one system of chains in the channels. If the chains are incommensurable both with the matrix and with each other, then there is a modulation vector for each system, and these vectors violate (*a*). In such cases, an interpretation similar to the dualistic one is possible only by allowing two or more modulation patterns – each of them periodic in space – to act on the same basic structure.

Nearly all known modulated structures, however, can straightforwardly be interpreted in a dualistic way. The type of modulation (displacement or scalar density variation) plays no role for the symmetry; displacements have to undergo the symmetry operations of G_M as vectors. Thus it is possible to visualize the symmetry of a modulated structure just as easily as that of a normal one. In particular, the lattice and all symmetry elements of G_M can be pinpointed in the direct space of the crystal. If a drawing is desired, it suffices to superimpose the symmetry element figures in *International Tables for X-ray Crystallography* (1969) for G_M and G_B. The graphic representation proposed earlier by the author (de Wolff, 1981) comes very close to such a superposition.

The author is indebted to Dr T. Janssen and Professor A. Janner (Institute for Theoretical Physics, University of Nijmegen) for reading the manuscript and for their very helpful remarks.

References

International Tables for Crystallography (1983). Vol. *A*. Dordrecht: Reidel.
International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.
JANNER, A., JANSSEN, T. & DE WOLFF, P. M. (1983). *Acta Cryst.* **A39**, 658–666.
JANSSEN, T., JANNER, A. & DE WOLFF, P. M. (1980). *Proc. Conf. on Group Theoretical Methods in Physics*, edited by M. A. MARKOV, pp. 155–162. Moscow: Nauka.
WOLFF, P. M. DE (1974). *Acta Cryst.* **A30**, 777–785.
WOLFF, P. M. DE (1977). *Acta Cryst.* **A33**, 493–497.
WOLFF, P. M. DE (1981). *Symmetries and Broken Symmetries in Condensed Matter Physics*, edited by N. BOCCARA, pp. 257–262. Paris: Idset.
WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* **A37**, 625–636.
YAMAMOTO, A. (1982). *Acta Cryst.* **B38**, 1451–1456.

Acta Cryst. (1984). **A40**, 42–50

Nomenclature and Generation of Three-Periodic Nets: the Vector Method

BY S. J. CHUNG AND TH. HAHN

Institut für Kristallographie der RWTH Aachen, Templergraben 55, *D*-5100 *Aachen, Federal Republic of Germany*

AND W. E. KLEE*

Institut für Kristallographie der Universität Karlsruhe, Kaiserstrasse 12, *D*-7500 *Karlsruhe, Federal Republic of Germany*

(*Received* 16 *June* 1983; *accepted* 26 *August* 1983)

Dedicated to Professors M. J. Buerger and A. F. Wells on the occasions of their 80*th and* 70*th birthdays*

Abstract

Three-periodic nets are connected graphs which permit embeddings having a threefold periodicity. To many crystal structures such nets can be meaningfully assigned and used to express the topology of the structures. It is shown that such a net can be fully characterized by a finite graph in which the edges are labelled in a suitable way. The reversal of the process of assigning a labelled finite graph to a given net can be used to generate nets of real and hypothetical crystal structures in a systematic fashion.

* To whom correspondence should be addressed.

1. Introduction

This exposition deals with the various ways in which the atoms in crystal structures may be connected to each other. For such a study it is convenient to use the language and the tools of graph theory. The relation between a crystal structure and a graph is established by identifying the atoms of the structure with the vertices of the graph and the chemical bonds with the edges. Such an assignment is straightforward for structures in which the bonds are largely covalent. For structures in which ionic, metallic or van der Waals bonds dominate, the method to be discussed may still be useful, but requires an assignment of

0108-7673/84/010042-09$01.50

bonds to pairs of atoms which may be arbitrary. If in a structure, for example that of a silicate, only a certain part is held together by covalent bonds, it is this part which is of interest. As an example consider the structure of nepheline, $Na_3K[AlSi_3O_8]_4$. Here the point of interest is the alumino-silicate framework in which each tetrahedral atom (silicon or aluminum) is connected to four oxygen atoms and each oxygen atom to two tetrahedral atoms. In assigning a graph to this framework a certain simplification is possible: It is sufficient to assign vertices to the tetrahedral atoms only and to connect two such vertices by an edge whenever the corresponding tetrahedral atoms are connected *via* an oxygen bridge. Such simplifications will be made in the case of all the silicates which are mentioned here.

The discussion will focus on certain types of graphs which are of particular interest: These are the three-periodic connected graphs which will also be called *three-periodic nets*. [Wells (1977) uses the term *three-dimensional nets*.] A systematic nomenclature for three-periodic nets has, to the knowledge of the authors, not yet been developed. The enumeration of such nets has been a subject of interest for some time. Including the procedure to be presented here three principal methods may be distinguished:

(*a*) The *orbit method*: The orbit of a point under all operations of a three-dimensional space group is formed. All pairs of points of the orbit which are less than a specified distance apart are then connected by a line. For literature on this method which is related to the construction of homogeneous sphere packings see Fischer (1973, 1982).

(*b*) The *aufbau method*: This name is given to methods in which more complex three-periodic nets are built up from simpler nets. This may be done, for example, by substituting a triangle graph K_3 for a trivalent vertex or a tetrahedron graph K_4 for a quadrivalent vertex (Heesch & Laves, 1933). The method may also involve an increase in the periodicity of the net when, for example, a three-periodic net is constructed by interconnecting two-periodic nets. Such methods have been used by Wells (1977, 1979) and have been extensively applied by Smith and co-workers (see Smith & Bennett, 1981). Regarding crystal structures as sets of interconnected layers is a viewpoint which has been advanced by Lima-de-Faria and Figueiredo (Lima-de-Faria & Figueiredo, 1976; Figueiredo, 1982).

