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Totally unimodular nets

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p-Periodic nets can be derived from a voltage graph G with voltages in Z^p, the free abelian group of rank p, if the cyclomatic number γ of G is larger than p. Equivalently, one may describe a net by providing a set of $(\gamma - p)$ cycle vectors of G forming a basis of the subspace of the cycle space of G with zero net voltage. Let $\mathbf{M}$ be the matrix of this basis expressed in the edge basis of the 1-chain space of G. A net is called totally unimodular whenever every sub-determinant of $\mathbf{M}$ belongs to the set $\{-1, 0, 1\}$. Only a finite set of totally unimodular nets can be derived from some finite graph. It is shown that totally unimodular nets are stable under the operation of edge-lattice deletion in a sense that makes them comparable to minimal nets. An algorithm for the complete determination of totally unimodular nets derived from some finite graph is presented. As an application, the full list of totally unimodular nets derived from graphs of cyclomatic numbers 3 and 4, without bridges, is given. It is shown that many totally unimodular nets frequently occur in crystal structures.

1. Introduction

Net enumeration is a long-standing problem in crystallography, going back as far as the works of Wells (1977). It is known that p-periodic nets can be represented by labelled quotient graphs (Chung *et al.*, 1984) and that, conversely, p-periodic nets can be derived from graphs with label assignment in Z^p, the free abelian group of rank p. For 3-periodic nets Chung *et al.* (1984) limited assignments to label vectors (h, k, l) with indices from the set $\{-1, 0, 1\}$. It is generally true, however, that infinitely many nets can be generated from a single graph. A noteworthy exception concerns minimal nets, which are in a one-to-one correspondence with finite graphs (Beukemann & Klee, 1992; Bonneau *et al.*, 2004). Minimal p-periodic nets owe their name to the property that deleting any edge lattice breaks the net into an infinite number of translationally equivalent $(p - 1)$-periodic nets. We propose here to derive a special class of p-periodic nets, called totally unimodular nets, which bear the properties that (i) deletion of certain edge lattices, chosen in a way to be made clear later on in this text, yields a p-periodic net homeomorphic to some minimal net and (ii) deletion of any number of edge lattices will not give a finite number of translationally equivalent interpenetrated p-periodic components. It results from the definition that only finitely many totally unimodular nets can be derived from any finite graph. These two properties of totally unimodular nets make them second in complexity after minimal nets. We shall also see that totally unimodular nets are widespread, representing the topology of a great number of crystal structures, for which we think they deserve more attention.

In §2 we summarize the essential graph-theoretical background necessary to an understanding of this work, hopefully making the paper self-contained enough. Definitions of the more important concepts are also recalled in the Appendix; these concepts are given in italic on their first appearance in the text. The Appendix also explains the nomenclature of some common graphs used in the paper. The reader will find the basic concepts of graph theory in Harary (1972) and some terminology used in solid-state chemistry in Delgado-Friedrichs & O'Keeffe (2005). Voltage graph theory was developed in Gross & Tucker (2001). A method of generating new nets by adding edge lattices directly to the quotient graph of minimal nets was discussed by Eon (2006). The results in this paper are based on similar ideas but exploit the observation that every periodic net can be described as the regular projection of some minimal net (Eon, 2007, 2011). This leads to the formal definition, in §3, of totally unimodular nets. The remainder of §3 and §4 are devoted to the analysis of the topological stability of these nets under the operation of edge-lattice deletion. Rutile is studied in §5 as an example of a net of genus 7 that is not totally unimodular. We describe in §6 an algorithm and software enabling one to find all totally unimodular nets derived from a given finite graph. The program was applied to get the complete list of 2- and 3-periodic totally unimodular nets derived from finite graphs with cyclomatic numbers 3 and 4 without bridges; the results are discussed in the last section (§7).

2. Nets as projections

Following Klee (2004), we consider that a net is a simple 3-connected graph, which is locally finite (*i.e.* any vertex has a finite number of neighbours; note that this condition was not explicit in Klee's paper). A p-periodic net (N, T) is given by a net N and a subgroup T of the automorphism group of N, denoted Aut(N), such that T is isomorphic to Z^p, the free abelian group of rank p, and the quotient graph $G = N/T$ is finite (see also Delgado-Friedrichs, 2005). Note that we do not impose that T is maximal; this will enable us to consider that two periodic nets (N, S) and (N, T) based on the same net N are distinct if the automorphism subgroups S and T are different. In order to simplify notations, we will speak of the periodic net N without direct reference to the translation group T whenever this is maximal in Aut(N). It results from these definitions that T, the translation group of (N, T), acts freely on N. Hence, the natural projection q_T mapping every vertex or edge of N on its orbit by T is a covering projection [*i.e.* it is direction-preserving and it maps the set of edges originating (respectively, terminating) at any vertex v one-to-one onto the set of edges originating (respectively, terminating) at $q_T(v)$]. It is then possible to assign *voltages* in T to the edges of G such that the derived graph is isomorphic to N. The corresponding voltage graph is called a labelled quotient graph of the net.

Let γ be the *cyclomatic number* of a graph G, that is, the dimension of its *cycle space* C. The minimal net M derived from G is a γ-periodic net. The set of the *cycle vectors* of G with zero *net voltage* forms a subspace, say K, of the cycle space. Since every cycle vector of C is associated with a translation of the minimal net, K determines a translation subgroup of M. We may then define the quotient M/K, which is clearly isomorphic to the net N. We can sum up the previous results in the following diagram:

$$M \to N = M/K \to G = N/T,$$

where the left-hand arrow is the regular projection, say q_K, of the minimal net M to the periodic net N, and the right-hand arrow is the projection q_T of the net to its quotient graph. The periodic net N appears then as a partial projection, between the minimal net and its quotient graph. The subspace K will be called the kernel of the projection. It is fully equivalent to define a p-periodic net by a voltage graph or by providing a basis of the kernel of the projection in the cycle space. It is the latter method we preferentially use in this paper; since each cycle vector in the basis of the kernel defines a translation as an element of a translation subgroup, we call it a relator of the net. A relator may be associated with a closed walk with zero net voltage. Relators will be expressed in the edge basis (*i.e.* the set of all oriented edges) of the quotient graph.

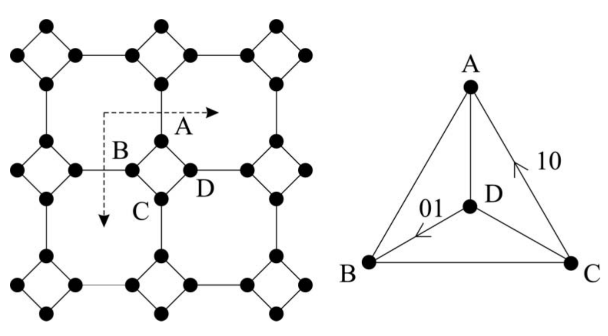

Figure 1
The net (4.8^2) (**fes**) and its labelled quotient graph $\mathcal{K}_4$.

