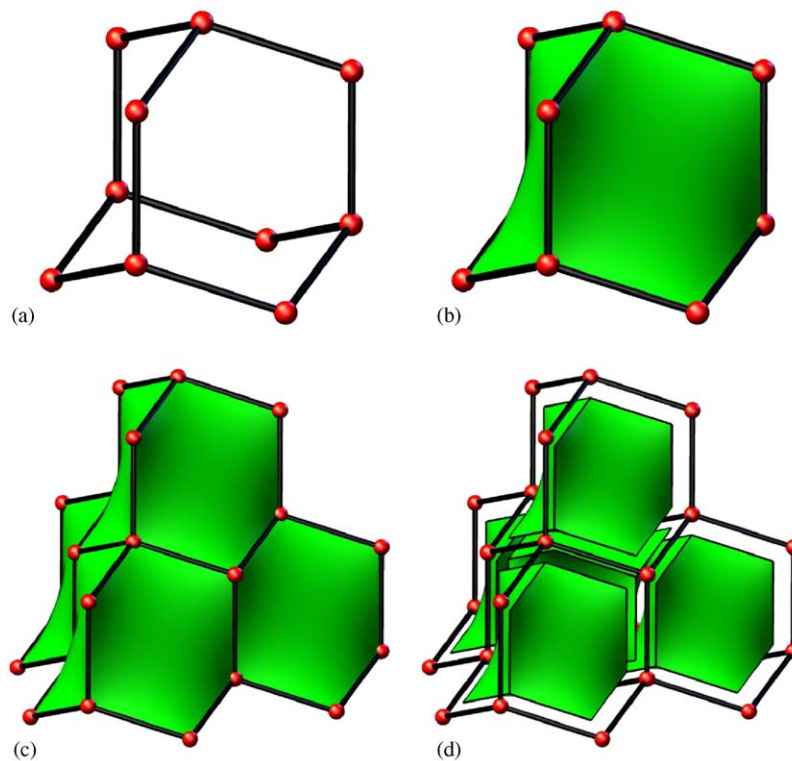

Fig. 11. (a) A C_{10} ("adamantine") unit of the diamond structure. (b) The same unit as a cage (tile). (c) Five tiles fused together showing development of the **dia** (diamond) net. (d) The same with the tiles shrunk to show how they fit together.
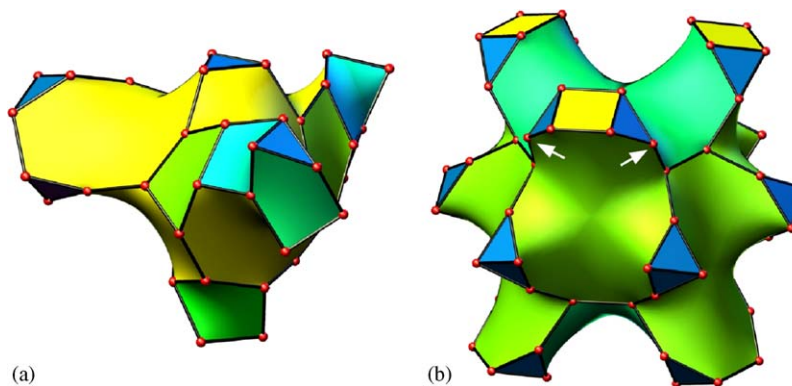

Fig. 12. Two tiles from isohedral tilings (a) **kts**. This polyhedron is topologically equivalent to a simple convex polyhedron. (b) **bcr**. Note that the graph of this tile is not three-connected as deleting e.g. the two vertices indicated by arrows will leave two unconnected parts, and this tile is not topologically equivalent to a convex polyhedron.
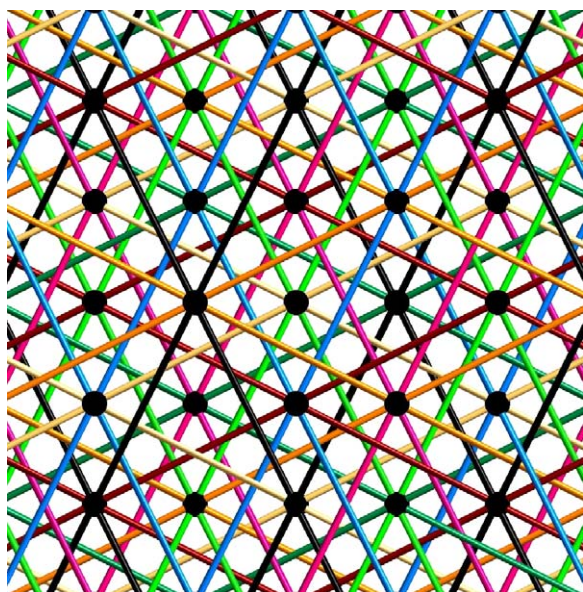
Fig. 13. Part of an eight-coordinated two-periodic net described in the text. The colors are to aid in distinguishing edges.

An enumeration of three-coordinated sphere packings (embeddings of type 1) found 55 structures of which six had embeddings of type **1c** ([27], see also [28]).

An empirical search [30] for uninodal four-coordinated nets with embeddings of types **1a** and **1b** has resulted in the recognition of 168 such structures. These are documented in a database described below.

There has of course been a long history of empirical searches for frameworks for zeolites and crystals in general starting from the pioneering work of Wells [31] half a century ago; for references to these see e.g. [32,33].

8. Some special nets and tilings

8.1. Regular nets

The coordination figure associated with a vertex is defined by the convex hull of the neighbors of a vertex. We require for a *regular* net in its maximum-symmetry embedding, that this figure be a regular polygon or polyhedron. We further require the vertex to have site symmetry in the net that is at least the rotation symmetry of that regular polygon or polyhedron.

It is easy to show [21] that there are exactly five such three-periodic nets with vertex figure triangle, square, tetrahedron, octahedron, and cube; these have symbols **srs**, **nbo**, **dia**, **pcu** and **bcu**, respectively. They are as important to chemistry as the five regular polyhedra and three regular two-periodic nets which have been known

since antiquity.[2] The regular nets are illustrated in Fig. 14 both as the net itself and as the *augmented* net in which each of the original vertices is replaced by its coordination figure.

An interesting property of the regular nets is that their natural tilings all have transitivity 1111. We know of no other nets that have this property.[3]

The dual of a natural tiling of a regular net is a natural tiling of a regular net. **srs**, **dia** and **pcu** are self-dual and **nbo** and **bcu** are a mutually dual pair.

8.2. Quasiregular net

A quasiregular polyhedron is one with one kind of edge and one kind of vertex. There are two: the cuboctahedron 3.4.3.4 and the icosidodecahedron 3.5.3.5. A quasiregular net is one in which the vertex figure is a quasiregular polyhedron. As 3.5.3.5 has icosahedral symmetry, the only possibility for the vertex figure of a three-periodic structure is 3.4.3.4. The net with this vertex figure is the net (**fcu**) of cubic closest sphere packing (also shown in Fig. 14) [21]. The transitivity of the natural tiling of **fcu** is 1112 reflecting that it consists of two types of tile (tetrahedra and octahedra). Again we know of no other *natural* tiling with transitivity 1112.

The dual of **fcu** has transitivity 2111 and the net (**flu**) is that of the fluorite (CaF_2) structure, with two tetrahedral vertices for each eight-coordinated (cubic) vertex. There is no other known binary structure with this transitivity so in a sense the **flu** structure is the most regular binary structure.[4]

8.3. Semiregular nets

Semiregular nets have been defined as those whose natural tilings have transitivity 11rs, $r > 1$. Fourteen with embeddings of type 1 or 2 (above) have been identified [15]. They include such familiar nets such as those of quartz (**qtz**) and sodalite (**sod**). We remark that there are infinite families of vertex- and edge-transitive nets analogous to the two-dimensional one described earlier, but these all have embeddings of type 4 and large coordination numbers (24 or 48).

---

[2] A reminder: the regular polyhedra are the tetrahedron 3^3, the octahedron 3^4, the icosahedron 3^5, the cube 4^3, and dodecahedron 5^3. The regular plane nets are the triangular lattice 3^6, the square lattice 4^4, and the honeycomb net 6^3.

[3] There are at least two more nets which are carried by tilings (not *natural tilings*) with transitivity 1111 [34].