(*c*) The *vector method*: This is the method presented here, so-called because it makes use of index triples which may be identified with vectors. It is in part based on a combinatorial method by Chung & Hahn (1975, 1976); see also Chung, Hahn & Klee (1983).

Other methods do not fit into a simple scheme because they are not free from intuition. To these belong certain procedures employed by Wells (1977, 1979) who did much to advance our knowledge of three-periodic nets.

2. Definitions

Only graph-theoretical terms which are of special importance in this context or which are not generally established will be defined here. Definitions of the others can be found in Harary (1969) or other books on graph theory. In contrast to Harary the terms *vertices* and *edges* are used here for the elements of a graph. *Space* means Euclidean space.

A graph is *simple* if it has no loops or multiple edges.

A graph is *n-regular* ($n = 0, 1, 2, \ldots$) if all of its vertices are n-valent, *i.e.* are of degree n.

A graph is a *net* if it is connected and has infinitely many cycles.

A graph is a *tree* if it is connected and has no cycles.

A subgraph of a given graph is a *spanning tree* of that graph if it is a tree and contains all the vertices of the graph.

An *embedding* of a graph in n-dimensional space ($n = 0, 1, 2, \ldots$) is a representation, in that space, of its vertices by points and of its edges by straight lines such that the incidence relations are preserved and no two lines intersect.

A graph is *n-dimensional* ($n = 1, 2, 3, \ldots$) if it can be embedded in n-dimensional space such that the distance between any pair of points is finite and if such an embedding is not possible in a space of lower dimension. The graph K_1 consisting of a single vertex is the only graph which can be embedded in zero-dimensional space and is called *zero-dimensional.*

A graph is *n-periodic* ($n = 1, 2, 3, \ldots$) if it can be embedded in space of sufficiently high dimension in such a way that among the isometric symmetry operations of the embedding there are translations in n, but for no such embedding there are translations in more than n independent directions. A graph which is not n-periodic is *zero-periodic.*

Two points of an embedding are *translationally equivalent* if there is a translation which maps one of the points onto the other and brings the embedding into coincidence with itself. A class of points which are equivalent with respect to all translations of an embedding is called a *point lattice* (more exactly an n-dimensional point lattice if there are n, but not more than n, independent translations). A *line lattice* is similarly defined for the lines connecting pairs of points of the embedding.

3. Quotient graphs

Consider an embedding of a three-periodic net in three-dimensional space. It will always be assumed that such an embedding is one of maximal translational symmetry, *i.e.* one with the smallest possible number of point lattices. Then a finite graph may be assigned to the three-periodic net *via* the given embedding as follows:

(*a*) The point lattices $\mathbf{P}_1, \mathbf{P}_2, \ldots, \mathbf{P}_p$ are mapped onto the vertices $P_1, P_2, \ldots, P_p$ of the finite graph.

(*b*) The line lattices are mapped onto the edges of the finite graph. This is done in such a way that a lattice of lines connecting the points in $\mathbf{P}_i$ with the points in $\mathbf{P}_j$ is mapped onto an edge incident with the vertices P_i and P_j.

In (*b*) the special case $\mathbf{P}_i = \mathbf{P}_j$ causes the vertex P_i to become incident with one or more loops. This occurs whenever a point in lattice $\mathbf{P}_i$ is connected to other points in the same lattice. If $\mathbf{P}_i \neq \mathbf{P}_j$ and if there is more than one lattice of lines connecting points of $\mathbf{P}_i$ with points of $\mathbf{P}_j$, then there will be a multiple edge incident with vertices P_i and P_j. So the finite graph is in general not simple.

The finite graph may be considered as the image of the three-periodic net under the mapping described above which makes use of a given embedding. Since this process is reminiscent of the mapping of a group onto one of its factor groups or quotient groups, the finite graph will be called the *quotient graph of the three-periodic net with respect to the given embedding* or, if there is no ambiguity, simply the *quotient graph of the three-periodic net* (the term *factor graph* has a different and well-defined meaning in graph theory). The mapping preserves certain properties of the three-periodic net like the valency of the vertices, but other information is lost. This is illustrated in Fig. 1 which shows that two non-isomorphic three-periodic nets may yield isomorphic quotient graphs.

4. Nomenclature for three-periodic nets

The assignment of a quotient graph to a three-periodic net, *via* a given embedding, is in general accompanied

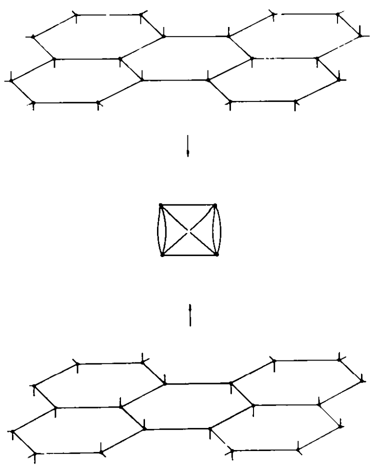

Fig. 1. Two non-isomorphic three-periodic nets with isomorphic quotient graphs. The upper net is that of mono-Ca[$Al_2Si_2O_8$] and the lower one that of Rb[$AlSiO_4$] (see Smith, 1977).