3. Totally unimodular nets

Let now G be a finite graph of cyclomatic number γ. We turn to the generation of p-periodic nets admitting G as their quotient graph. As stated in the previous section, we just need to define the set of relators of the periodic net, which can be written in a matrix form. Hence, we introduce the *relator matrix* R whose entry $\mathsf{R}_{i,j}$ is the coefficient of edge j in the relator i. It results from the definition that the relator matrix has n rows with $n = \gamma - p$.

Definition 3.1. Let (N, T) be a periodic net defined by a graph G with m edges and an $n \times m$ relator matrix R. (N, T) is a totally unimodular net if every $n \times n$ submatrix of R has determinant 0 or ± 1.

Matrices with this property are known as *totally unimodular matrices*, so we could re-phrase our definition by saying that a periodic net is *totally unimodular* whenever its relator matrix is totally unimodular.

Consider, for example, the 2-periodic net **fes**, also named (4.8^2), and its labelled quotient graph shown in Fig. 1. Hereafter, the RCSR (Reticular Chemistry Structure Resource) three-letter symbols (if available) are used to designate net topologies (O'Keeffe *et al.*, 2008). The quotient graph $\mathcal{K}_4$ of **fes** has six edges e_i $(i = 1, \ldots 6)$, which may be oriented and ordered following the lexicographic order. Thus, $e_1 = AB$ is oriented from A to B *etc.* Since $\mathcal{K}_4$ has cyclomatic number $\gamma = 6 - 4 + 1 = 3$, a single relator $(n = 3 - 2)$ is needed to define the kernel of the projection from **srs**, the minimal net derived from $\mathcal{K}_4$, to the 2-periodic net **fes**. This relator corresponds to the cycle $(ABCD)$ and is associated with the cycle vector $e_1 + e_4 + e_6 - e_3$ with zero net voltage. Opposite orientation of the cycle $(DCBA)$ is an equivalent choice. The relator matrix reads

$$\mathsf{R} = (1\ 0\ {-1}\ 1\ 0\ 1),$$

which shows that **fes** is a totally unimodular net.

We observe that deleting the edge AB from the labelled quotient graph $\mathcal{K}_4$ yields a graph *homeomorphic* to $\mathcal{K}_2^{(3)}$ with two independent voltages 10 and 01. The derived net, which can be obtained directly from **fes** by deleting the whole *edge lattice* AB, is thus homeomorphic to the hexagonal net **hcb**, the minimal net derived from $\mathcal{K}_2^{(3)}$. On the other hand, deleting the edge AC from $\mathcal{K}_4$ also yields a graph homeomorphic to $\mathcal{K}_2^{(3)}$ but with the unique voltage 01 in Z^2. The derived graph, which can also be obtained directly by deleting the edge lattice AC from **fes**, contains infinitely many isomorphic, 1-periodic components parallel to direction 01. It is easily verified that deleting edge BD yields a similar result along direction 10. In the same way, deleting any other edge from the cycle ($ABCD$) yields a 2-periodic net homeomorphic to **hcb**. The following lemma generalizes these observations.

Let G be a graph with cyclomatic number γ and pairwise distinct voltages $a, b, \ldots$ taken from a minimum set Σ of generators of Z^{γ}, assigned to the chords of a spanning tree of G. Note that any cycle vector of G may be written as a *word* in Σ and, conversely, any word in Σ defines a unique cycle vector of G. This allows us, in particular, to define relators as words in Σ.

Lemma 3.1. Let G be a graph with cyclomatic number γ and voltages in Σ as above. Let (P, T) be a periodic net with translation group T and quotient graph $G = P/T$, defined through a set of relators **r**, such that the edge with voltage a is not contained in any relator of **r**. Define a new relator $\mathsf{s} = na + \mathsf{w}$ independent of the set **r**, where n is a positive integer and w is an arbitrary word in Z^{γ}, not containing a. Let $G \setminus a$ be the graph obtained after deleting the edge with voltage a, otherwise with the same voltages as in G assigned to the remaining edges. The periodic graph $P_{\mathsf{s}} \setminus a$ obtained after deleting the edge lattice that is the pre-image of the deleted edge in the derived graph $P_{\mathsf{s}} \equiv P/\langle \mathsf{s} \rangle$ contains exactly n translationally equivalent components, which are isomorphic to the periodic graph derived from $G \setminus a$. If $n = 0$, the periodic graph derived from $G \setminus a$ has one dimension less than P_{s} so that $P_{\mathsf{s}} \setminus a$ consists of an infinite family of translationally equivalent periodic graphs.

Proof. Assign a new voltage $\varphi(x)(x = a, b, \ldots)$ in a free abelian group to the edge with former voltage x, in such a way that the set of relators $\mathbf{r} \cup \mathsf{s}$ is a basis of the subspace of the cycle space of G with zero net voltage. Notice that the derived periodic net is the quotient $P_{\mathsf{s}} = P/\langle \mathsf{s} \rangle$. There is no cycle vector in $G \setminus a$ with net voltage $p\varphi(a)$ for $0 < p < n$ [but there is one with net voltage $n\varphi(a)$]: otherwise, there would exist another relator $pa + \mathsf{w}\prime \neq \mathsf{s}$ in **r**. Now, $\varphi(a)$ is a translation vector of P_{s}, and thus of the periodic graph $P_{\mathsf{s}} \setminus a$ obtained after deleting the referred edge lattice, since the translation group is conserved after deletion. Hence $P_{\mathsf{s}} \setminus a$ contains n components isomorphic to the net derived from $G \setminus a$. In particular, $P_{\mathsf{s}} \setminus a$ is connected and isomorphic to the net derived from $G \setminus a$ for $n = 1$. The two periodic graphs P_{s} and $P_{\mathsf{s}} \setminus a$ have the same dimension since the new relator, s, must be removed as soon as the edge with voltage a is deleted. In the case $n = 0$, however, the set of relators is maintained, so that removal of the edge decreases by one the dimension of the derived periodic graph.

The proof of Lemma 3.1 implies that $P_{\mathsf{s}} \setminus a$ contains n disconnected isomorphic periodic nets in the case $n > 1$. Since we are interested in crystal nets, it seems quite natural to speak of n *interpenetrated* nets where in fact the embeddings of these nets are interpenetrated. We will keep to this (mis)use for the sake of clarity. Note that the n components are translationally equivalent when considered as subgraphs of the whole periodic net. Consider, for instance, the labelled quotient graph $\mathcal{B}_4$ of the net known as **ilc**, which is represented in Fig. 2. Since $\mathcal{B}_4$ has cyclomatic number $\gamma = 4$ and the net is 3-periodic, the kernel is one-dimensional and generated by a single cycle vector. The sum of the voltages assigned to edges e_1, e_2 and e_3 is 110 + 101 + 011 = 222, twice the voltage of edge e_4, so that the cycle vector $C = e_1 + e_2 + e_3 - 2e_4$ has zero net voltage. Because of coefficient 1 of edge e_1, for instance, C cannot be a multiple of any shorter cycle vector; hence C (or $-C$) is the relator of **ilc** and the relator matrix is given by the coordinates of C in the edge basis