[4] If we color alternate vertices of e.g. the **pcu** structure black and white, we get of course the NaCl structure; the transitivity of the natural tiling of this *colored* structure is 2111. However, we do not admit the possibility of colored nets in this discussion.
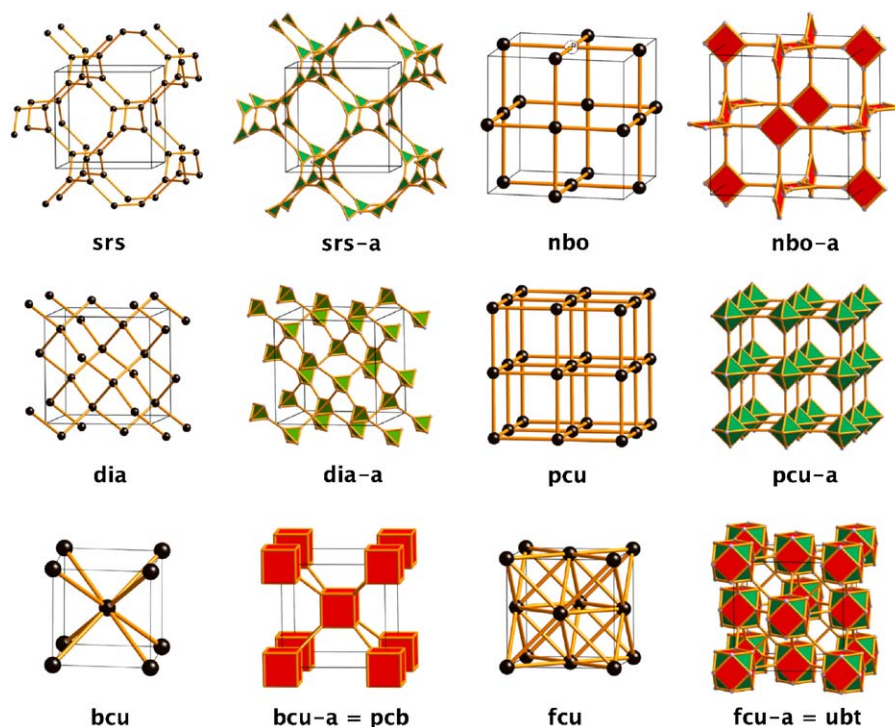
Fig. 14. The regular and quasiregular nets in their standard and augmented (**-a**) forms. Note that **pcu-a** is also known a polycubane (**pcb**) and **fcu-a** is also known as UB_{12} (**ubt**).

8.4. Edge-transitive nets

Nets with two kinds of vertex (usually two kinds of vertex figure) and one kind of edge are of particular interest in the design of materials [5]. A number have been described in our earlier tutorial [2]. Familiar examples are the fluorite (**flu**), PtS (**pts**) and NiAs (**nia**) nets. A systematic description of those with embeddings of type 1 or 2 is planned [35]. We currently know 25 such structures and believe that this comprises "most" of them.

8.5. Uniform tilings

Uniform tilings are ones in which both the individual tiles and the tiling are vertex transitive. Alternatively stated, the structure is a uninodal net formed by tilings of regular and/or Archimedean polyhedra. There are 28 of them [36] and it has been observed that most occur in common crystal structures [37]. We believe that this classification, which focuses on the individual tile, is less useful than one that focuses on the *tiling*, as in the classification by transitivity. In particular, four of our five regular nets are not uniform tilings (the vertices of individual tiles are not related by symmetry, although in the assembled tiling all the vertices are so related).

Wells [38] has used the term "uniform net" in a quite different sense: that of a net in which the shortest cycles at each vertex are all the same size.

8.6. Simple tiling

A simple tiling is a tiling by simple polyhedra in which three tiles meet at an edge and four at a vertex (the minimum number in each case). Foams, grains in polycrystalline material, and cellular materials are simple tilings, albeit usually not periodic. The structures of many important zeolites are, however, based on periodic simple tilings.

It follows from the definition just given, that the tiles of a tiling dual to a simple tiling have triangular faces and four vertices, i.e. they are tetrahedra. It turns out that with modern methods of combinatorial tiling theory complete enumerations of tilings by tetrahedra can be carried out [22,23] and it has been established that there are exactly 9, 117, and 1351 tilings by one, two, and three kinds of tetrahedra, respectively.[5]

An important example of a simple tiling is the so-called Kelvin structure, known to chemists as the sodalite structure, which results from a tiling of space by truncated octahedra (Fig. 15). The net symbol is **sod**. The dual of the sodalite tiling is the packing of congruent tetrahedra for which the net is **bcu-x** shown in Fig. 5.

The isohedral tilings by tetrahedra are of special interest. In an often-cited article [39] Marjorie Senechal

---

[5]The number of tile-3-transitive tilings corrects a small error in Ref. [23].
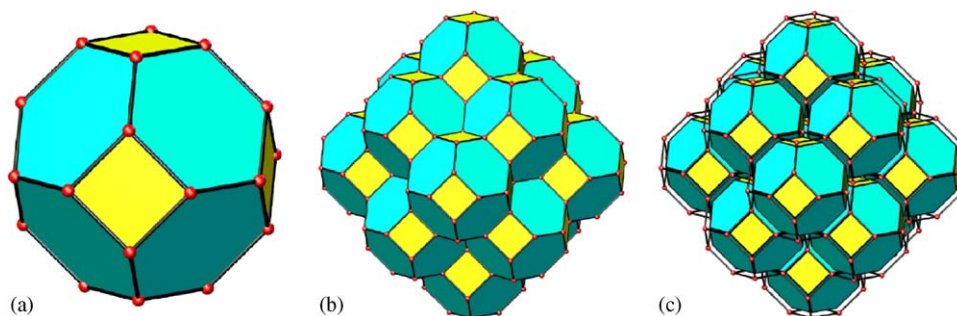
Fig. 15. (a) A truncated octahedron–an example of a simple polyhedron. (b) A simple tiling (space filling) by truncated octahedra. (c) The same with the polyhedra slightly shrunk. The vertices and edges form the **sod** net.
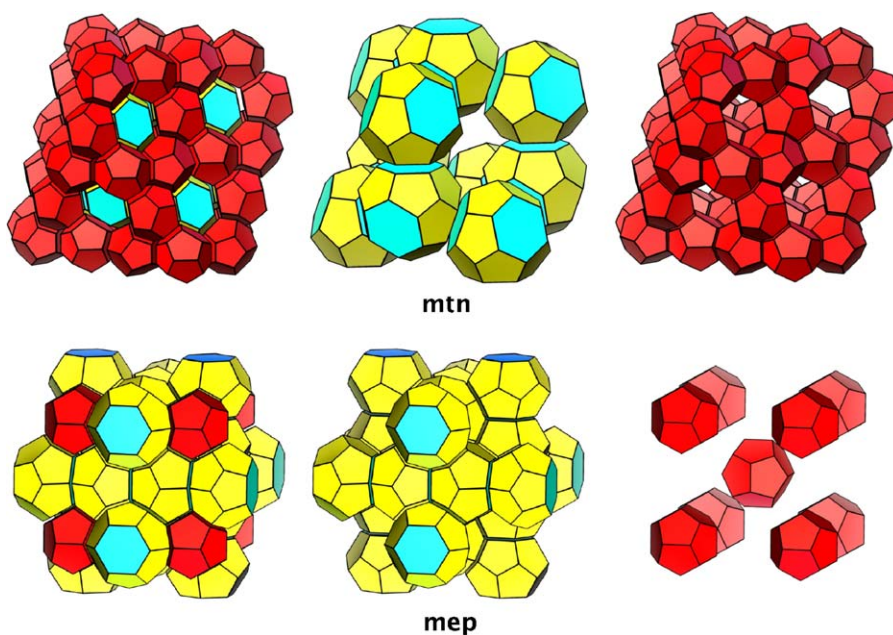

Fig. 16. Tilings carrying the nets **mtn** and **mep**. Left: all tiles. Center and right: each of two kinds of tile separately.

asks "Which tetrahedra fill space?" noting that "filling space by congruent polyhedra … is one of the oldest and most difficult of geometric problems", so that problem is solved at least for *isohedral* tilings by tetrahedra (there could, in principle, be tilings by congruent tetrahedra that are not all related by symmetry—such a tiling is termed *monohedral*). The duals are the nine simple tilings with one kind of vertex (vertex transitive). Interestingly, seven of these correspond to known zeolite nets, and all nine have long been known to crystal chemists [12,40]. Of course before the tiling work [22], it was not known that the list was complete.