by a loss of information. In particular, while it is still known which point lattices are connected to each other by how many lattices of lines, it is not known anymore which individual point is connected to which other point. This information can be restored by a suitable system of labelling the edges of the quotient graph. Consider a three-periodic net and its quotient graph with respect to a given embedding. For each point lattice $\mathbf{P}_i$ of the embedding a coordinate system is introduced which consists of an origin and three basis vectors. Each lattice is given its own origin, but the basis vectors are chosen common to all of the lattices. As origin in the lattice $\mathbf{P}_i$ an arbitrary point is taken and labelled $P_i(000)$. As basis vectors three linearly independent translation vectors **a**, **b** and **c** are chosen such that each translation vector is an integral linear combination of these. An arbitrary point of the embedding may then be identified by a symbol such as $P_i(rst)$, where the index i refers to the ith point lattice and the indices r, s and t indicate that the vector from the origin $P_i(000)$ to the point in question is $r\mathbf{a} + s\mathbf{b} + t\mathbf{c}$.

The system of labelling the edges of the quotient graph will now be discussed. Consider an edge of this graph which is incident with vertices P_i and P_j. This edge is the image of a lattice of lines of the embedding which connect points of lattice $\mathbf{P}_i$ with points of lattice $\mathbf{P}_j$. Assume that an arbitrary representative of the lattice of lines connects a point $P_i(rst)$ with point $P_j(uvw)$. In the quotient graph an arrow is then assigned to the corresponding edge, pointing from vertex P_i to vertex P_j, and the edge is labelled with the index triple $u-r$, $v-s$, $w-t$. The special case $i=j$ (loop) is treated in the same fashion. The labelling of the edges of the quotient graph is continued until all the edges are exhausted. It follows from the construction that the embedding of the three-periodic net is uniquely determined by the labelled quotient graph together with the coordinate systems. The three-periodic net itself is determined, up to isomorphism (in the graph-theoretical sense), by the labelled quotient graph alone, because different choices of coordinate systems cannot affect the way in which the points are connected to each other. Since the index triples may be identified with triples of vector coefficients the procedure just outlined will be called the *vector method of symbolizing three-periodic nets.*

A few conventions help to simplify the nomenclature of the quotient graph: Since the two ends of a loop cannot be distinguished, the reversal of the direction of an arrow on a loop cannot result in the labelling of a different three-periodic net. It follows that an arrow on a loop can be dispensed with altogether. Similarly, reversing the direction of an edge labelled 000 does not lead to a different net. Thus, arrows on such edges are likewise superfluous. Also, the convention will be adopted not to write indices 000, *i.e.* to leave an edge unlabelled if it is associated with the index triple 000. In Fig. 2 it is shown how such a labelled quotient graph is obtained from an embedding of the three-periodic net of mono-$Ca[Al_2Si_2O_8]$.

In cases where a representation of the labelled quotient graph by a drawing does not appear acceptable (*e.g.* when computer storage is desired), the quotient graph with its labelling can also be given in matrix form or in the form of some other tabular arrangement.

5. Equivalences

Whereas a labelled quotient graph uniquely determines a three-periodic net up to isomorphism, the labelling itself is not uniquely determined by the three-periodic net. There may be several labellings describing isomorphic three-periodic nets, depending on the choice of the coordinate systems and other factors. Two labellings will be called *equivalent* when they determine isomorphic three-periodic nets. In the following the various operations which lead to equivalent labellings of a given labelled quotient graph will be discussed.

(*a*) Reversal of the direction of an arrow accompanied by an inversion of the indices, *i.e.* by changing the indices *rst* to $\bar{r}\bar{s}\bar{t}$, where the bars stand for minus signs.

(*b*) Change of coordinate system.

Change of basis vectors: Let there be a change from the basis vectors **a**, **b**, **c** to new basis vectors **a**′, **b**′, **c**′ and let, in matrix notation,

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}.$$

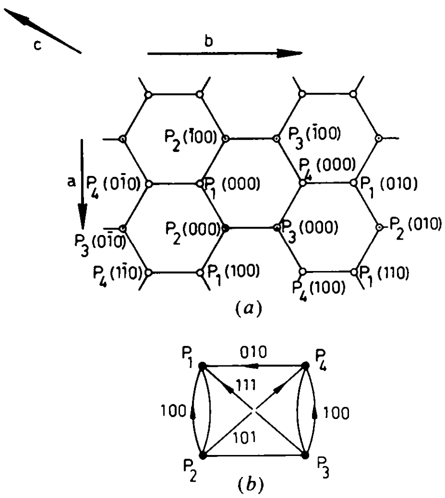

Fig. 2. Labelling the quotient graph of a three-periodic net. (*a*) Embedding and coordinate systems for the mono-$Ca[Al_2Si_2O_8]$ net. Dotted and open circles indicate perpendicular lines upward and downward, respectively. (*b*) The labelled quotient graph.