$$\mathsf{R} = (1\ 1\ 1\ {-2}).$$

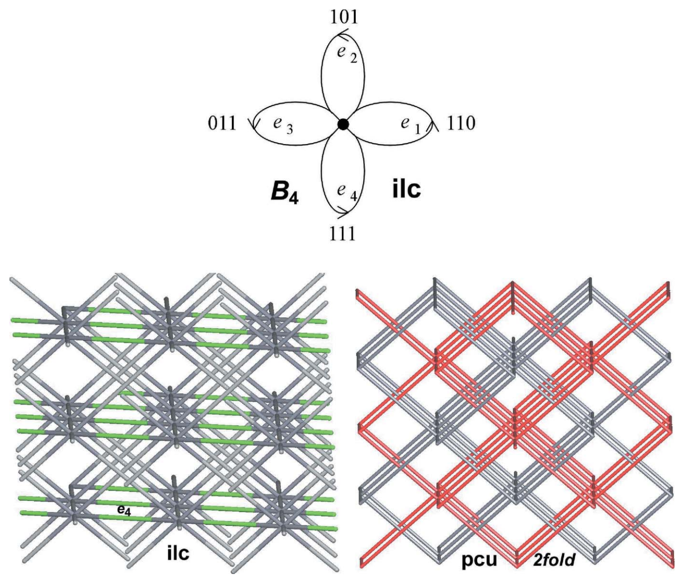

Figure 2
(Top) The labelled quotient graph $\mathcal{B}_4$ of the net **ilc**, (bottom left) the net **ilc** and (bottom right) twofold **pcu** obtained after deleting edge lattice e_4 (green).

Because of the last entry (−2) in R, **ilc** is not totally unimodular. Next, we observe that removal of any edge (loop) in $\mathcal{B}_4$ yields the bouquet $\mathcal{B}_3$, which is the quotient graph of **pcu**, the primitive cubic net. Direct application of Lemma 3.1 shows that withdrawal of any edge lattice associated with edges e_1, e_2 or e_3 with entry 1 in R yields a single primitive cubic net. Withdrawal of the edge lattice associated with edge e_4 with entry 2 in R yields two interpenetrated primitive cubic nets. Interpretation of the splitting of the net is straightforward and follows closely the proof of the lemma. Edge e_4 is indeed the only path in **ilc** from any vertex to its translated image by 111 whereas the walk $e_1 + e_2 + e_3$ leads to its translated image by 222. It may also be observed that the three voltages 101, 011 and 111 over edges e_2, e_3 and e_4 generate Z^3 while voltages 110, 101 and 011 over edges e_1, e_2 and e_3 generate a subgroup of index 2 in Z^3.

We are now in a position to investigate the effect of deleting more than one edge at a time in a 3-periodic net. Let us first recall that the *support* of a cycle vector in a graph G is the set of edges with non-zero coefficients.

Theorem 3.1. Consider a 3-periodic net N defined by a finite graph G with cyclomatic number γ and a set $\mathbf{r}$ of $(\gamma - 3)$ relators associated with a set $\mathcal{S}$ of cycle vectors of G. Deletion of a set $\mathcal{E}$ of $n \le (\gamma - 3)$ edges from the support of $\mathcal{S}$ in G yields a 3-periodic connected net if, for at least one subset $\mathbf{s} \subseteq \mathbf{r}$ of n relators, the $n \times n$ matrix M, whose entry M_{ij} is the coefficient associated in relator $\mathrm{i} \in \mathbf{s}$ to edge $j \in \mathcal{E}$, has determinant ± 1.

Proof. Write an $n \times m$ matrix R_n whose rows correspond to the cycle vectors associated with the n relators of $\mathbf{s}$ expressed in the standard (edge) basis of the edge space. Since $\det(\mathsf{M}) = \pm 1$, the rows of the product matrix $\mathsf{M}^{-1}.\mathsf{R}_n$ define a set of relators that is equivalent to the set **s**. However, the unit matrix appears in the place formerly occupied by matrix M in matrix R_n. Hence, each of the $(\gamma - 3) - n$ relators of the complementary set in $\mathbf{r}$ can be modified by adding to it the linear combination of these n new relators that cancels out the coefficient of the edges in $\mathcal{E}$. This provides an equivalent set of relators in which each of the edges of $\mathcal{E}$ belongs to a single relator and has coefficient +1 in the respective cycle vector. As a consequence $\mathcal{E}$ is not a *cut set*; repeated application of Lemma 3.1 completes then the proof.

Consider for example, the net **pts** with labelled quotient graph $G = \mathcal{C}_4^{(2)}$ drawn in Fig. 3. We may find two independent cycle vectors with zero net voltage in G, namely $e_1 - e_2 - e_5 + e_6$ and $e_3 - e_4 + e_7 - e_8$, which form a basis of the kernel of the projection. The net **pts** is thus defined by the graph $\mathcal{C}_4^{(2)}$ and the relator matrix describing these two cycle vectors

$$\mathsf{R} = \begin{pmatrix} 1 & \bar{1} & 0 & 0 & \bar{1} & 1 & 0 & 0 \\ 0 & 0 & 1 & \bar{1} & 0 & 0 & 1 & \bar{1} \end{pmatrix}.$$

Any set of two columns in R yields a submatrix with two 0 on the same row or two 0 on one of the diagonals; hence the determinant of any 2×2 submatrix is 0 or ± 1. **pts** is thus a totally unimodular net. Removal of edges e_1 and e_3 from $\mathcal{C}_4^{(2)}$ leads to a graph homeomorphic to $3(3^2, 4)1$ (Beukemann & Klee, 1992) while the respective 2×2 submatrix in R has determinant 1. Hence, removal of the corresponding edge lattices from **pts** yields a 3-periodic net that is homeomorphic to the minimal net **tfa** (see Fig. 4 and Fig. 5). On the other hand, removal of edges e_1 and e_7 from $\mathcal{C}_4^{(2)}$ leads to the graph 4(3)2, and determinant 1 for the associated submatrix, so that removal of the corresponding edge lattices from **pts** yields a 3-periodic net that is isomorphic to the minimal net **ths**. It may be checked that only **tfa** and **ths** may arise (eight times each) from deletion of two edge lattices associated with determinant ± 1.

It is interesting to look also at the 3-periodic net that describes the topology of α-cristobalite, with labelled quotient graph drawn in Fig. 6 that is based on the same $\mathcal{C}_4^{(2)}$ graph. The net is isomorphic to **dia**, the diamond net, but α-cristobalite realizes a periodic embedding of **dia** defined by a translation subgroup of index 2 of the full translation group of the net. We

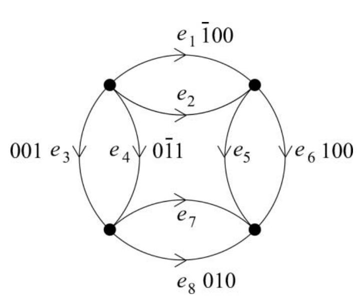

Figure 3
The labelled quotient graph $\mathcal{C}_4^{(2)}$ of **pts**.

