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TOPOLOGICAL ASPECTS OF CRYSTALLOGRAPHY

W. E. Klee

Institut für Kristallographie der Universität
D-7500 Karlsruhe

Summary: Topological and in particular graph-theoretical methods may be used for

1. the classification of crystal structures,
2. the derivation of the different structural types which are possible from a topological point of view,
3. the prediction of the maximum symmetry which a structure of a given type may possess,
4. the solution of special problems such as the determination of those Si/Al-distributions in silicates which are compatible with Loewenstein's Si-Al avoidance rule.

0. Introduction

We show how graph-theoretical methods can be used to describe and characterize certain topological properties of crystal structures. We mean those properties which depend on the way in which the atoms are connected to each other. We shall assume that for the crystal structure in question or for the relevant part of it we are given the information which pairs of atoms are connected by a chemical bond and which are not. With this information we can associate graphs of various types with the crystal structure and study the properties of these graphs. In constructing the graphs we shall make use of the following concepts:

i) We call a graph a simple graph if it has no loops or multiple edges.

ii) We call a graph n-periodic (n=0,1,2,...) if it can be embedded in a euclidean 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 n+1 linear independent directions. We call two vertices translationally equivalent with respect to a given embedding of the graph, if there is a translation which maps one of the vertices onto the other and brings the embedding into coincidence with itself.

iii) We call a graph n-dimensional ($n=1,2,3$) if it allows an embedding in n-dimensional, but not (n-1)-dimensional euclidean space. The graph K_1 consisting of a single vertex is the only graph which can be embedded in 0-dimensional space and is called 0-dimensional. The 0-, 1- and 2-dimensional graphs are the planar graphs.

Obviously we are only considering locally finite graphs, i. e. graphs in which all vertices are of finite degree. For graph-theoretical terms not explained in this paper see Harary (1969).

The crystalline silicates are well suited to exemplify the arguments discussed here. If we leave certain high-pressure modifications out of discussion the silicates are characterized by the presence of TO_4 tetrahedra, where T stands primarily for Si which may, however, be partly replaced by Al, B, and other elements which form sufficiently small cations. The T-atoms, the tetrahedral atoms, occupy the centres of the tetrahedra and the four O-atoms to which each T-atom is bonded are at the corners. The arrangement is generally such that two tetrahedra share at most one oxygen atom and that each oxygen atom belongs to at most two tetrahedra. We shall assume that all the silicates which are discussed here are of this type. Possible distortions of the tetrahedra from their ideal symmetry are of no consequence for our topological considerations.

With a given silicate structure we can associate several types of graphs which all give information about the mode of linking of the TO_4 tetrahedra in the structure:

Graphs of the first type, the silicate graphs S", contain two kinds of vertices, called tetrahedral vertices and oxygen vertices. The first-mentioned vertices represent the tetrahedral atoms and the last-mentioned vertices the oxygen atoms, while the edges of such a graph correspond to the chemical bonds between the atoms.

crystal structure of sanbornite, $Ba[Si_2O_5]$ (see Douglass, 1958)

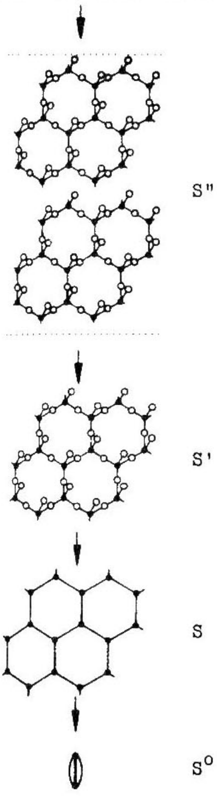


Fig. 1. Different types of graphs which can be derived from the crystal structure of sanbornite

A silicate graph S" may or may not be connected. In the latter case its components will in general be isomorphic and we select one such component for further study. Otherwise we select one component from each of the two or more isomorphism classes and consider these components separately. In any case we shall assume that from now on we are only dealing with connected graphs, and we shall call the connected graphs obtained by the method just outlined the <u>silicate graphs S'</u>.

Graphs of the third type, which are more convenient for many applications, contain only vertices representing tetrahedral atoms and are called <u>silicate graphs S</u>. We obtain such a graph S from a graph S' by deleting each monovalent oxygen vertex and by replacing each divalent oxygen vertex together with its two incident edges by a single edge. Note that we can reconstruct S' from S if we remember that each tetrahedral vertex in S' is tetravalent and that two tetrahedral vertices in S' are connected via an oxygen vertex whenever the corresponding vertices in S are adjacent.