Let the index triple *rst* change to $r's't'$. Since only the reference system has been changed and not the embedding, it follows from $r\mathbf{a}+s\mathbf{b}+t\mathbf{c}=r'\mathbf{a}'+s'\mathbf{b}'+t'\mathbf{c}'$ that

$$\begin{pmatrix} r' \\ s' \\ t' \end{pmatrix} = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}^{-1} \begin{pmatrix} r \\ s \\ t \end{pmatrix}.$$

Change of origin: Consider, in the labelled quotient graph, an edge *rst* running from vertex P_i to vertex P_j. Let there be, in the coordinate system for the point lattice $\mathbf{P}_i$ of the embedding, a change of origin from point $P_i(000)$ to point $P_i(0'0'0') = P_i(lmn)$, where the indices *lmn* refer to the old system. Any point $P_i(uvw)$ in the old system must then be re-labelled $P_i(u-l, v-m, w-n)$ in the new system. Similarly, let there be a change of origin in the point lattice $\mathbf{P}_j$, from point $P_j(000)$ to point $P_j(0'0'0') = P_j(opq)$. This entails a re-labelling of the point $P_j(xyz)$ to $P_j(x-o, y-p, z-q)$. Under the mapping of the embedding onto the quotient graph precisely those lines of the embedding which run from points $P_i(uvw)$ to points $P_j(xyz)$ are mapped onto the (P_i, P_j) edge *rst* for which $x-u=r, y-v=s, z-w=t$. It follows that the edge *rst* must be re-labelled

$$r' = r - o + l$$

$$s' = s - p + m$$

$$t' = t - q + n.$$

Combination of both: By using 4×4 matrices it is possible to express by a single equation the effect of the change of both basis vectors and origins. For the (P_i, P_j) edge *rst* one obtains

$$\begin{pmatrix} r' \\ s' \\ t' \\ \hline 1 \end{pmatrix} = \left(\begin{array}{ccc|c} \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}^{-1} & & & \begin{matrix} l-o \\ m-p \\ n-q \end{matrix} \\ \hline 0 & 0 & 0 & 1 \end{array}\right) \begin{pmatrix} r \\ s \\ t \\ \hline 1 \end{pmatrix},$$

where r', s' and t' are the new indices and where the meaning of the other symbols is as before. The vertical and horizontal lines in the matrices serve merely as a guide to the eye and have no other meaning.

(*c*) Performance of an automorphism of the quotient graph: The concept of an automorphism, generally defined as an adjacency-preserving permutation of the vertices, is extended here to include the permutation of loops which are incident with the same vertex and the permutation of edges which are incident with the same pair of vertices. Obviously the performance of such an automorphism of the labelled quotient graph leads to an isomorphic three-periodic net.

All the operations discussed above are illustrated in Fig. 3.

6. Generation of three-periodic nets: principles

The process of generating three-periodic nets is essentially a reversal of the vector method of symbolizing three-periodic nets which has been outlined in § 4. It will therefore be called the *vector method of generating three-periodic nets.* It is carried out in three or four steps as follows.

(*a*) *Generation of all connected graphs with a given number of vertices of specified valence*

The graphs serve as quotient graphs for the three-periodic nets to be generated and may therefore have loops and multiple edges.

(*b*) *Labelling of the quotient graphs*

This means the assignment of an index triple to each edge and the assignment of a direction to those edges which are not loops and to which the index triple 000 has not been assigned. (Recall the convention to leave the latter type of edges unlabelled.) The following instructions guarantee that the labelling of the quotient graph does indeed define a three-periodic net.

(i) Select, in the given quotient graph, a spanning tree and assign to its edges the index triple 000, *i.e.* leave the edges unlabelled. One such choice of spanning tree suffices to generate all of the three-periodic nets which meet the conditions outlined below. Recall that each vertex of the quotient graph stands for a point lattice in an embedding of the three-periodic nets to be generated and that each edge of the quotient graph stands for a lattice of lines. From each point lattice of the embedding and from those line lattices which are associated with the edges of the spanning tree select one representative in such a way that the selected points and lines form a tree themselves. Take the points of this tree as origin points $P_1(000)$, $P_2(000), \ldots, P_p(000)$ for the different point lattices. From this choice it follows that the edges of the spanning tree of the quotient graph are to be assigned the index triples 000.

(ii) Assign indices *rst* (with 000 not being excluded) and, where applicable, arrows to the remaining edges, subject to the following restrictions.

(α) $r, s, t \in \{-1, 0, +1\}$

This is an arbitrary restriction which guarantees that only a finite number of three-periodic nets can be generated from a given quotient graph. Generation is thereby restricted to those three-periodic nets which permit an embedding and a choice of a primitive unit cell for this embedding such that the origin points $P_1(000)$, $P_2(000), \ldots, P_p(000)$ all lie in the cell and are connected only to points in the same or in neighbouring cells (a neighbouring cell is a cell which has at least one point of the Euclidean space in common with the given cell). The nets which are excluded are therefore not likely to be those of real crystal structures.

(β) Choose index triples for loops which are different from 000.

This is in order to avoid loops in the three-periodic nets.

(γ) Choose index triples for multiple edges such that for each pair of edges of a multiple edge the sum of the index triples is different from 000 when the orientation of the edges is antiparallel or, when the orientation is parallel, such that the difference is unequal to 000.

This is in order to avoid multiple edges in the three-periodic nets.

(δ) Ensure that among the index triples *rst* there is at least one with $r \neq 0$, at least one different one with $s \neq 0$, and a third one with $t \neq 0$.

This is in order to avoid a lower than threefold periodicity for the nets to be generated.

(*c*) *Partitioning the set of labelled quotient graphs into equivalence classes*

Using the criteria given in § 5 the labelled quotient graphs should be tested for possible equivalences and assigned to equivalence classes. From each equivalence class one representative may then be selected. When testing for equivalence it may be found that a quotient graph which is labelled in accordance with the established rules is equivalent to one which is labelled in contradiction to them. Such an equivalence is the consequence of restricting the indices to the integers −1, 0 and +1 by using arguments based on the concept of a unit cell: Whether two adjacent points lie in the same or in neighbouring unit cells or do not may depend on the way in which the unit cell has been chosen.