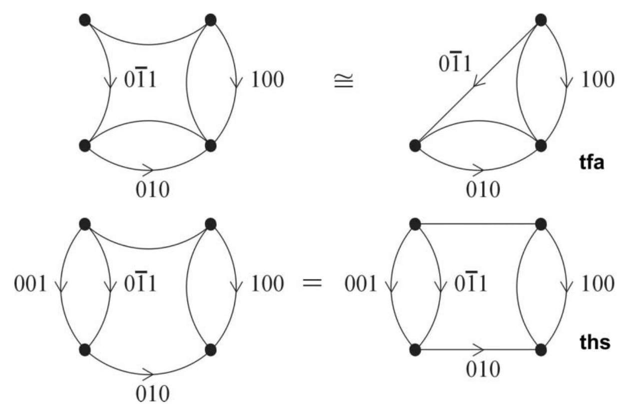

Figure 4
Labelled quotient graph of **pts** after deletion of edges (top) e_1 and e_3 yielding a net homeomorphic to **tfa** and (bottom) e_1 and e_7 yielding **ths**.

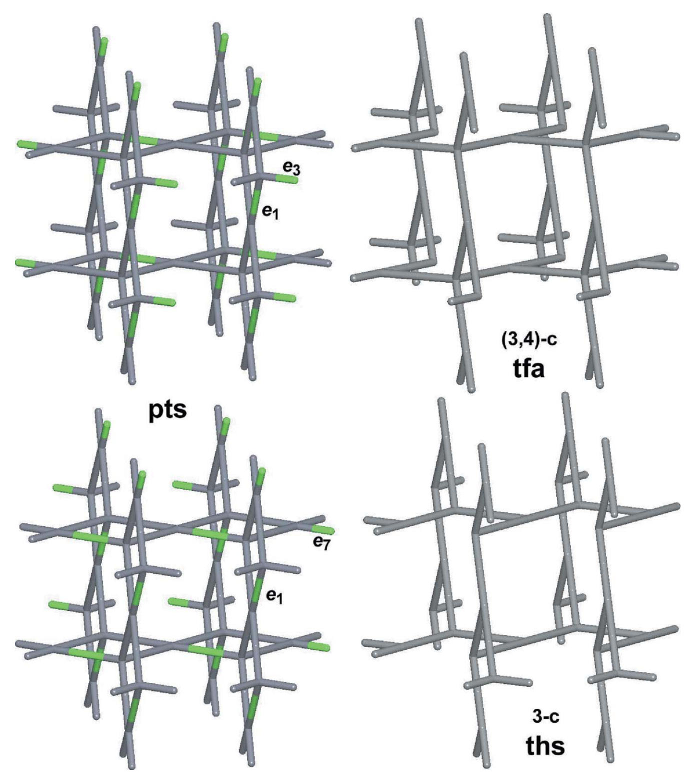

Figure 5
A representation of (top and bottom left) the net **pts**, (top right) a net homeomorphic to **tfa** obtained after deleting edges e_1 and e_3 and (bottom right) a net homeomorphic to **ths** after deleting edges e_1 and e_7. Deleted edges in **pts** are shown in green.

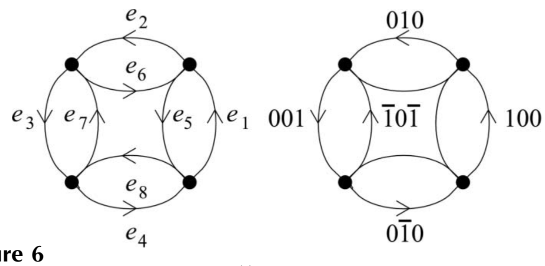

Figure 6
The labelled quotient graph $C_4^{(2)}$ of α-cristobalite.

will speak of the cristobalite net to emphasize that every edge lattice of **dia** is split into two edge lattices in α-cristobalite. It may be checked that the voltage assignment in the labelled quotient graph drawn in Fig. 6 is equivalent to the description of the cristobalite net through the relator matrix

$$\mathsf{R} = \begin{pmatrix} 1 & 0 & 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 \end{pmatrix}.$$

Again, R is totally unimodular and removal from the cristobalite net of the two edge lattices that project on edges e_1 and e_2 of its quotient graph yields a 3-periodic net homeomorphic to the minimal net **tfa**. In this case, **tfa** is the only minimal net contained in the initial net and is produced by the removal of any one of the 16 possible pairs of edges associated with submatrices of determinant ± 1. We are thus naturally drawn to the conclusion that the cristobalite net is totally unimodular. As a net, however, cristobalite is isomorphic to **dia**, a minimal net. It should be emphasized that there is no contradiction: **dia** is a 3-periodic, $\gamma = 3$ minimal net while cristobalite is a $\gamma = 5$, 3-periodic net. Withdrawing an edge lattice in **dia** amounts to withdrawing two correlated edge lattices in cristobalite that disconnect the net. The phenomenon is quite general: 3-periodic minimal nets can always be generated as 3-periodic nets of higher *genus* but with lower translational symmetry.

Theorem 3.1 admits a partial converse.

Theorem 3.2. Let N be a p-periodic net defined by a graph G and a set $\mathbf{r}$ of n relators projecting on a set $\mathcal{S}$ of cycle vectors of G, and suppose that one can find n edge lattices whose removal leaves a connected graph with the same periodicity as N and such that its quotient graph is a spanning subgraph of G. Then, the $n \times n$ matrix M associated with the coefficients of the respective edges in the set $\mathcal{S}$ has determinant $\pm$ 1.

Proof. Assign voltages in Z^p to the edges of G in order to satisfy the set of relators $\mathbf{r}$. Call P the periodic graph left after deleting the n referred edge lattices of N, and G^* its quotient graph. Because P is connected, G^* also is connected and so the cyclomatic numbers of G and G^* verify $\gamma(G^*) = \gamma(G) - n$. Let $\mathbf{b}$ be the set of relators that define P, then $|\mathbf{b}| = |\mathbf{r}| - n = 0$, so that $\mathbf{b} = \emptyset$ and P is homeomorphic to some minimal net. Since P is connected and has the same periodicity as N, there is a set $\mathcal{B}$ of cycle vectors of G^* with net voltages $10\ldots0, 010\ldots0, \ldots, 00\ldots1$ in Z^p. Inserting back any removed edge e_i in G^* is possible since G^* spans G, and increases its cyclomatic number by one unit. One can thus find an independent cycle in $G^* + e_i$ containing the edge e_i and add the right combination of cycle vectors of the set $\mathcal{B}$ to get a cycle vector of zero net voltage in G; this defines a new relator s_i of N containing the edge e_i. The $n \times n$ matrix of the coefficients of these edges in the new relator set $\mathbf{s}$ is clearly the unit matrix. But $\mathbf{r}$ and $\mathbf{s}$ are equivalent sets of relators; hence the change-of-basis matrix between both sets, which is exactly the matrix M, has determinant ± 1.