Simple tilings by polyhedra that have only five- and six-sided faces are also of special interest. It appears, though it has never been proved, that only four polyhedra (with 12, 14, 15 or 16 faces, respectively) can occur in such tilings. The duals of these tilings are the so-called Frank–Kasper "tetrahedrally close packed" structures. The two most important of these

tilings (**mtn** and **mep**, Fig. 16) correspond to the structures of the type I and type II clathrate hydrates, and their duals are the structures of $MgCu_2$ and Cr_3Si respectively—see e.g. Ref. [12]. These two simple tilings both have three kinds of vertex. Because of the enumeration of simple tilings described above, it is known that they are the only such tilings with less than four kinds of vertex.

It should be noted that, although the dual of a simple tiling is a tiling by tetrahedra, according to our strict definition of simple tilings the converse is not true. The tiling for which one tile is shown in Fig. 12(b) is the dual of a tiling by tetrahedra but as discussed above, the tile is not a simple polyhedron.

8.7. Isohedral simple tilings

In related work, isohedral simple tilings by tiles with $\leqslant 16$ faces have been determined [25]. It was found that there are 0, 23, 136, and 710 distinct isohedral tilings for

Table 2
The numbers of known (to us) uninodal nets with order of site symmetry $\geqslant 4$ or $\geqslant 8$

c.n.	3	4	5	6	7	8	9	10	11	12	Total
Order $\geqslant 4$	3	16	9	26	9	11	4	9	1	3	91
Order $\geqslant 8$	0	4	3	6	0	5	1	2	0	2	23

"c.n." refers to coordination number.

tiles with < 14, 14, 15, and 16 faces, respectively. Most of these are rather low symmetry and have many different kinds of vertex (already for 14-face tilings there can be as many as ten kinds of vertex in a tiling). The Kelvin structure (Fig. 15) is one such isohedral tiling with a tile with 14 faces and was described by Lord Kelvin in 1887; interestingly no more appear to have been described until two more were discovered in 1968 (see Ref. [25] for details).

8.8. Symmetrical nets

It was hypothesized [2] and fully verified from an extensive search of the literature [4], that "only a small number of simple, high-symmetry structures will be of overriding general importance" as the underlying topology of crystals made by assembly of molecular building blocks. "High-symmetry" here refers to the order of the point symmetry at the vertices of the net in their maximum-symmetry embeddings. In a periodic net the site symmetry can range from 48 in a cubic lattice to 1 for the generic case. However, the number of nets with order of point symmetry $\geqslant 4$ is just a small fraction of the total and with order of point symmetry $\geqslant 8$ one arrives at a select few.[6]

Table 2 lists the numbers of symmetrical nets from our collection (more that 500, see the discussion of databases below) of uninodal nets. Of about 170 uninodal four-coordinated nets (one of the more important categories) only four have order of point symmetry $\geqslant 8$. These have all been mentioned already in this article. They are (with order of point symmetry) **dia** [24], **nbo** [16], **sod** [8] and **cds** [8]—see Figs. 14, 15, and 1, respectively.

8.9. Minimal nets and minimal surfaces

Minimal periodic nets are ones for which deletion of any edge, and all its translates, would result in a structure that is no longer connected. A very nice result is that there are exactly 15 such three-periodic nets [41]

and of these only eight correspond to nets without collisions [42]. Of these, five have self-dual natural tilings (it is easy to show that the dual of a tiling of a minimal net must carry a net that is also minimal see [42]).

Minimal surfaces are surfaces for which the average curvature is everywhere zero. Three-periodic minimal surfaces (PMSs) are of very considerable interest to many aspects of crystal chemistry and physical chemistry (see e.g. Refs. [43,44]). A serious discussion of their properties here would take us too far afield; suffice it to say that the five most important such surfaces are those with the minimal genus (in a sense the "minimal minimal surfaces") named *P*, *D*, *G*, *CLP*, and *H*. The labyrinth (channel) systems of these five surfaces are the five minimal nets with self-dual natural tilings, viz. **pcu**, **dia**, **srs**, **cds**, and **hms.** The first four (all met earlier in this article, see Figs. 14 and 1) are uninodal and of crucial importance to the next topic. Tiles of these nets with interpenetrating duals are illustrated in Fig. 17. Imagine now that the edges of pairs of interpenetrating nets are hollow tubes that are inflated uniformly until they meet at a common surface: this surface is the corresponding minimal surface.

8.10. Nets as tilings of minimal surfaces

It has been recognized for some time [43] that many three-periodic nets are usefully considered as tilings of minimal surfaces. Indeed, this looks like being another promising way to approach the systematic enumeration of nets [44–46]. The most important surfaces in this context are *P*, *D*, and *G* and it is often found [45] that the same two-dimensional tiling produces different three-dimensional nets for each surface.

In a two-dimensional tiling of the plane by polygons, the sum of the angles at the vertices of the polygons that meet at each vertex must be $360°$, as e.g. for the tiling 3^6. If the sum of angles is less than $360°$, as for 3^5, the tiling is of a surface of positive curvature and one gets a finite polyhedron (the icosahedron in this instance). If the sum is greater than 360, e.g. for 3^7, the surface being tiled must have negative curvature as is the case for the hyperbolic plane. These tilings of the hyperbolic plane can also sometimes be projected onto Euclidean space as tilings of minimal surfaces [44,45].

As an example we describe three tilings $4^3.6$ of these three surfaces in Fig. 18—in this case the sum of angles

---

[6]We have mentioned earlier certain infinite families of nets with embeddings of type 4. From the two-periodic example given (see Fig. 12) one can derive an infinite family of 10-coordinated three-periodic nets with symmetry $P4/mmm$ with site symmetry $4/mmm$ (order $= 16$). The data in Table 1 refer mostly to nets which have embeddings of types 1–3.
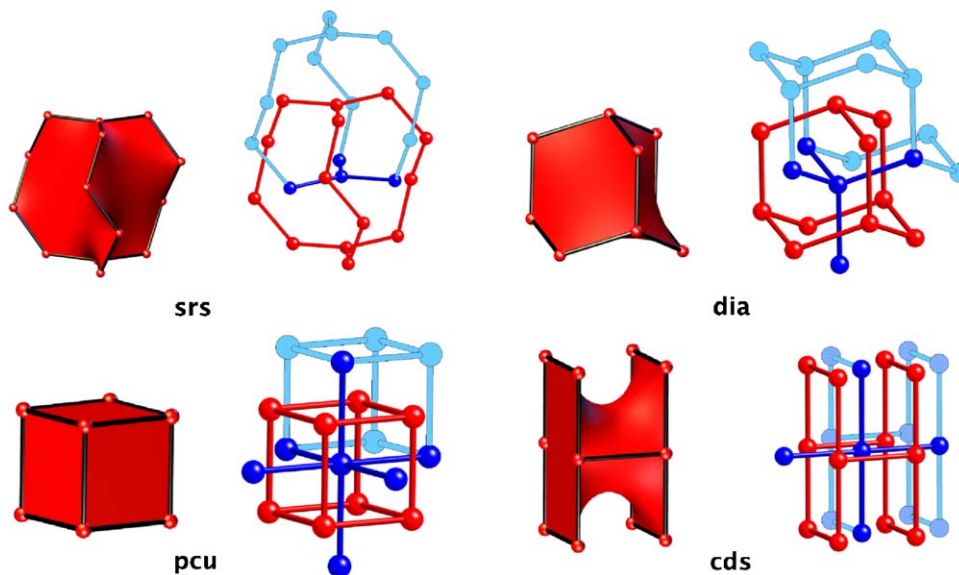
Fig. 17. The uninodal nets of naturally self-dual tilings. One tile is shown in red, and a vertex in the tile and its immediate neighbors are shown in dark blue. The light blue parts complete one dual tile.

is 390°. As infinite periodic surfaces are being tiled with polygons, infinite periodic polyhedra [12,38] are produced. The first structure (**rho**) is the net of the zeolite RHO shown as a tiling of the P surface forming an infinite polyhedron in Fig. 18. Note that the polyhedron shown fills half of space, and the empty space (the *complementary polyhedron*) is identical. Note too that the natural three-dimensional tiling is a space filling by the Archimedean polyhedra $4^2.8$ (octagonal prism) and 4.6.8 (truncated cuboctahedron) and it is an example of a uniform tiling. It is also one of the nine uninodal simple tilings. The symmetry of one infinite polyhedron is the same as that of **pcu**, i.e. $Pm\bar{3}m$, but that of the two polyhedra together, and hence that of **rho**, is $Im\bar{3}m$.