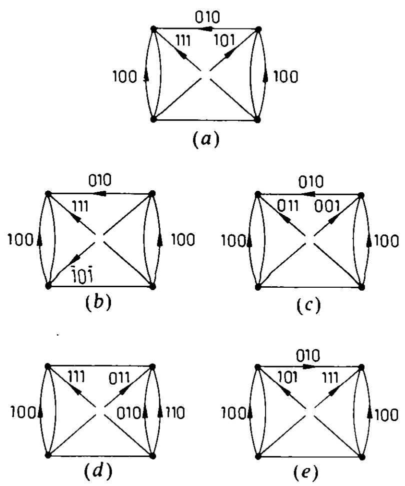

Fig. 3. Equivalent labelled quotient graphs. (*a*) Labelled quotient graph as in Fig. 2(*b*). (*b*) Reversal of a direction with re-labelling $rst \to \bar{r}\bar{s}\bar{t}$. (*c*) Change of basis vector **c** to $\mathbf{c}' = \mathbf{a} + \mathbf{c}$. (*d*) Change of origin point $P_4(000)$ to $P_4(0'0'0') = P_4(0\bar{1}0)$. (*e*) Automorphism induced by the permutation $(P_1P_4)(P_2P_3)$.

(d) Embedding the three-periodic nets

Although the three-periodic nets are already determined after execution of step (*c*) it may still be desirable to construct embeddings of the nets in three-dimensional space. After having chosen *p* origin points, one for each vertex of the labelled quotient graph, as well as three basis vectors, the *p* point lattices can be drawn. Then the straight lines are added in accordance with the labelling of the quotient graph. It may be found that with a particular choice of coordinate systems an embedding is not possible because of intersecting lines. Such a situation can always be remedied by a suitable displacement of certain points of the embedding (which may necessitate a lowering of translational symmetry).

7. Generation of three-periodic nets: examples

For purposes of illustration some three-regular three-periodic nets with quotient graphs of order six will be generated. The generation follows the pattern established in § 6.

(*a*) The first step is the calculation of all three-regular graphs with six vertices which are to serve as quotient graphs for the three-periodic nets to be generated. The resulting 17 graphs are shown in Fig. 4. A discussion of their calculation is beyond the scope of this paper.

(*b*) and (*c*) Let quotient graph no. 1 be selected for further consideration. The task is to label its edges and then to check for equivalent labellings. The choice of a spanning tree is indicated by the heavy lines in Fig. 5(*a*). Each of the four remaining edges is then to be labelled with index triples *rst*, where $r, s, t \in \{-1, 0, +1\}$. Recall that there must be at least one index triple with $r \neq 0$, a second one with $s \neq 0$, and a third one with $t \neq 0$. Consider all sets of four such

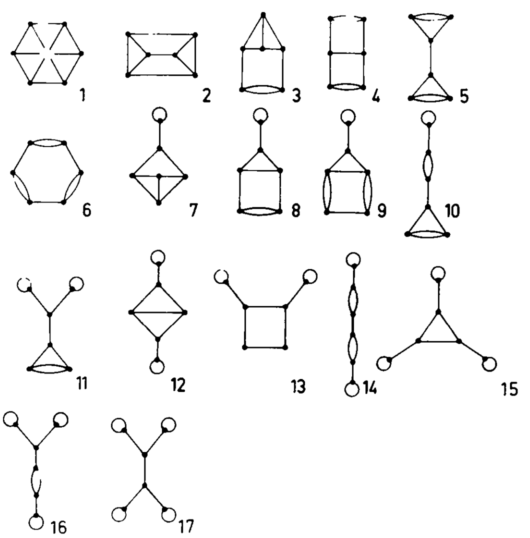

Fig. 4. The 17 three-regular graphs of order six.

Table 1. *Non-equivalent sets of four index triples to be used for labelling quotient graphs with s + 4 edges, where s is the number of edges of a spanning tree*

{100, 010, 001, 000}
{100, 010, 001, 100}
{100, 010, 001, $\bar{1}$00}
{100, 010, 001, 110}
{100, 010, 001, $\bar{1}\bar{1}$0}
{100, 010, 001, 111}
{100, 010, 001, $\bar{1}$11}
{100, 010, 001, $\bar{1}\bar{1}\bar{1}$}

triples and let two sets belong to the same class when they can be transformed into each other by a change of basis vectors. It will be found that there are eight classes. From Table 1, which lists one representative from each class, the first quadruple 100, 010, 001, 000 is arbitrarily selected. There are $4! = 24$ ways of distributing four index triples among four edges and, for each such choice, $2^3 = 8$ ways of assigning directions to the three edges not labelled 000. It will not be necessary to go through all these possibilities, as the high symmetry of the quotient graph permits a much simplified approach: Since edges (P_1, P_4) and (P_3, P_6) of the quotient graph are equivalent with respect to an automorphism which leaves the spanning tree invariant, there are only three non-equivalent ways of assigning the index triple 000 to one of the four edges in question. The remaining index triples 100, 010 and 001 can then be distributed at will, since they are all equivalent with respect to suitable basis transformations. This holds true also for the assignment of the arrows. The three labelled quotient graphs shown in Figs. 5(*b*), (*c*) and (*d*) are thus obtained. Each of these defines a different three-regular three-periodic net.