Graphs of the fourth type are called <u>finite silicate graphs S^o</u> and can be constructed from the silicate graphs S in a unique way as follows: If a given graph S is 0-periodic and therefore (since we restrict our considerations to crystalline silicates) finite, we put $S^o = S$. If S is 1-, 2- or 3-periodic, then we partition the set of vertices of S into classes V, W, ... of translationally equivalent vertices and identify these classes with the vertices v^o, w^o, ... of S^o. We connect two vertices v^o and w^o in S^o by as many edges as a vertex in class V has neighbours among the vertices in class W. The special case V = W causes one or more loops to be incident with

$v^o = w^o$. Note that the graph S^o may be looked upon as a kind of homomorphic image of S.

The graphs S", S', S and S^o which can be derived from the crystal structure of the barium silicate sanbornite are shown in Fig. 1.

1. Classification of the silicate structures

A classification of the silicate structures can be based on the periodicity and the dimension of the silicate graphs S and also on the number of classes of translationally equivalent vertices in these graphs, i. e. on the order of the finite graphs S^o. A still finer classification may be obtained by placing two silicate structures in the same class if and only if their finite silicate graphs S^o are isomorphic. In the finest classification according to graph-theoretical properties two structures will be placed in the same class if and only if their silicate graphs S are isomorphic. Let us consider a few examples: Quarz and tridymite, two of the numerous modifications of SiO_2, have finite silicate graphs of different order, the graphs being  and , resp. $K[AlSiO_4]$, kalsilite, and $Rb[AlSiO_4]$ synth. (Klaska and Jarchow, 1975) have finite graphs of the same order, but these graphs,  for $K[AlSiO_4]$ and  for $Rb[AlSiO_4]$, are non-isomorphic. $Rb[AlSiO_4]$ and mono-$Ca[Al_2Si_2O_8]$ (Takéuchi et al., 1973) have finite silicate graphs S^o which are both isomorphic to , but their silicate graphs S are non-isomorphic. Kalsilite and tridymite, finally, have not only isomorphic finite graphs S^o, but also isomorphic graphs S.

A classification scheme, together with a few examples, is shown in Table 1.

The system of classification illustrated here is rigorous in the sense that its categories are mutually exclusive and it is exhaustive in the sense that all silicates of the type discussed here find their place in it, including any that may be discovered in the future. It may not be equally useful in all areas of silicate science, but it does provide a most convenient basis from which all possible silicate graphs may be generated in a systematic way as explained in the next section.

Table 1. A classification scheme for the crystalline silicates as based on the properties of the silicate graphs S. The number n is the order of S (if S is 0-periodic) or the number of classes of translationally equivalent vertices in S (if S is 1-, 2- or 3-periodic)

Structures with		Examples of such structures	S.R.[⊕]
0-periodic acyclic graphs	with n=1,2,...	phenacite, $Be_2[SiO_4]$, n=1	37A,342
0-periodic cyclic graphs	with n=3,4	benitoite, $BaTi[Si_3O_9]$, n=3	34A,380
1-periodic 1-dimensional graphs	with n=1	jadeite, $NaAl[Si_2O_6]$, n=1	31A,228
1-periodic 2-dimensional graphs	with n=2,3,...	vlasovite, $Na_4Zr_2[Si_8O_{22}]$, n=4	40A,289
1-periodic 3-dimensional graphs	with n=3,4,...	litidionite, $Cu_2Na_2K_2[Si_8O_{20}]$, n=8	41A,386
2-periodic 2-dimensional graphs	with n=1,2,...	sanbornite, $Ba[Si_2O_5]$, n=2	22, 490
2-periodic 3-dimensional graphs	with n=4,5,...	cymrite, $Ba[Si_2Al_2O_8]\cdot H_2O$, n=4	41A,381
3-periodic 3-dimensional graphs	with n=2,3,...	cristobalite, SiO_2, n=2	39A,338
several non-isomorphic graphs		zoisite, $Ca_2Al_3[SiO_4 \mid Si_2O_7 \mid OH \mid O]$, n=1,2	33A,475

[⊕] In this column the volume and page numbers of STRUCTURE REPORTS are given, where more information about the structures and where the references to the original literature can be found.