The next structure (**uks**) is a $4^3.6$ tiling of the D surface. Again the infinite polyhedron is the same as its complement. The symmetry of one polyhedron is the same as that of **dia**, i.e. $Fd\bar{3}m$, but that of the two polyhedra together, and hence that of **uks**, is $Pn\bar{3}m$. The structure is not a simple tiling, but as may be seen from the figure the natural tiling is the combination 2 $[4^6.12^2]+[4^6.6^4.12^4]$ (in a symbol for a tile m^n means that there are n faces that are m-gons, see [7]).

The third structure (**gie**) is the net of the zeolite like material UCSB-7 [47] and is a $4^3.6$ tiling of the G surface, again to produce an infinite polyhedron identical to its complement. The symmetry of one polyhedron is the same as that of **srs**, i.e. $I4_132$, but that of the two polyhedra together, and hence that of **gie**, is $Ia\bar{3}d$. The natural tiling is $3[4^4.10^2]+2[4^3.6^2.10^3]$.

The above three nets are of course to be found in W. Fischer's list of cubic sphere packings [11]; the

correspondence is **rho** = 4/4/c4, **uks** = 4/4/c7, **gie** = 4/4/c20.

We give here two examples of tilings $3^2.4.3.6$ (angle sum = 390°) of the G surface. Note in passing that $3^2.4.3.4$ (angle sum = 360°) is an example of an Archimedean (vertex-transitive) tiling of the plane, a surface of zero curvature, and $3^2.4.3.3 = 3^4.4$ (angle sum = 330°) is an Archimedean polyhedron, a tiling of a surface of positive curvature. It is interesting that although there is just one tiling[7] $3^2.4.3.6$ of the hyperbolic plane, there are at least two of the G surface. Fragments of these structures (**fcy** and **fcz**) are shown in Fig. 19. They have some interesting similarities: both have the same symmetry, $Ia\bar{3}d$, and unit cell edge at minimum density. Their vertex symbols are the same $3.3.3.4.6.10_2.10_4.10_8.10_8.10_{12}$. However, we can be sure that they are different nets as the coordination sequences are different starting from the sixth coordination shell. They also have different natural tilings: for **fcy** the tiles are $3[4^2.10^2] = 2[31^2.6^2.10^3]$ and for **fcz** they are $3[3^8.4^2.10^2]+2[62.10^3]$, see Fig. 19. The Fischer symbols for these two structures are 5/3/c41 and 5/3/c42 [11].

In contrast to the case of $3^2.4.3.6$ there are two distinct hyperbolic uninodal tilings $4^3 6$. Accordingly there must be more tilings of the minimal surfaces in addition to those shown in Fig. 18. We illustrate the structure (**fau**) which is the net of the faujasite (FAU) family of zeolites. Here we have a $4^3.6$ tiling of a surface with the same topology as the D surface, but the actual surface does not divide space into equal parts (imagine

---

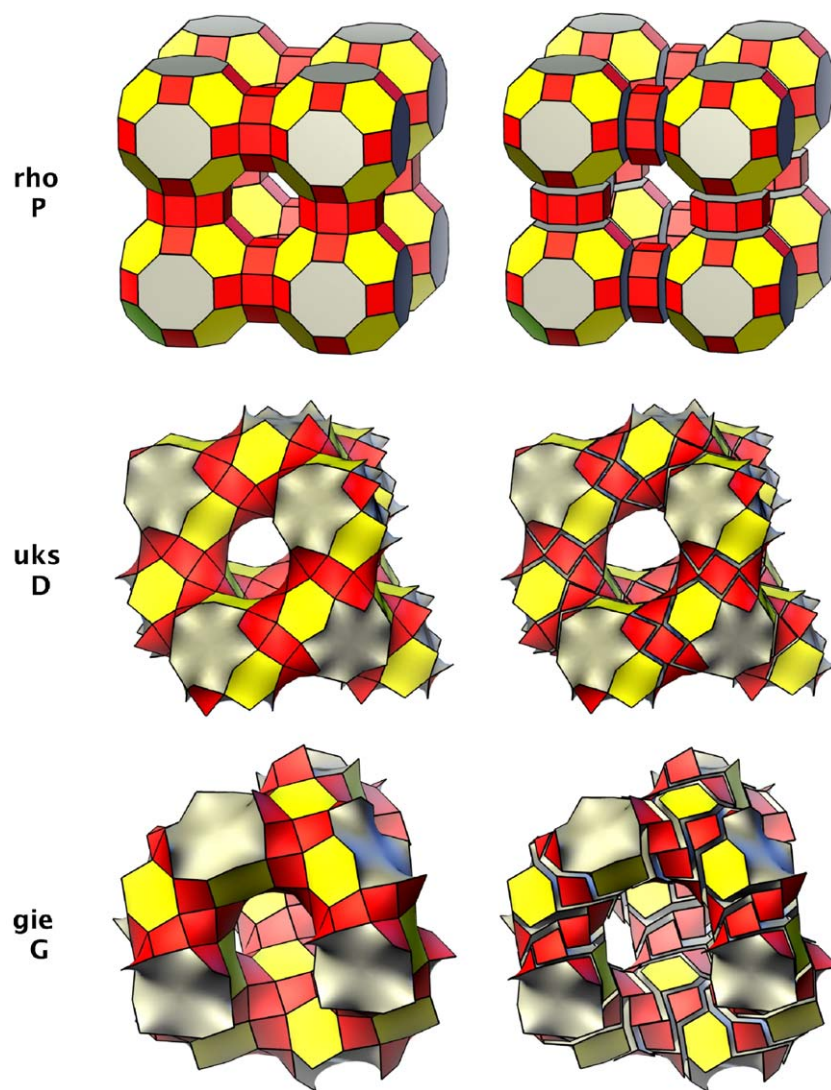[7]This is readily done using Delaney–Dress symbols—see e.g. [48].

Fig. 18. $4^3.6$ tilings of the P, D and G surfaces. On the right the structures are shown as three-dimensional natural tilings with the tiles slightly shrunk. Note that in each case only half the three-dimensional tiles are shown (the "empty" space would be filled by an identical set of tiles).

the two interpenetrating **dia** nets as being unevenly inflated) and the complementary polyhedron is not the same. As shown in Fig. 20, the first polyhedron can be considered as assembled from three-dimensional tiles that are hexagonal prisms and truncated octahedra (sodalite cages) and the complementary polyhedron, which is different, is made up of large tiles known as *supercages*. Now the symmetry of either infinite polyhedron or their combination is the same as that of **dia**, i.e. $Fd\bar{3}m$. Of course, the three sorts of three-dimensional tile combine to fill space and the tiling is the natural tiling for **fau**. It is another example of a uninodal simple tiling. The two-dimensional tiling in **fau** may be seen to be different from that in **uks** by noticing that in **uks** (and in **rho** and **gie**) one of the quadrilaterals shares edges only with other quadrilaterals and no quadrilateral in **fau** has this property.

8.11. Self-dual tilings, interpenetrating nets, and entanglements

As already mentioned, some nets admit tilings that are self-dual. In at least one case there can be an infinite family of self-dual tilings all carrying the same net [34]. However for natural tilings, which are almost always unique for a given net, the property of self-duality appears to be rather rare. Indeed, we know of only four uninodal nets that are naturally self-dual—the nets alluded to above (**srs**, **dia**, **pcu**, and **cds**) and illustrated in Fig. 17.