(*d*) Embeddings of the nets in space will now be drawn. To this end three basis vectors and six origin points are chosen for each of the three labelled quotient graphs in Fig. 5 in such a way that the

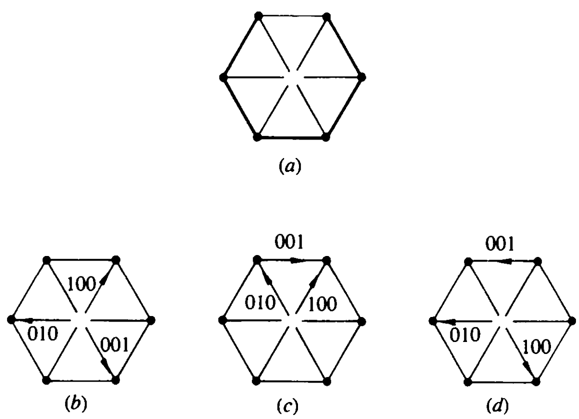

Fig. 5. Generation of three-periodic nets. (*a*) The quotient graph (with a spanning tree indicated by heavy lines). (*b*), (*c*) and (*d*) Three labellings of the quotient graph which define non-equivalent three-periodic nets.

embeddings exhibit the maximal possible symmetry. The embeddings are shown in Figs. 6(*a*), (*b*) and (*c*). The first net is Archimedean, in the nomenclature of Wells (1977), and is identical with the net 6×12^2 on p. 83 of Wells (1977). The space group of the embedding is $R\bar{3}m$. The second and third nets are neither Platonic nor Archimedean and are not listed by Wells. The space groups of the embeddings are $I\bar{4}m2$ and Cm, respectively. For both embeddings it holds that of the six points in a primitive unit cell four are of the type 4×12^2 and two of the type 12^3.

8. Generation of three-periodic nets: applications

The vector method is the only procedure known to the authors which permits a straightforward generation of three-periodic nets with quotient graphs of a given order. The restrictions which were imposed on the integers to be used for labelling the edges of the quotient graphs were arbitrary and can be modified or supplemented at will.

For quotient graphs of sufficiently low order it may happen that after the choice of the spanning tree there remain just three edges for further labelling. To these edges three independent directions must be assigned. Since all sets of three independent index triples are equivalent it follows that each such quotient graph yields only one three-periodic net. This happens, for example, in the case of the five three-regular quotient graphs of order four. There are thus five three-regular nets with quotient graphs of this order, *i.e.* five three-regular nets which permit embeddings with four points per unit cell. Note that in each case the unit cell is primitive, because the assumption of a centered unit cell with four points would imply the existence of a primitive cell with fewer points and this is not possible with three-regular three-periodic nets.

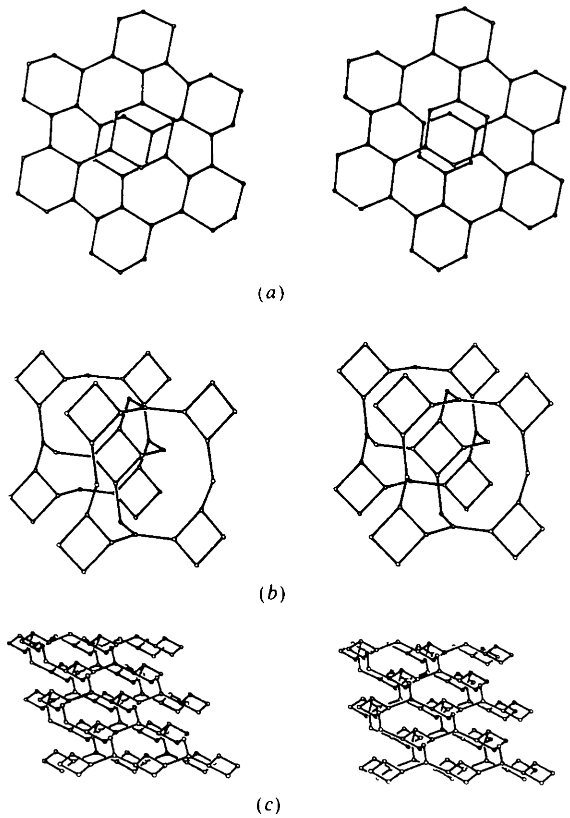

Fig. 6. Embeddings of the three-periodic nets defined by the labelled quotient graphs in Fig. 5 (stereo pairs). (*a*) Embedding of net (*b*) with symmetry $R\bar{3}m$. This is the Archimedean 6×12^2 net listed by Wells (1977, p. 83). (*b*) Embedding of net (*c*) with symmetry $\bar{I}4m2$. (*c*) Embedding of net (*d*) with symmetry Cm.

It will be found that the number of quotient graphs as well as the number of three-periodic nets to be generated from a given quotient graph increases enormously with the order of the quotient graph. For specific applications, however, only certain types of three-periodic nets may be of interest, for example those derived from vertex-transitive or edge-transitive quotient graphs, these being quotient graphs in which all vertices or all edges are equivalent with respect to an automorphism of the (unlabelled) graph. Such quotient graphs are much more limited in number. Of the 17 quotient graphs illustrated in Fig. 4 the first is both vertex and edge transitive, while nos. 2 and 6 are vertex but not edge transitive. All the others are neither vertex nor edge transitive.

The principal motive for generating three-periodic nets comes from the relationship of their embeddings with real or hypothetical crystal structures. There are classes of crystal structures for which certain bond lengths or angles are typical. Embeddings which are to be associated with such structures should display these lengths and angles. It is therefore of interest to know whether a given three-periodic net is capable of such an embedding or not. Refinement methods like the distance least-squares method of Meier & Villiger (1969) may be of help in answering this question.