4. Characterization of totally unimodular nets

In this section, we want to come to a full characterization of totally unimodular nets by analysing the effect of deleting specific edge-lattice sets. We consider a p-periodic net N defined by a graph G with m edges and an $n \times m$ relator matrix R. Then, we choose a set $\mathcal{S}$ of n edges in G; call $G \setminus \mathcal{S}$ the graph obtained from G after deleting this edge set. We will examine the properties of the periodic graph obtained after removing the n associated edge lattices as a function of the determinant D of the respective $n \times n$ submatrix $\mathsf{R}_{\mathcal{S}}$ of R.

The result expressed in Theorem 3.1 may be extended easily to nets of an arbitrary periodicity; hence a connected p-periodic graph is obtained if $D = \pm 1$. Since this graph is p-periodic, has no relator and its quotient graph is connected, this quotient $G \setminus \mathcal{S}$ must have cyclomatic number p. Hence, notwithstanding possible dangling edges, the periodic graph is homeomorphic to some p-periodic minimal net.

Suppose now that $|D| > 1$ and choose a largest $k \times k$ submatrix M of $\mathsf{R}_{\mathcal{S}}$ with determinant ± 1. If such a submatrix exists, we change the order of edges and relators so that it is now located on the upper left of $\mathsf{R}_{\mathcal{S}}$; then we left multiply R by the $n \times n$ matrix obtained from the unit matrix I_n after insertion of M^{-1} on its upper left side. Applying the same procedure as in the proof of Theorem 3.1, we get an equivalent relator matrix where the upper-left $k \times k$ submatrix is the unit matrix I_k and only zero entries appear below this matrix. The lower-right $(n-k) \times (n-k)$ submatrix R_{n-k} of $\mathsf{R}_{\mathcal{S}}$ has then determinant $\pm D$ and no entry equal to ± 1 (otherwise M would not be the largest submatrix of determinant ± 1). Let d be the greatest common divisor of the entries of the left column in R_{n-k}. We may apply Euclid's algorithm (Heath, 1956) to the $(n-k)$ lower rows of R to get an equivalent relator matrix where only one non-zero entry remains in the left column of R_{n-k}; clearly this entry is d and can be brought to the first row of R_{n-k} by re-ordering of the relators. The same procedure may be applied again to the lower-right $(n-k-1) \times (n-k-1)$ matrix until we get an equivalent upper triangular matrix $\mathsf{T}_{\mathcal{S}}$ with non-zero values along the diagonal. Since every edge of $\mathcal{S}$ belongs to an independent relator, $\mathcal{S}$ is not a cut set. In accordance with Theorem 3.1, deleting the edge lattices that are the pre-images of the first k edges still yields a connected p-periodic graph. In accordance with Lemma 3.1, removal of the next edge lattice splits the graph into d translationally equivalent, interpenetrated p-periodic connected graphs. Repeated application of the lemma to the remaining edges of $\mathcal{S}$ shows that, after removal of all the corresponding edge lattices, the net is finally split into $|D|$ translationally equivalent, interpenetrated p-periodic connected graphs. Excepting the possible existence of dangling edges, as in the first case, every periodic component is homeomorphic to some p-periodic minimal net.

Consider finally the case $D = 0$. Applying again Euclid's algorithm, and re-ordering rows when necessary, we get an upper triangular matrix that is equivalent to $\mathsf{R}_{\mathcal{S}}$. This time, however, some diagonal entries should be zero. As it is always possible to exchange edges (columns) during the algorithm, we may suppose that all zero entries are located on the lower part of the diagonal. Let then e_k be the first edge with zero entry and Δ be the product of non-zero entries in the diagonal. Deletion of edge lattices that are the pre-images of edges e_i with $i < k$ yields, as above, a set of $|\Delta|$ translationally equivalent (interpenetrated) p-periodic connected graphs. Now, edge e_k does not belong to any relator of the resulting periodic graph. Hence its removal will not decrease the number of relators. If e_k is not a bridge, Lemma 3.1 shows that the resulting periodic graph consists of an infinite family of translationally equivalent $(p-1)$-periodic graphs. If e_k is a bridge, each periodic component is split into two translationally non-equivalent periodic graphs. Eventually, deleting a cut set $\mathcal{S}$ of G will split the net into a number of translationally non-equivalent periodic components of possibly different periodicities. The splitting of the net depends on both the rank of matrix $\mathsf{R}_{\mathcal{S}}$ and the relationship between the cut set and the support of the relators. Owing to the large number of non-equivalent possibilities, we think it better to analyse a concrete example in the next paragraph. Before this, however, we may summarize the results of this section into the following.

Corollary 4.1. A p-periodic net is totally unimodular if and only if it cannot be split into a finite number of translationally equivalent interpenetrated p-periodic components.

Proof. Consider the whole set of $n \times n$ submatrices of the $n \times m$ relator matrix. The previous analysis showed that a net can only split into a finite number of translationally equivalent interpenetrated nets when some of these submatrices have determinant D with $|D| > 1$.

Notice that minimal nets form a subclass among totally unimodular nets. In fact we may consider that the relator matrix of minimal nets is identically null so that withdrawal of any edge lattice disconnects a p-periodic minimal net into an infinite family of translationally equivalent $(p-1)$-periodic graphs.

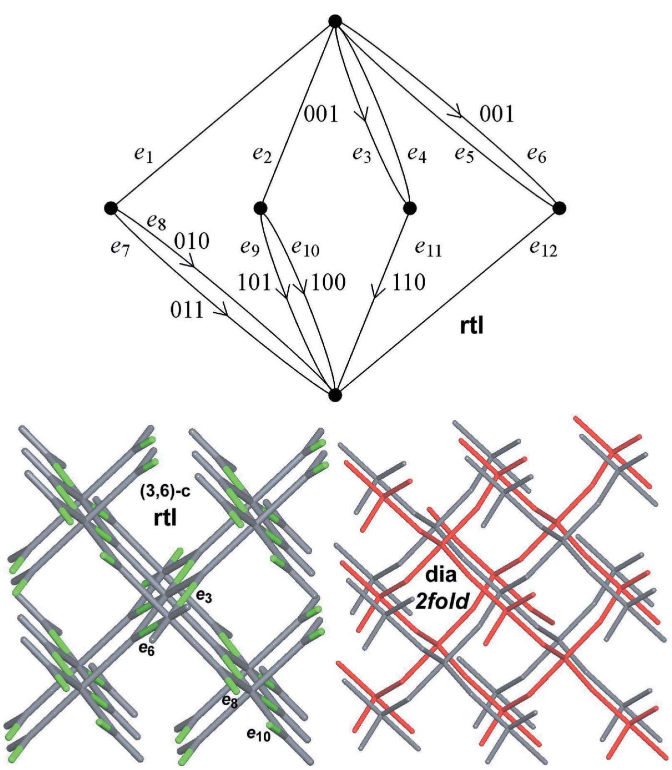

Figure 7
(Top) Labelled quotient graph of **rtl**, (bottom left) representation of **rtl** and (bottom right) twofold **dia** obtained after deleting the edge set $\mathcal{S}_2 = \{e_3, e_6, e_8, e_{10}\}$ enhanced in green in **rtl**.