2. Generation of the silicate graphs

As is not untypical in graph theory the following constructions are easy to carry out only as long as the number of vertices involved, which here means the order of the finite silicate graphs S^o, remains small. The derivation of the silicate graphs S may be effected in two steps, the first step being the generation of all finite graphs S^o of a given order, and the second step being the generation of all graphs S which belong to a particular S^o. The techniques which are employed depend on the periodicity of the graphs to be constructed.

o) 0-periodic silicate graphs S:

In the first step we require all connected simple graphs S^o of a given order, subject to the condition that the degree of any vertex does not exceed 4. The number of such graphs of a given order is, of course, finite. At least up to order 6 they can be obtained by direct inspection of graph diagrams such as the ones given by Harary (1969).

The second step is trivial, since for the 0-periodic graphs $S = S^o$.

i) 1-periodic silicate graphs S:

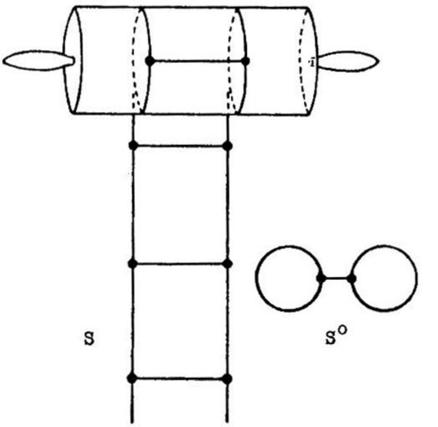


Fig. 2. A 1-periodic 2-dimensional graph S which is obtained from an embedding of the finite graph S^o in the surface of a cylinder

The first step involves the derivation of all connected but not necessarily simple graphs S^o, again subject to the condition that the degree of any vertex does not exceed 4. The number of such graphs of a given order is, of course, finite.

The 1-periodic 1- and 2-dimensional silicate graphs S correspond, in a unique way, to certain embeddings of the graphs S^o in the surface of a cylinder, as is illustrated in Fig. 2. The embeddings have to be such that the resulting graphs S are connected and have no loops or multiple edges.

The 1-periodic and 3-dimensional silicate graphs S can be constructed from 1- and 2-dimensional subgraphs by methods which are not difficult to employ in practice but which have not yet been put on a systematic basis.

ii) 2-periodic silicate graphs S:

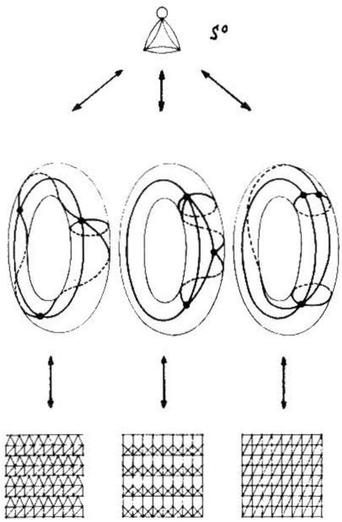


Fig. 3. Three 2-periodic 2-dimensional graphs which result from different embeddings of the finite graph S^0 in the surface of a cylinder (taken from Guigas and Klee, 1976)

The first step requires the generation of the finite graphs S^0 as in ii).

With regard to the second step it should be noted that the 2-periodic and 2-dimensional silicate graphs S correspond to certain embeddings of the finite silicate graphs S^0 in the surface of a torus, as illustrated in Fig. 3. For details of the procedure see Guigas and Klee (1976). Of particular interest are those graphs S which allow a convex-polygonal embedding in the plane, i. e. an embedding in which every face is a convex polygon. The property of permitting such an embedding is connected with a purely graph-theoretical property through the following

<u>Theorem</u> (Mani-Levitska, Guigas and Klee, 1979): A 2-periodic and 2-dimensional simple graph allows a convex-polygonal embedding in the plane if and only if it is 3-connected.

The 2-periodic and 3-dimensional silicate graphs S can be constructed from 1- and 2-dimensional subgraphs by methods which are not difficult to employ in practice but which have not yet been put on a systematic basis.

iii) 3-periodic silicate graphs:

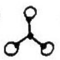
The derivation of the 3-periodic and 3-dimensional graphs is not quite analogous to that of the 2-periodic and 2-dimensional ones. The last-mentioned graphs, when embedded in the plane, partition the plane into points, lines and faces. The first-mentioned graphs, however, when embedded in 3-dimensional space, do not necessarily partition the space into points, lines, faces and volume elements in a unique way. The derivation of these graphs can therefore not be based on methods which aim at such partitions of 3-dimensional space. Three possible approaches to the problem will be discussed.