9. Limitations

It may be asked why the relations between three-periodic nets and quotient graphs have been defined with the aid of embeddings of the nets and why a purely graph-theoretical method which side-steps the embeddings has not been used. The answer is that there are nets to which a quotient graph cannot be assigned in a unique way by using graph-theoretical considerations alone. These are the nets which allow two or more embeddings with non-isomorphic quotient graphs. The different cases which may occur are illustrated in Fig. 7. Recall that only embeddings with maximal translational symmetry are considered. Embeddings which yield the same partitioning of the points into point lattices may be called *equivalent*. The example in Fig. 7(*a*) is the SCCSCC net of Smith

(1977). In Fig. 7(*b*) a non-equivalent embedding is obtained from the given one by interchanging two monovalent points with a common neighbour. The case illustrated in Fig. 7(*c*), in which non-isomorphic quotient graphs are obtained from different embeddings, is supposedly rare. It does not invalidate the vector method, but calls for a certain caution: From the fact that two three-periodic nets have non-isomorphic quotient graphs (even if these are of the same order) it cannot be inferred that the nets themselves are non-isomorphic.

Note that the automorphism group of a net which permits non-equivalent embeddings cannot be isomorphic to a space group with its uniquely determined translation subgroup. It follows that for a net with an automorphism group which is isomorphic to a space group all embeddings are equivalent. These nets, which are the most important ones, have a uniquely defined quotient graph. The example in Fig. 7(*b*) shows that the above-mentioned group isomorphism, while being sufficient, is not a necessary condition for the existence of a unique quotient graph.

10. Extensions

The vector method of symbolizing and generating three-periodic nets can be easily extended to one- and two-periodic nets or indeed to nets of any periodicity greater than zero. Fig. 8 gives examples of one-, two- and four-periodic nets and their labelled quotient graphs. For simplicity of nomenclature a net with a quotient graph of order n may be called *a net of order n.* Extending the arguments given in the second paragraph of § 9 to four-dimensional space leads to the result that there are 17 three-regular four-periodic nets of order six, one for each quotient graph in Fig. 4. Likewise there are four four-regular four-periodic nets of order three, there are three five-regular four-periodic nets of order two, and there is one eight-regular four-periodic net of order one. The order of a net, as defined above, is the number of points per unit cell of an embedding of highest translational symmetry. In the examples just listed all the orders refer to primitive unit cells, because lower orders than the ones given are not compatible with the specified regularity and periodicities.

Further extensions of the vector method will be dealt with in a forthcoming publication, where it will be shown how three-periodic nets can also be mapped into one- and two-periodic graphs by identifying not all of the translationally equivalent points, but only those which are equivalent with respect to a certain subgroup of the group of all translations.

SJC and ThH are indebted to the Deutsche Forschungsgemeinschaft (DFG) for support of this work. WEK expresses his gratitude to Professor A. F. Wells (Storrs, Connecticut) for a stimulating and fruitful discussion. All authors thank Dr H Behm (Karlsruhe) for drawing the stereo figures.

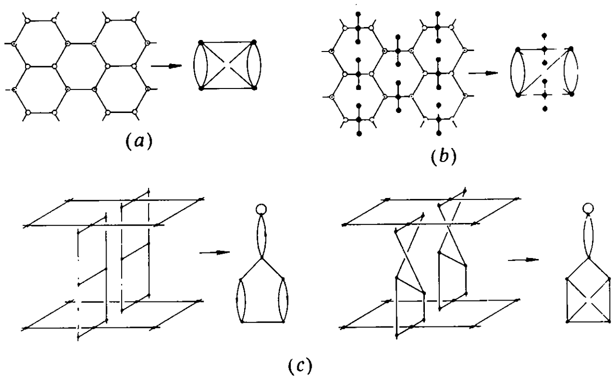

Fig. 7. Possible relations between nets, their embeddings (of highest translational symmetry) and the corresponding quotient graphs. (*a*) All embeddings of this net lead to the same partitioning of the set of points into point lattices. The quotient graph is uniquely defined. (*b*) Different embeddings of this net may lead to different partitionings of the set of points into point lattices. The quotient graph is nevertheless uniquely defined. (*c*) Two embeddings of the same net load to different partitionings of the set of points into point lattices. The quotient graphs are not isomorphic.

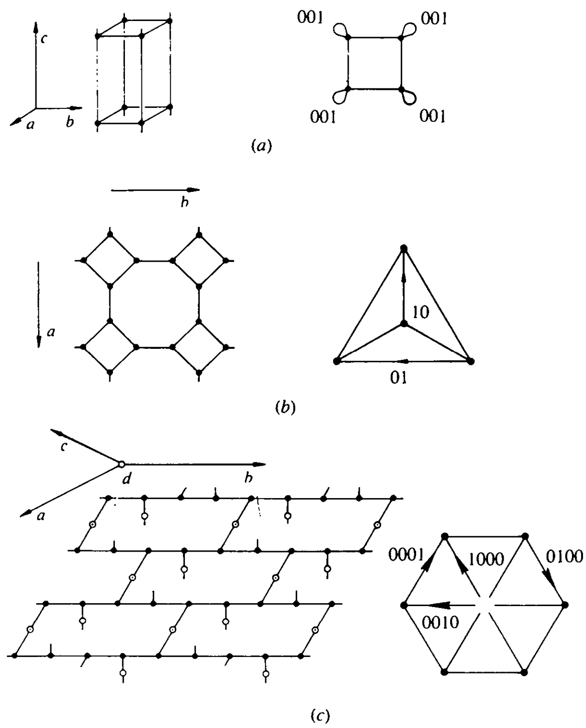

Fig. 8. Graphs of various periodicities and their labelled quotient graphs. (*a*) A one-periodic three-dimensional four-regular graph. (*b*) A two-periodic two-dimensional three-regular graph. (*c*) A four-periodic four-dimensional three-regular graph. From dotted and open circles there are lines going in the [0001] and [000$\bar{1}$] directions, respectively.