If two self-dual nets interpenetrate, all the edges of one net penetrate the rings (tile faces) of the other and vice versa so that all the essential rings (faces of tiles) of one net are catenated with rings of the other and the nets are *fully catenated*. The topic of interpenetrating nets in
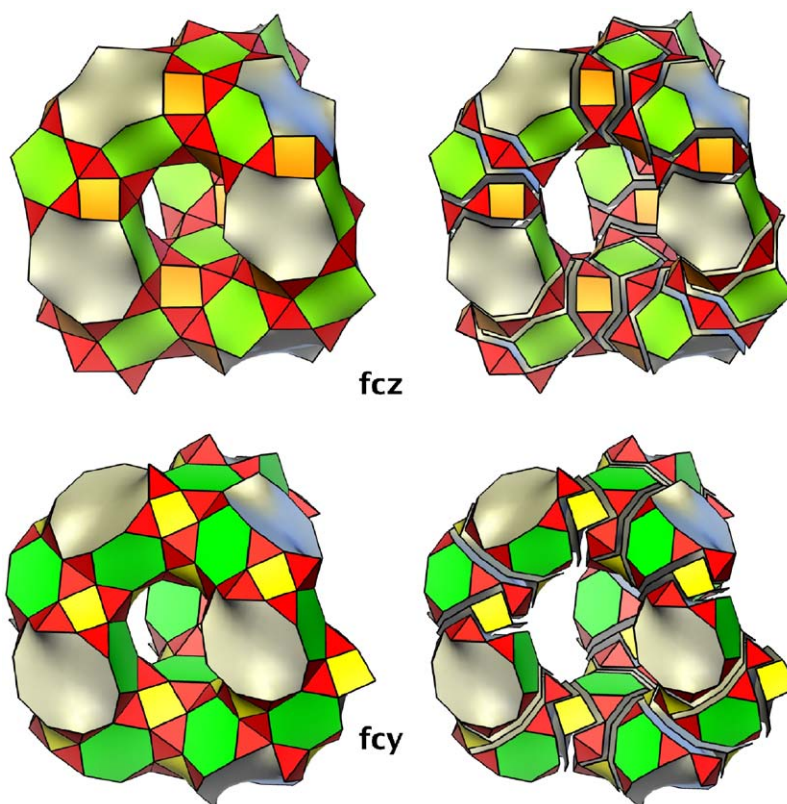
Fig. 19. Two $3^2.4.3.6$ tilings of the G surface. On the right the structures are shown as three-dimensional natural tilings with the tiles slightly shrunk. As in Fig. 18, only half the tiles are shown.
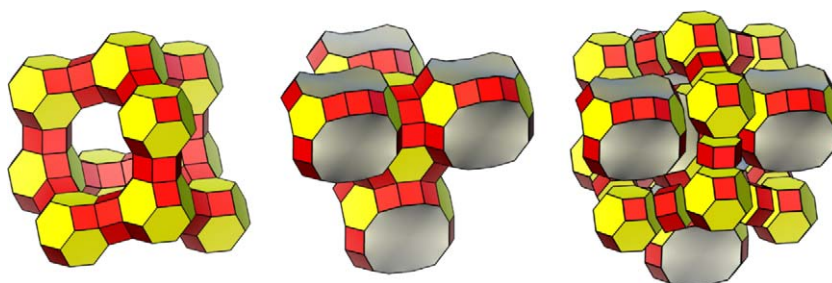

Fig. 20. The **fau** structure as a $4^3.6$ tiling of the D surface shown left and center as complementary polyhedra, and on the right as a three-dimensional natural tiling with the tiles slightly shrunk.

crystal structures is currently of great interest and has been reviewed [49–51] and studied in the context of porosity in MOFs [52,53]. It is clear that the propensity for inter-penetration is confined predominantly to very few nets. In a paper on minimal nets [42] the authors remarked "we believe that the only vertex-transitive naturally self-dual nets are … **pcu**, **dia**, **srs** and **cds**…. We believe that, in most cases of crystal structures based on interpenetrating nets, the net topology will be derived from one of these four basic nets." This turned out to be an accurate prediction. A subsequent analysis [50] of all 301 interpenetrating MOF structures published up to 2003 showed that structures based on one of these four nets accounted for 70% of the total. An additional four nets (**rtl**, **pts**, **ths** and **sra**) accounted for an additional 11%. The first two of these nets are simply related to **cds** [13] and the second two to **dia** (42 and to be published). Similar trends are found in the analysis of inorganic structures reported in this issue [51].

Some well-known nets are self-catenated. The four-coordinated net, **coe**, of the coesite form of silica is a well-known example [10,54]. Other examples that occur in this paper are **tcb** and **ten** (Fig. 7). We illustrate two more examples in Fig. 21. The first, **fnu** is five-coordinated and is derived from **bcu** (body-centered cubic) by omission of 3/8 of the bonds; its symmetry is
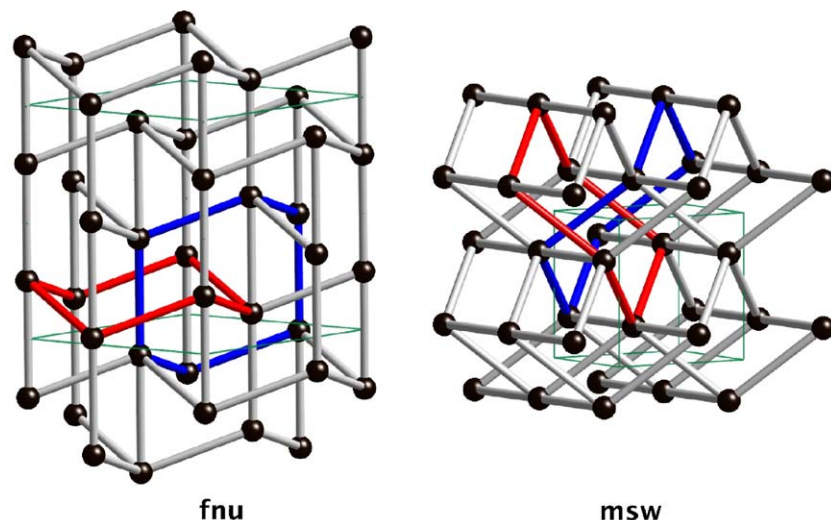
Fig. 21. Two self-catenated nets. The rings emphasized in red and blue are catenated.
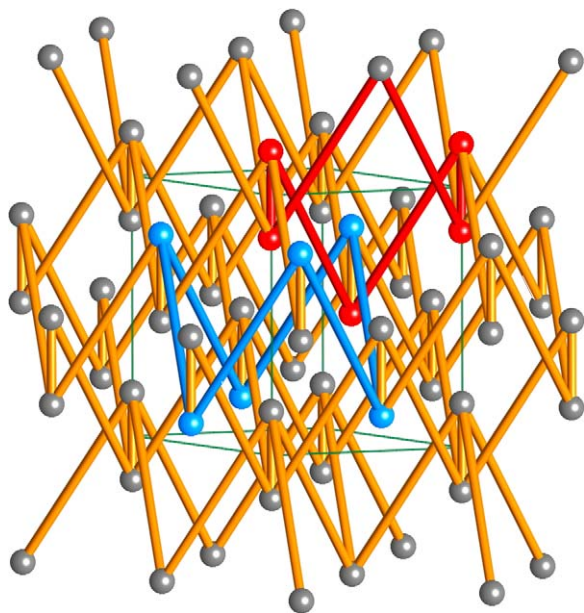

Fig. 22. Fragment of an embedding of the net of diamond (**dia**). Two catenated six-rings are shown in blue and red. Redrawn after Fig. 11 of Carlucci et al. [55].

Table 3
Some important uninodal nets

net	Regular	Minimal	Self-dual
srs	x	x	x
nbo	x		
dia	x	x	x
pcu	x	x	x
bcu	x		
ths		x	
cds		x	x

"Self-dual" refers to the nets of naturally self-dual tilings.

and the nets are both **dia**; it is just the *embedding* that is different in the two cases.

It is possible that at least some of these self-catenated nets are not carried by a tiling, at least in the usual sense, as rings that are tile faces cannot be catenated with other rings. It is not at all clear whether some of them may have embeddings without self-catenation as in the diamond example. This is a difficult question that requires close attention to the question of what exactly constitutes a ring in this context. These are interesting topics we must leave for another day.

We also do not consider other entanglement phenomena such as catenation of bidimensional layers. Many examples of these exceptional topologies have been shown recently [54,56].

8.12. So what are the most important nets?

Importance is of course subjective, and will depend on context. However, we have mentioned three special kinds of net: regular, minimal, and those with naturally self-dual tilings. Uninodal nets with these properties are listed in Table 3. **ths** refers to the familiar net of Si in

$R\bar{3}m$. The second **msw** recently turned up in a hydrogen-bonded framework [55]. It is derived from **bct**, the 10-coordinated body-centered tetragonal lattice with $c/a = \sqrt{(2/3)}$, by omission of $\frac{2}{5}$ of the bonds; its symmetry is $P4_2/nnm$.

A net may well have separate embeddings with and without catenated rings. A very nice example is provided by the familiar diamond net (**dia**, Fig. 11). This has been found [56] to occur in a self-catenated form shown in Fig. 22. We emphasize that the two graphs for which fragments are shown in Figs. 11 and 22 are the same,

ThSi$_2$ [2]. We believe that description of these structures, together with the binodal structures identified in [2], belongs in every serious textbook concerned with chemical structures.