5. The rutile net

The rutile net (**rtl**) provides an interesting example of the different cases considered in the previous section. The labelled quotient graph G is shown in Fig. 7 with all edges e_i oriented up–down. The reported voltages lead to the following relator matrix:

$$\mathsf{R} = \begin{pmatrix} 0 & 0 & 1 & \bar{1} & 1 & \bar{1} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & \bar{1} & 1 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & \bar{1} & 0 & 0 & 1 & \bar{1} & 0 & 0 \\ \bar{1} & \bar{1} & 0 & 1 & 1 & 0 & 0 & \bar{1} & 0 & \bar{1} & 1 & 1 \end{pmatrix}.$$

The submatrix associated with the edge set $\mathcal{S}_1 = \{e_3, e_5, e_7, e_9\}$ has determinant 1. Since the graph $G \setminus \mathcal{S}_1$ is homeomorphic to $\mathcal{K}_2^{(4)}$, the 3-periodic graph obtained after deleting the respective edge lattices in **rtl** is homeomorphic to **dia**.

Although removal of the set $\mathcal{S}_2 = \{e_3, e_6, e_8, e_{10}\}$ from G also leaves a graph homeomorphic to $\mathcal{K}_2^{(4)}$, the determinant of the submatrix $\mathsf{R}_{\mathcal{S}}$ is 2, so that the net is split into two interpenetrated components homeomorphic to **dia** (see Fig. 7). This shows that **rtl** is not totally unimodular.

The submatrix associated with the cut set $\mathcal{S}_3 = \{e_1, e_2, e_{11}, e_{12}\}$ of G has determinant 0. The graph $G \setminus \mathcal{S}_3$ has two components homeomorphic to $\mathcal{B}_2$ and the periodic graph obtained after deleting the respective edge lattices in **rtl** still has three relators since the four edges of $\mathcal{S}_3$ are only involved in one relator (the rank of $\mathsf{R}_{\mathcal{S}}$ is 1). The graph consists of two infinite families of 1-periodic graphs. In each family, the 1-periodic graphs are all translationally equivalent. They correspond to ribbons of rhombi and may be correlated to edge-linked octahedral chains usually considered to describe rutile topology in crystal chemistry.

As a last example, the submatrix associated with the edge set $\mathcal{S}_4 = \{e_3, e_4, e_5, e_6\}$ also has determinant 0, but rank 3. Hence, there is still one relator after deleting the four edges. Since $G \setminus \mathcal{S}_4$ is connected, the periodic graph obtained after deleting the respective edge lattices in **rtl** contains an infinite family of 2-periodic graphs, all translationally equivalent in one direction. Notwithstanding dangling edges, the quotient $G \setminus \mathcal{S}_4$ is homeomorphic to $3(3^2, 4)1$ and each 2-periodic component of the infinite graph is homeomorphic to the plane net $(4.6.4.6)(4.6^2)_2$.

6. Generating totally unimodular nets

We used the theory described above to create a computer program *UniNet* for generating all possible totally unimodular nets from a given quotient graph G. The algorithm of the program includes the following steps:

(i) Reading the adjacency matrix of G.

(ii) Determining the spanning tree and all (γ) chords of G.

(iii) Determining the basis of the cycle space C for G.

(iv) Assigning voltages from Z^γ to the chords and, as a result, obtaining a labelled quotient graph of a γ-periodic minimal net M and a set of basis cycle vectors corresponding to C.

(v) Enumerating all closed trails by summing the basis cycle vectors, searching for all acceptable cycle vectors with zero net voltage (relators) and forming all subspaces K of C.

(vi) Searching for all projections M/K, where K runs over all projection kernels with totally unimodular relator matrices and, as a result, obtaining all totally unimodular nets $N = M/K$.

We applied this procedure to generate all $(\gamma - 1)$-periodic totally unimodular nets from γ-periodic minimal nets for $\gamma = 3$ and 4 (*i.e.* for the minimal nets enumerated by Beukemann & Klee, 1992). There are 111 quotient graphs with $\gamma = 4$ from which we excluded 68 that have at least one bridge because they give only nets with vertex collision which are very rare in crystal chemistry (Delgado-Friedrichs & O'Keeffe, 2005). Analogously we excluded seven graphs from the 15 quotient graphs with $\gamma = 3$. As a result, we found 14 2-periodic and 210 3-periodic totally unimodular nets. The corresponding crystallographic data are available as supplementary material.[1]

The embeddings of the nets were generated using the program *Systre* (Delgado-Friedrichs & O'Keeffe, 2003; http://www.gavrog.org) and were topologically identified with both *Systre* and *TOPOS* (Blatov, 2006; http://www.topos.ssu.samara.ru). At this step, only non-isomorphic nets were selected and characterized by a number of their topological indices to be used for classification (Blatov, 2007). The indices were included in the *TOPOS TTD* collection (Blatov & Proserpio, 2009) that allows us to reveal the totally unimodular nets in the crystal structures of newly synthesized compounds. To find how the 3-periodic totally unimodular nets occur in known crystal structures we searched through the *TOPOS TTO* collection that currently contains more than 13 000 examples of 3-periodic (single or interpenetrated) *underlying nets* realized in inorganic compounds, coordination networks and organic hydrogen-bonded supramolecular architectures [see Alexandrov *et al.* (2011) and Blatov & Proserpio (2011) for details on the possible different representations called 'standard' or 'cluster' stored in *TOPOS* databases]. To estimate the occurrence of 2-periodic totally unimodular nets we explored underlying nets in 10 458 two-dimensional coordination polymers, the crystallographic data of which were taken from the Cambridge Structural Database (release 5.32; Allen, 2002).

Table 1
Occurrence of totally unimodular nets among 2-periodic nets [see Blatov *et al.* (2009) for the definition of point and vertex symbols].

Name	Point symbol	Vertex symbol	Occurrence
sql	4^4	[4.4.4.4]	4019
hcb	6^3	[6.6.6]	1935
fes	4.8^2	[4.8.8]	611
3,4L13	$(4.6^2)_2(4^2.6^2)$	$[4.6.6]_2[4.6.4.6]$	294
hxl	3^6	[3.3.3.3.3.3]	121
3,5L52	$(3.5^2)(3^2.5^3)$	[3.5.5][3.5.3.5.5]	44
KIb	(4.10^2)	$[4.10_2.10_6]$	16
3,4L21	$(3.7^2)_2(3.7^3)$	$[3.7.7]_2[3.7.7.7]$	16
4L1	$(4^2.6^3.8)$	$[4.4.6_2.6_2.6_4.*]$	14
hnb	$(3.9^2)_3(9^3)$	$[3.9.9]_3[9.9.9]$	6
cem-d	$(5^3)_2(5^4)$	$[5.5.5]_2[5.5.5.5]$	3
4,4L27	$(3.6^4.8)(3^2.6.7^2.8)$	$[3.*.6.6.6.6][3.3.6_2.*.*.*]$	3

7. Occurrence of totally unimodular nets

We found examples of the occurrence of ten out of 14 2-periodic totally unimodular nets in coordination polymers (Table 1). Among them are two minimal 2-periodic nets, **sql** and **hcb**, that emerge as totally unimodular nets of a lower translational symmetry as was shown above for the cristobalite and diamond nets. Some of these 2-periodic nets which are less known, or have been newly found, are shown in Fig. 8. It is noteworthy that the first four most abundant 2-periodic nets are totally unimodular, and all ten nets are topologically rather simple (uninodal or binodal). Furthermore, three 2-periodic nets (**KIb**, 4L1 and 4,4L27) have good embeddings (with no edge crossings) only in three-dimensional space as shown in the figure.