References

CHUNG, S. J. & HAHN, TH. (1975). *Acta Cryst.* **A31**, S1.
CHUNG, S. J. & HAHN, TH. (1976). *Z. Kristallogr.* **144**, 427.
CHUNG, S. J., HAHN, TH. & KLEE, W. E. (1983). *Z. Kristallogr.* **162**, 51–53.
FIGUEIREDO, M. O. (1982). *Fortschr. Mineral. Beih.* **60**, 26–27.
FISCHER, W. (1973). *Z. Kristallogr.* **138**, 129–146.
FISCHER, W. (1982). *Fortschr. Mineral. Beih.* **60**, 23–24.
HARARY, F. (1969). *Graph Theory*. Reading, MA: Addison-Wesley.
HEESCH, H. & LAVES, F. (1933). *Z. Kristallogr.* **85**, 443–453.
LIMA-DE-FARIA, J. & FIGUEIREDO, M. O. (1976). *J. Solid State Chem.* **16**, 7–20.
MEIER, W. M. & VILLIGER, H. (1969). *Z. Kristallogr.* **129**, 411–423.
SMITH, J. V. (1977). *Am. Mineral.* **62**, 703–709.
SMITH, J. V. & BENNETT, J. M. (1981). *Am. Mineral.* **66**, 777–788.
WELLS, A. F. (1977). *Three-dimensional Nets and Polyhedra*. New York: Wiley.
WELLS, A. F. (1979). *Further Studies of Three-Dimensional Nets. ACA Monogr.* No. 8. Pittsburgh: Polycrystal Book Service.

Acta Cryst. (1984). **A40**, 50–57

Crystallographic Refinement of Macromolecules having Non-crystallographic Symmetry

BY T. ALWYN JONES AND LARS LILJAS

Department of Molecular Biology, Wallenberg Laboratory, Box 562, Uppsala, Sweden

(*Received* 22 *April* 1983; *accepted* 30 *August* 1983)

Abstract

Some very large biological macromolecules, such as viruses, exhibit a high degree of non-crystallographic symmetry. A method is described to refine crystallographically such large structures using a combination of molecular averaging in real space, automatic real-space refitting and interactive refitting using computer graphics. The method has been successfully applied to a small plant virus, satellite tobacco necrosis virus, containing 11 700 amino acids in the crystallographic asymmetric unit. The starting model for the refinement was built with 3·7 Å phases. These have been refined and the resolution extended to 2·5 Å.

Abbreviations used in the text: STNV satellite tobacco necrosis virus, SBMV southern bean mosaic virus, TBSV tomato bushy stunt virus, FFT fast Fourier transform, n.c.s., non-crystallographic symmetry.

Introduction

The first macromolecules to be crystallographically refined were small proteins containing about fifty amino acids in the asymmetric unit. Rubredoxin was refined using difference-Fourier and reciprocal-space least-squares methods (Watenpaugh, Sieker, Herriot, & Jensen, 1973), and pancreatic trypsin inhibitor by cyclic application of real-space refinement (Deisenhofer & Steigemann, 1975; Diamond, 1971). Since then reciprocal-space refinement has been improved by introducing extra observations in the form of restraints to bond lengths, angles *etc.* (Konnert, 1976; Hendrickson & Konnert, 1980), by using constraints and elastic restraints (Sussman, Holbrook, Church & Kim, 1977), and by the use of FFT methods (Agarwal, 1978; Jack & Levitt, 1978). These methods are not automatic and require manual intervention at various stages. Fortunately, this aspect has been greatly simplified by the use of computer graphics systems such as *FRODO* (Jones, 1982) and *BILDER* (Diamond, 1982). It is now possible to refine successfully protein molecules containing 750–800 residues in the asymmetric unit. However, it is still very difficult and time consuming to build and refine macromolecules starting from maps that are poorly phased with data extending to 3·0–3·5 Å resolution. This requires a lot of manual intervention and many cycles of refinement [*e.g.* the immunoglobin Fc fragment refined by Deisenhofer (1981)].

Many interesting macromolecules contain multiple copies of a protein subunit. Viruses in particular contain many copies of a single polypeptide chain. Three spherical plant viruses have been extensively studied by X-ray crystallography, STNV, TBSV and SBMV (Liljas *et al.*, 1982; Harrison, Olson, Schutt, Winkler, & Bricogne, 1978; Abad-Zapatero *et al.*, 1980). All three have icosahedral symmetry. In the classification of Caspar & Klug (1962) STNV is of the simplest $T = 1$ type, possessing exact icosahedral symmetry and therefore having 60 identical subunits in its protective coat. It turns out that when STNV crystallizes the asymmetric unit is the complete virus particle. Both TBSV and SBMV are $T = 3$ particles with 180 subunits making up the particle. When they crystallize some of the icosahedral symmetry elements become space-group symmetry elements so that TBSV has 15 and SBMV 30 protein subunits in the crystallographic asymmetric unit.

0108-7673/84/010050-08$01.50