9. Databases

Here we briefly describe some databases of three-periodic structures that are useful in one or another aspect of crystal chemistry.

9.1. RCSR

This database, currently at http://okeeffe-ws1.la.asu.edu/RCSR/home.htm, and very much still under development, is devoted to the simpler nets that arise, or might arise, in crystal chemistry. It contains most of the Fischer–Koch–Sowa sphere packings with embeddings of type **1a** or **1b** (although many of these, e.g. diamond, are known in other contexts as well!). Most of the structures are uninodal or binodal and include the nets of common crystal structures such as those of feldspar and rutile. All the structures mentioned in this paper are to be found there. At present, there are approximately 1200 structures in a database that is searchable by symbol, name, keyword, and properties.

Symbols, such as **dia** or **srs-a**, are assigned to each structure. Many nets have a three-letter symbol, for others there are three letters and an extension. Thus **srs-a** refers to the net derived from **srs** by replacing each vertex by its vertex figure to produce an *augmented* net. **srs-e** refers to the net derived by replacing the original net with one derived from vertices in the positions of the original edges—the *edge* net (some examples have been met in this article). Note that the net **srs-e** is sufficiently "important" to have its own, rather than a derived, symbol. This is **lcv**. Search of the database by either symbol will result in the entry for **lcv** where one finds that the net has "alternate symbol" **srs-e**. Similarly **sod** has alternate symbol **nbo-e**. A full explanation of the construction of net symbols is given at the web site.

> *Names* are names commonly used, such as "diamond".
> *Keywords* refer to special classes such as "simple tiling" or "regular net".
> *Properties* refer to properties such as number of kinds of vertex, space group number, and density.

For each structure, symmetry, coordinates of vertices and edges, and unit cell parameters are given for an optimal embedding. The data are presented in a way that allows one to read off the number of variables in the structure and the number of kinds of edge. Some topological properties such as vertex symbols, coordina-

tion sequences and transitivity (when known) are also given. It is planned to extend the database to other kinds of structure such as two-periodic layers and to polyhedra and cages. As it is still in a development stage, suggestions and feedback are very welcome (send to M.O.K.).

9.2. Hypothetical zeolites database

A hypothetical zeolite database, currently at www.hypotheticalzeolites.net, is a collection of zeolite structures generated by the symmetry-constrained intersite-bonding search (SCIBS) method of Treacy et al. [32,33]. It contains a collection of zeolitic frameworks that were refined from graphs that are obtained by systematically searching over all possible four-coordinated arrangements of *p* unique vertices in each space group. For each of the 230 space groups all combinatorial possibilities for uninodal ($p = 1$) and binodal ($p = 2$) nearest-neighbor connections have been computed. For some select space groups such as number 191 (*P*6/*mmm*) the set of graphs up to $n = 6$ crystallographically unique vertices have been computed and refined. The refinement of the zeolite structures as an SiO$_2$ composition is two-fold, one coarse grained refinement using a cost function due to Boisen et al. [57], and the other with more computationally expensive interatomic potential methods [58], dividing the database into BRONZE and SILVER sections, respectively. Several zeolite framework types coexist in different space groups, so a large number of duplicate structures are found, therefore the GOLD section of the database attempts to filter and present the unique topologies in their highest refinement level for uninodal and binodal framework types.

The graph search and refinement process are performed on a large computer cluster. For the uninodal graphs, approximately 40,000 graphs were computed, which can easily be accomplished in a few hours on one PC. For the binodal graphs, over 440 million graphs were computed, resulting in months of computation on 64 processors. Currently, we are computing space groups with $<10^8$ graphs for $p = 3$, 4, and 5.

For each space group, there is a combinatorial explosion of graphs as the number of unique vertices increases. The number of graphs N found for each space group is found to grow as $N = AB^p$. For space group *P*6/*mmm* (No. 191) we get $A_{191} = 0.084$, $B_{191} = 24.6$ whereas for space group $Ia\bar{3}d$ (No. 230) we get $A_{230} = 0.053$, $B_{230} = 1310$. The coefficient B determines the largest practical value of p that can be examined, which for $Ia\bar{3}d$ is $p \leqslant 4$. Interestingly, most space groups fall into one of two categories, with either a high or low B value, epitomized by B_{191} and B_{230}. Fig. 23 shows a plot showing $\ln(N)$ versus p for seven space groups showing the bimodal distribution of slopes.
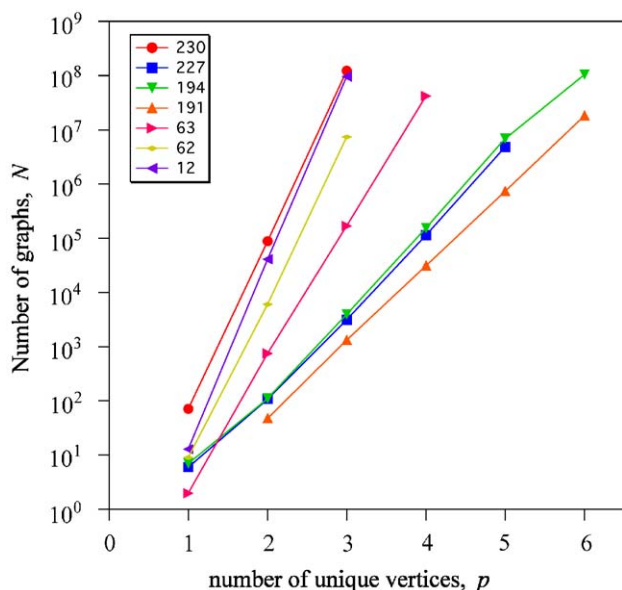
Fig. 23. Plots of the number of graphs found N as a function of the number of unique vertices p for a selection of space groups. There is a clear exponential relationship $N = AB^p$ (A and B are constants for each space group), which shows that the SCIBS method is limited by a combinatorial explosion of graphs as p increases. Some space groups, such as $P6/mmm$ (No. 191) have relatively low values of B, allowing p to be as high as 6.

In addition, as N increases, the fraction of viable nets falls dramatically. Consequently, as p increases, the efficiency of the SCIBS search decreases. For example, to find the **MFI** framework, which has $p = 12$, in space group *Pnma*, our present strategy will need to sift through more than 10^{35} graphs! Such combinatorial explosions are an inherent limitation of such geometric search methods. However, efficient pre-filtering of the graphs may mitigate the combinatorial explosion of graphs. For example, inspection of the topological density TD_{10} (the averaged sum of the first 10 shells of the coordination sequence) quickly reveals graphs with density greater than that for quartz ($TD_{10} = 1230$, contrast **elv**, for which $TD_{10} = 23922$). Other topological indicators of graph viability are needed.

The polyhedral tiling method of Delgado Friedrichs et al. [22–25], offers an efficient approach to framework discovery because the open polyhedron is an essential element of all useful zeolites. The polyhedral tiling approach is relatively immune from generating the self-catenated frameworks, such as **ten** (see Fig. 7), and offers much promise for discovering high p frameworks.

Another strategy due to Deem and co-workers [59], is to adopt a statistical mechanics approach, and to allow p unique vertices to anneal within the constraints of a given space group. This is an efficient method for discovering the high p frameworks (such as **MFI**), but by its very nature, it bypasses many of the topologically interesting (but chemically less likely) frameworks such as **ten** and **elv**.

Despite the limitations of the various methods, these databases are already proving useful for structure determination. The framework of ZSM-10 [60] was unambiguously identified [61] by searching all 18 million graphs in space group $P6/mmm$, with $p = 6$, for the lowest energy framework that matches the known powder pattern. Rietveld powder pattern refinements are problematic for ZSM-10, partly because of the small crystallite size, and partly because of the difficulty in removing all of the cations from the framework [60]. Fig. 24 shows aspects of the structure and its relationship to the tripled cell of the zeolite LTL. The two structures have columns of large tiles with planar 12-ring faces. These are surrounded by six columns of tiles, alternating hexagonal prisms and "cancrinite cages", with planar six-ring faces (colored blue in the figure). In LTL the centers of the six-ring tiles are on 6^3 nets; in ZSM-10 they are on 3.4.6.4 nets. The two nets are easily interconverted by $30°$ rotation of the groups of columns as indicated in the figure (see also Ref. [12, p. 201]). It might be noted how useful a natural tiling is in delineating the cages in zeolite structures. The ZSM-10 tiling is quite complex: the transitivity is 6 15 16 8.