Of the 210 3-periodic totally unimodular nets, 55 are described in the databases on periodic nets (Blatov, 2007; O'Keeffe *et al.*, 2008; Ramsden *et al.*, 2009; Blatov & Proserpio, 2011) and 40 are realized as underlying nets (Table 2), ten of which were not known before this study (named #, # . . . *T*# according to Alexandrov *et al.*, 2011). Moreover, three out of the four nets at the top of the table (**bcu**, **bnn**, **nbo**) occupy also a top place among the first 20 most frequent underlying nets recently reported (Alexandrov *et al.*, 2011). Closer inspection of the latter list shows that out of the ten first most abundant nets (**pcu**, **dia**, **bcu**, **pts**, **rtl**, **cds**, **srs**, **sra**, **bnn**,

[1] Supplementary material includes drawings of all the 15 and 111 quotient graphs with $\gamma = 3$ and 4 (genus3.jpg and genus4.jpg), and the coordinates for the embedding of the nine 2-periodic totally unimodular nets not listed in the RCSR (2periodic_9nets.cgd). For the 3-periodic nets we give the coordinates for the 65 (known or observed) nets and separately for the 145 new and not yet observed nets (145new_TotUnMod.cgd, 65known_TotUnMod.cgd). The coordinates are text files in *Systre* .cgd format that include the edges, and together with each name we also give the corresponding quotient graph name as given by Beukemann & Klee (1992). For the 145 new nets we also assign a name according to *TOPOS TTO/TTD* rules as reported in the file all_new145.xls. The material is available from the IUCr electronic archives (Reference: WX5007). Services for accessing these data are described at the back of the journal.

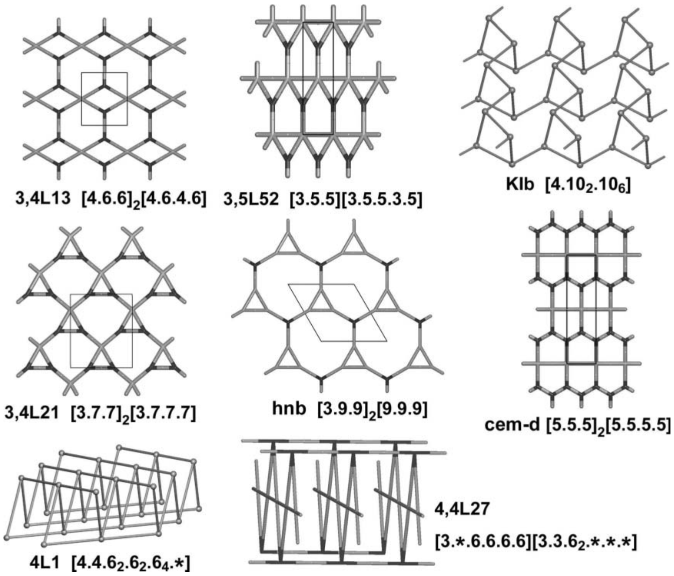

Figure 8
Eight less-known or newly found 2-periodic nets listed in Table 1. **Klb** was described in Fig. 28b in Koch & Fischer (1978).

nbo), nine are totally unimodular with $\gamma = 3$ to 5 (including the minimal nets **pcu**, **dia**, **srs**, **cds** with $\gamma = 3$); the only exception is **rtl**. As an example Fig. 9 shows a representation of three nets listed in Table 2 that are not in the RCSR database. The remaining 145 3-periodic totally unimodular nets that have not yet been observed in any crystal structure have new topologies not described before. Interestingly three of them are non-crystallographic nets (Moreira de Oliveira & Eon, 2011) for which a maximum symmetry embedding cannot be computed with *Systre*. For the remaining 142 nets the number of non-equivalent nodes varies from 1 to 5; there are one uninodal, 20 binodal, 76 trinodal, 34 tetranodal and 11 pentanodal nets.

Since the proportion of 3-periodic totally unimodular underlying nets is rather large (40 *versus* 210; 19.0%) in comparison to the probability of occurrence of a randomly generated net (1–2%) (Blatov & Proserpio, 2009), the property of unimodularity can be considered as crystallochemically important. At the same time, it does not predetermine a high occurrence of the net. Obviously, other properties should be taken into account, in particular, high net symmetry (Ockwig *et al.*, 2005). Thus, most of the observed totally unimodular nets are uninodal or binodal (33 out of the 40 3-periodic and all 12 2-periodic) (see Tables 1 and 2), while the 145 new 3-periodic nets are mainly trinodal or tetranodal.

8. Concluding remarks

Totally unimodular nets were introduced as a class of periodic nets defined from a finite graph and a totally unimodular relator matrix. They generalize the concept of minimal nets for which the relator matrix may be considered to be identically null, a very special case of unimodularity.

Corollary 4.1 determines the physical meaning of total unimodularity for periodic nets: they cannot be split into an interpenetrating array of the same periodicity like minimal nets cannot be transformed into low-coordinated nets of the same periodicity. Thus, minimal and totally unimodular nets can be considered as 'simple' nets in the sense that they do not contain, respectively, one or several subnets of the same periodicity.

Upon further generalization of the concept, more 'complex' nets could be classified according to the spectrum of absolute values for $n \times n$ determinants in their $n \times m$ relator matrix. Indeed, the analysis of **rtl** suggests that periodic nets associated with many common crystal structures are not totally

Table 2
Occurrence of totally unimodular nets among 3-periodic nets.