This work also showed that one can produce nets that look identical in projection (along [0 0 1] in this instance) and which have very similar unit cell parameters, but which are really quite different. Fig. 25 shows the column of cages with planar six-sided faces of the previous paragraph and also a related column with an identical projection taken from one of several additional low-energy frameworks that emerged from the search. Interestingly, these other frameworks contain five-rings and are potentially interesting high-silica synthetic targets.

It is clear that the next decade is going to witness a rapid growth in the number of known hypothetical framework materials, including mixed coordination nets. A concomitant growth in targeted-synthesis techniques is much needed.

9.3. Atlas of zeolite structure types

This well known database, whose address is http://www.iza-structure.org/databases/ is devoted exclusively to the frameworks of known zeolites; currently there are 165 entries. Virtually, everything one would want to know about zeolite structures (symmetry, coordinates, etc.) is accessible from this database which is maintained by the international zeolite association. The structures are assigned an "official" three-letter code e.g. FAU for faujasite. Generally, when structures from this database appear in RCSR they are assigned the same three-letter code, but now lower case. Visitors to both sites will recognize the debt owed by RCSR to the zeolite database.
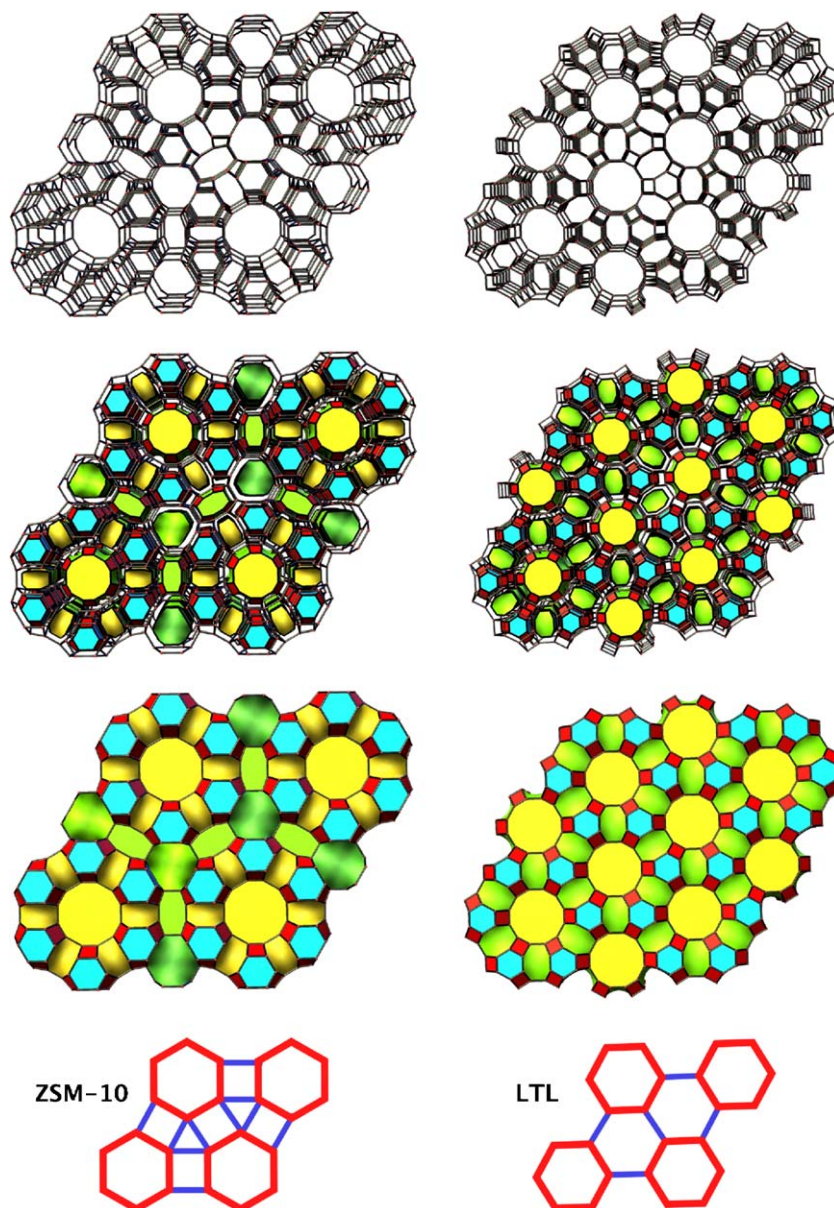
Fig. 24. Aspects of the nets of ZSM-10 (left) and LTL (right). Top the nets. Below that the nets with shrunken natural tiles. Below that the tiles fitted together. At the bottom is shown the pattern of columns of tiles with plane hexagon faces (colored blue in the tiling pictures above).

9.4. Tetrahedral frameworks of zeolites, clathrates and related materials

A large collection of known and hypothetical structures and secondary building units (SBUs) relevant to zeolite and related structures has been published as a volume of *Landolt–Börnstein* [62].

10. Computer programs

Here we briefly describe three programs designed for topological analysis of structures.

10.1. TOPOS

The program package TOPOS 4.0 with an advanced graphical interface (available at http://www.topos.ssu. samara.ru) [63] was recently improved for the automatic determination and classification of the interpenetration degree [50,51]. The program is also able to analyze and simplify complex groups (including H-bonded networks) and to assign the topology of the resulting network according to the RCSR proposed symbol. As a result, typical crystal structure of organic, inorganic, or coordination compound may be processed in a few minutes from the .res or .cif files, to get a comprehensive
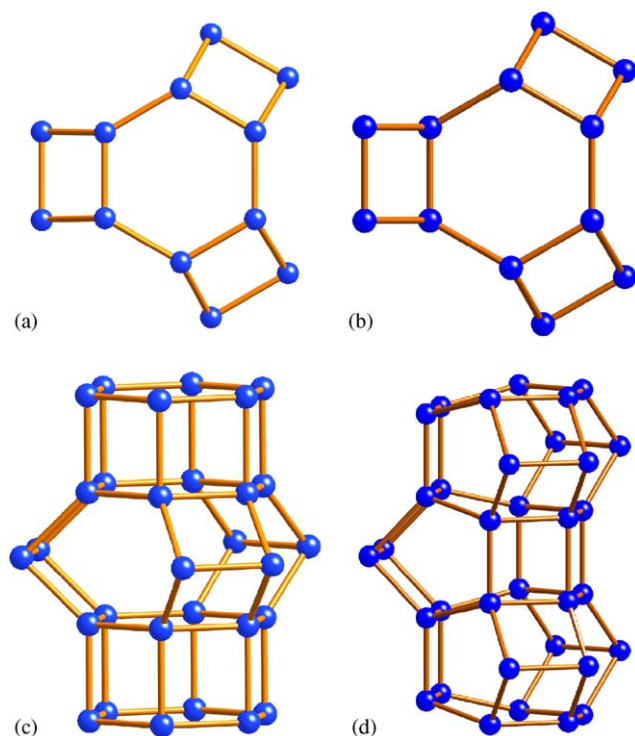
Fig. 25. Left: column of cages found in LTL and ZSM-10 (alternating hexagonal prisms and "cancrinite cages"). Right; column from a hypothetical network. The projections down [0 0 1] shown in (a) and (b) are almost identical but views almost normal to **c** reveal that they are quite different.

description of the topology and of the interpenetration (if any). Automatic analysis and classification of polycatenation is planned for the near future [64]. A detailed analysis of Voronoi–Dirichlet partition of crystal space and estimation of related crystallochemical parameters are also available in TOPOS [63].

10.2. Systre

The program Systre [8] is designed to determine the symmetry of a net, to determine whether it is a known structure and to provide a refined embedding. The name is derived from these three aspects: **sy**mmetry, **st**ructure, **re**fine. Input can be in terms of coordinates, or coordinate-free (purely topological). If some coordinate representation is given, the net is first reduced to its basic topology. An equilibrium placement is then derived. If at this point the net is determined to be collision free, the isomorphisms (symmetry operations) relating vertices are determined, a primitive cell determined and the space group identified. The next step is to determine a *canonical form* which is essentially a set of integers that is unique to a particular net, and which is always computed to be the same for every input of the same underlying topology. Thus, for nets without collisions, it solves the graph isomorphism problem: it

unambiguously determines whether two nets have the same or different topologies. Finally, starting from the equilibrium placement, a minimum density embedding in the maximum symmetry is found. For a more detailed account, including a worked example, see Ref. [8].

10.3. TOTOPOL

The program TOTOPOL was written originally to analyze bond distances, inter-bond angles, coordination sequences and vertex symbols of four-coordinated nets such as zeolites. However, it is flexible enough to handle nets with up to 12-coordination. TOTOPOL reads a .cif file corresponding to a framework material. To minimize framework ambiguities, extra-framework atoms should be removed from the .cif file. In some instances, framework cations may need to be replaced by Si, or simply "T". The program computes T–O distances (where "T" is nominally the framework cation, such as Si), as well as O–T–O, T–O–T angles. The coordination sequence, vertex symbol and circuit symbol for each unique framework T-atom is computed and compared with an archive that includes the known zeolite framework types. The program does not need bridging oxygen atoms to work. Without the bridging atoms, it computes T–T distances and T–T–T angles. The atom cluster involved in each vertex symbol or circuit symbol is displayed in an interactive window. The TOTOPOL program can be used on the web at http://www.hypotheticalzeolites.net.

The occurrence of two distinct tilings (e.g. **fcy** and **fcz** of Fig. 19) of the G surface corresponding to a unique hyperbolic tiling has been shown [65] to arise for the G surface only (i.e. not for P or D) and if, and only if, the hyperbolic tiling is chiral. The **fcz** structure has recently been found [66] to be the underlying net of a complex mesoporous germanate.

References

[1] E. de Vere, The labouring man, that tills the fertile soil, 1573.
[2] M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O.M. Yaghi, J. Solid State Chem. 152 (2000) 3–20.
[3] O.M. Yaghi, M. O'Keeffe, M. Kanatzidis (Eds.), Design of solids from molecular building blocks: golden opportunities for solid state chemistry, J. Solid State Chem. 152 (2000) 1–321.

[4] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176–182.

[5] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705–713.

[6] D. Braga (Ed.), New trends in crystal engineering. Cryst. Eng. Comm. 6 (2004) 344–521.

[7] O. Delgado-Friedrichs, M. O'Keeffe, J. Solid State Chem. (2005), this issue.

[8] O. Delgado-Friedrichs, M. O'Keeffe, Acta Crystallogr. A 59 (2003) 351–360.

[9] O. Delgado-Friedrichs, Discr. Comput. Geom. 33 (2005) 67–81.

[10] M. O'Keeffe, Z. Kristallogr. 196 (1991) 21–37.

[11] W. Fischer, Acta Crystallogr. A 60 (2004) 246–249.

[12] M. O'Keeffe, B.G. Hyde, Crystal structures: I Patterns and symmetry, Mineral. Soc. Am. (1996).

[13] O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Solid State Sci. 5 (2003) 73–78.

[14] E. Koch, H. Sowa, Acta Crystallogr. A 60 (2004) 239–245.

[15] O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acta Crystallogr. A 59 (2003) 515–525.

[16] B.F. Abrahams, M.J. Hardie, B.F. Hoskins, R. Robson, E.E. Sutherland, J. Chem. Soc. Chem. Comm. 1049 (1994).

[17] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 127 (2005) 1504–1518.

[18] J.-F. Ma, J. Yang, G.-L. Zheng, L. Li, J.-F. Liu, Inorg. Chem. 42 (2003) 7531–7534.

[19] M.-L. Tong, X.-M. Chen, S.R. Batten, J. Amer. Chem. Soc. 125 (2003) 16170–16171.

[20] M. Kurmoo, C. Estourne, Y. Oka, H. Kumagai, K. Inoue, Inorg. Chem. 44 (2005) 217–224.

[21] O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acta Crystallogr. A 59 (2003) 21–27.

[22] O. Delgado-Friedrichs, D.H. Huson, Discr. Comput. Geom. 21 (1999) 229–315.

[23] O. Delgado-Friedrichs, A.W.M. Dress, D.H. Huson, J. Klinowsky, A.L. Mackay, Nature 400 (1999) 644–647.

[24] O. Delgado-Friedrichs, D.H. Huson, Discr. Comput. Geom. 24 (2000) 279–292.

[25] O. Delgado-Friedrichs, M. O'Keeffe, Acta Crystallogr. A 61 (2005) 358–362.

[26] W. Fischer, E. Koch, Acta Crystallogr. A 58 (2002) 509–513.

[27] E. Koch, W. Fischer, Z. Kristallogr 210 (1995) 407–414.

[28] H. Sowa, E. Koch, Acta Crystallogr. A 61 (2005) 331–342.

[29] W. Fischer, Acta Crystallogr. A 61 (2005) in press.

[30] M. O'Keeffe, N.E. Brese, Acta Crystallogr. A 48 (1992) 663–669.

[31] A.F. Wells, Acta Crystallogr. 7 (1954) 535–544.

[32] M.M.J. Treacy, K.H. Randall, S. Rao, J.A. Perry, D.A. Chadi, Z. Kristallogr. 212 (1997) 768–791.

[33] M.M.J. Treacy, I. Rivin, E. Balkovsky, K.H. Randall, M.D. Foster, Microporous Mesoporous Mats. 74 (2004) 121–132.

[34] C. Bonneau, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi. in preparation.

[35] O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, In preparation.

[36] B. Grünbaum, Geombinatorics 4 (1994) 49–56.

[37] M. Deza, M. Shtogrin, Eur. J. Combin. 21 (2000) 807–814.

[38] A.F. Wells, Three Dimensional Nets and Polyhedra, Wiley, New York, 1977.

[39] M. Senechal, Math. Mag. 54 (1981) 227–243.

[40] A.F. Wells, Further Studies of Three-dimensional Nets, Amer. Crystallogr. Ass. Monograph 8 (1979).

[41] A. Beukemann, W.A. Klee, Z. Kristallogr 201 (1992) 37–51.

[42] C. Bonneau, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acta Crystallogr. A 60 (2004) 517–520.

[43] S. Andersson, S.T. Hyde, K. Larsson, S. Lidin, Chem. Rev. 88 (1988) 221–242.

[44] S.T. Hyde, S. Ramsden, in: D. Bonchev, D.H. Rouvray (Eds.), Chemical Topology: applications and Techniques, Gordon & Breach, Amsterdam, 2000 (Chapter 2).

[45] S.T. Hyde, A.-K. Larssen, T. Di Matteo, S. Ramsden, V. Robins, Aust. J. Chem. 56 (2003) 981–1000.

[46] R. Nesper, S. Leoni, CHEMPHYSCHEM 2 (2001) 413–422.

[47] T.E. Gier, X. Bu, P. Feng, G.D. Stucky, Nature 395 (1998) 154–157.

[48] A.W.M. Dress, D.H. Huson, Geom. Ded. 24 (1987) 295–310.

[49] S.R. Batten, R. Robson, R. Angew. Chem. Int. Ed. 37 (1998) 1461–1494.

[50] V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, Cryst. Eng. Comm. 6 (2004) 377–395.

[51] I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, J. Solid State Chem. **xxx** (2005) xxx-xxx, this issue.

[52] T.M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 4843–4844.

[53] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, J. Am. Chem. Soc. 126 (2004) 5666–5667.

[54] L. Carlucci, G. Ciani, D.M. Proserpio, Coord. Chem. Rev. 246 (2003) 247–289.

[55] N. Malek, T. Maris, M. Simard, J.D. Wuest, J. Am. Chem. Soc. 127 (2005) 5910–5916.

[56] L. Carlucci, G. Ciani, D.M. Proserpio, Cryst. Eng. Comm. 5 (2003) 269–279.

[57] M.B. Boisen, G.V. Gibbs, M.T. Bukowinski, Phys. Chem. Miner. 21 (1994) 269–284.

[58] J.D. Gale, J. Chem. Soc. Faraday Trans. 93 (1997) 629–637.

[59] M.W. Deem, J.M. Newsam, J. Am. Chem. Soc. 114 (1992) 7189–7198.

[60] J.B. Higgins, K.D. Schmitt, Zeolites 16 (1996) 236–244.

[61] M.D. Foster, M.M.J. Treacy, J.B. Higgins, I. Ritvin, E. Balkovsky, K.H. Randall, submitted.

[62] J.V. Smith, Landolt-Börnstein New Series IV/14 Subvolume A, Springer, Berlin, 2000.

[63] V.A. Blatov, Cryst. Rev. 10 (2004) 249–318.

[64] I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, in preparation.

[65] V. Robins, S.J. Ramsden, S.T. Hyde, Eur. Phys. J. (2005) in press.

[66] X. Zou, T. Conradsson, M. Klingstedt, M.S. Dadachov, M. O'Keeffe. Nature (2005) in press.