Name	Occurrence	Name	Occurrence
bcu	285	**nor**-3,4-*C*2/*m*	3
hex	164	3,4,4-c *sqc*69	3
bnn	151	**fsg**	2
nbo	97	4,6T19	2
mog	81	3,6T1	2
sqp	64	**cdz**	1
fsc	62	**ftb**	1
qtz	55	**fsf**	1
qzd	50	**tcj**-4,6-*Cmcm*	1
etb	17	**fsg**-3,4-*Cmmm*	1
fsc-3,4-*Imm*2	12	**thj**-3,4-*C*222	1
pcu-h	11	3,3,4-c *sqc*164	1
bbe-3,4-*Cmmm*	10	3,4T24	1
tfo	10	3,6T44	1
mot	9	4,4T26	1
bto	7	3,3,3T5	1
3,6-c *sqc*27	7	3,3,3T9	1
eta	5	3,3,4T28	1
moc	4	3,3,4T31	1
sit	3	3,3,3,3,4T1	1

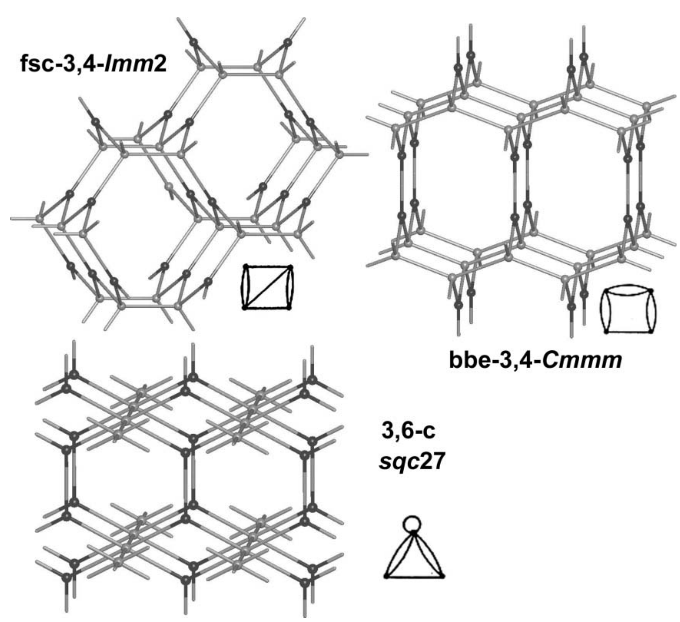

Figure 9
Three 3-periodic nets listed in Table 2 that are not in the RCSR. The quotient graph related to each of them is added to the right, at the bottom of the net.

unimodular. Our occurrence analysis showed that more than 80% of 3-periodic nets are not totally unimodular. It is also highly probable that the occurrence of totally unimodular nets decreases with increasing cyclomatic numbers. Hence, a less demanding property is needed to better characterize important nets for crystal chemistry. We propose to call unimodular a net such that the smallest positive absolute value for $n \times n$ determinants in the relator matrix, if it exists, is $|D| = 1$. According to this definition, totally unimodular nets (including minimal nets) are also unimodular nets. The present study shows that, for unimodular nets, there exists a set of n edge lattices whose deletion yields a connected graph of the same periodicity which is homeomorphic to some minimal net.

Finally, we note that crystallochemical analysis of the topology of crystal structures often corresponds to a decomposition into structural 1- or 2-periodic subunits such as simple or multiple chains, or two-dimensional layers. This can be done more routinely by considering null $n \times n$ determinants in the $n \times m$ relator matrix of the associated 3-periodic net.

APPENDIX *A*
Terminology

Bouquet $\mathcal{B}_n$: graph with a single vertex and n loops.
$\mathcal{C}_m^{(n)}$: graph of the cycle with m vertices and multiple (n-folded) edges.
Cut set: a set of edges whose deletion yields a disconnected graph.
Cycle space: the vector space built upon the set of cycle vectors.
Cycle vector: any linear combination of cycles.
Cyclomatic number: the number of independent cycles of a graph, γ = number of edges − number of vertices + 1.
Edge lattice: the set of edges in a periodic net (N, T) that are equivalent under the translation group T.
Genus: the genus of a periodic net (N, T) is the cyclomatic number of its quotient graph N/T.
Homeomorphism: two graphs are homeomorphic if it is possible to transform them into isomorphic graphs by a sequence of edge subdivisions (*i.e.* deletion of an edge uv and addition of a vertex w together with two edges uw and wv).
$\mathcal{K}_m$: complete graph with m vertices.
$\mathcal{K}_m^{(n)}$: complete graph with m vertices and multiple (n-folded) edges.
Net voltage: sum of the voltages along the edges of a walk.
Underlying net: the net whose nodes and edges correspond to structural units and connections between them. It is the result of some structure simplification (Blatov & Proserpio, 2011).
Voltage: vector label assigned to an arc (*i.e.* oriented edge), indicating the vector difference between the unit cells containing the terminating and its originating vertices.
Word in Σ: a linear combination of generators from the set Σ with integer coefficients.

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References

Alexandrov, E. V., Blatov, V. A., Kochetkov, A. V. & Proserpio, D. M. (2011). *CrystEngComm*, **13**, 3947–3958.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Beukemann, A. & Klee, W. E. (1992). *Z. Kristallogr.* **201**, 37–52.
Blatov, V. A. (2006). *IUCr Compcomm. Newsl.* **7**, 4–38.
Blatov, V. A. (2007). *Acta Cryst.* A**63**, 329–343.
Blatov, V. A., O'Keeffe, M. & Proserpio, D. M. (2009). *CrystEngComm*, **12**, 44–48.
Blatov, V. A. & Proserpio, D. M. (2009). *Acta Cryst.* A**65**, 202–212.
Blatov, V. A. & Proserpio, D. M. (2011). In *Modern Methods of Crystal Structure Prediction*, edited by A. R. Oganov. Weinheim: Wiley-VCH.
Bonneau, C., Delgado-Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2004). *Acta Cryst.* A**60**, 517–520.
Chung, S. J., Hahn, Th. & Klee, W. E. (1984). *Acta Cryst.* A**40**, 42–50.
Delgado-Friedrichs, O. (2005). *Discrete Comput. Geom.* **33**, 67–81.
Delgado-Friedrichs, O. & O'Keeffe, M. (2003). *Acta Cryst.* A**59**, 351–360.
Delgado-Friedrichs, O. & O'Keeffe, M. (2005). *J. Solid State Chem.* **178**, 2480–2485.
Eon, J.-G. (2006). *Z. Kristallogr.* **221**, 93–98.
Eon, J.-G. (2007). *Acta Cryst.* A**63**, 53–65.
Eon, J.-G. (2011). *Acta Cryst.* A**67**, 68–86.
Gross, J. L. & Tucker, T. W. (2001). *Topological Graph Theory*. New York: Dover.
Harary, F. (1972). *Graph Theory*. New York: Addison-Wesley.
Heath, T. L. (1956). *The Thirteen Books of Euclid's Elements*. New York: Dover.
Klee, W. E. (2004). *Cryst. Res. Technol.* **39**, 959–968.
Koch, E. & Fischer, W. (1978). *Z. Kristallogr.* **148**, 107–152.
Moreira de Oliveira, M. & Eon, J.-G. (2011). *Acta Cryst.* A**67**, 240–251.
Ockwig, N. W., Delgado-Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2005). *Acc. Chem. Res.* **38**, 176–182.
O'Keeffe, M., Peskov, M. A., Ramsden, S. J. & Yaghi, O. M. (2008). *Acc. Chem. Res.* **41**, 1782–1789.
Ramsden, S. J., Robins, V. & Hyde, S. T. (2009). *Acta Cryst.* A**65**, 81–108.
Wells, A. F. (1977). *Three Dimensional Nets and Polyhedra*. New York: Wiley.