α) It is always possible to embed a 3-periodic and 3-dimensional graph in 3-dimensional space in such a way that its vertices are arranged in parallel layers and it is usually possible to do it in such a way that the vertices and edges in any particular layer form a connected subgraph. 3-periodic and 3-dimensional graphs may therefore be obtained by interconnecting 2-periodic and 2-dimensional graphs in various ways. This method has been applied successfully by Wells (see Wells, 1977) for constructing graphs of silicates and other structures, and more recently by Smith (1977, 1978, 1979) for constructing graphs especially of the tectosilicates. Many of the graphs thus generated correspond to frameworks which have actually been found in nature. It is, however, difficult to see which general principles underly the distinction between those graphs which have been generated by the authors mentioned and those which have not.

β) Whether a meaningful connection can be established between the 3-periodic and 3-dimensional silicate graphs S and certain embeddings of the finite silicate graphs S^o in the pretzel (double torus) surface or in orientable closed surfaces of higher genus remains to be investigated.

γ) A combinatorial method which is certainly capable of further development has been employed by Chung and Hahn (1976). The approach is essentially as follows: In a given finite silicate graph S^o a connected spanning subgraph is chosen. Those edges of S^o which belong to the subgraph are considered to represent connection (via oxygen atoms) between tetrahedral atoms within a primitive unit cell of the silicate, whereas the remaining edges of S^o are considered to represent connections (via oxygen atoms) to tetrahedral atoms in certain of those 26 neighbouring cells which have a face, an edge, or a corner in common with the given unit cell. The desired silicate graphs are obtained by choosing different connected spanning subgraphs in S^o and, for a given choice of subgraph, assigning to each edge of S^o which does not belong to the subgraph one of 26 colours, where each colour stands for a different neighbouring cell. Actually the edges are given a direction and so the number of colours which are required is reduced to 13. The procedure can be modified in such a way as to make the results independent of the choice of the primitive unit cell.

We add a few general remarks which apply to 1-, 2- and 3-periodic silicate graphs.

It may happen that to a given finite graph S^o there does not belong even a single graph S of prescribed periodicity and dimension. From S^o =  , for example, no 1-periodic and 2-dimensional silicate graphs S can be obtained, because S^o cannot be embedded in the surface of a cylinder in such a way that the construction leads to a simple and connected graph S.

It may also happen that to a given finite graph S^o there exist infinitely many graphs S. Two of the infinitely many 3-periodic and 3-dimensional graphs S which can be constructed from S^o =  are illustrated in Fig. 4. Of such a set of infinitely many silicate graphs which belong to a particular finite graph at most a few can be expected to be graphs of actual silicate structures. It is therefore wise to restrict the number of allowed graphs S in an arbitrary but meaningful way. This may be done as follows.

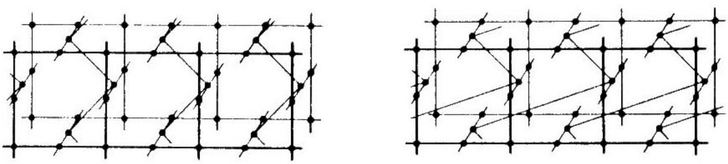


Fig. 4. Two of the infinitely many 3-periodic 3-dimensional graphs S which can be generated from the finite graph S^o (see text)

Let a finite graph S^o with vertices v^o, w^o, ... be given. As we know, these vertices represent classes V, W, ... of translationally equivalent vertices in the graphs S which are to be constructed from S^o. Suppose that we want to construct graphs of periodicity n, where $n \in \{1,2,3\}$. Then we label each vertex in V by an n-tuple of whole numbers (negative, zero, or positive) such that the vertices and the n-tuples are in a one-to-one correspondence, and do likewise for each vertex in W. Now, we agree to consider only those graphs S for which the following condition holds: If a pair of vertices v and v' in class V is adjacent to the same vertex w in class W ($V \neq W$), or if a pair of vertices v and v' in class V is mutually adjacent, then $v_i - v_i' \in \{-1,0,+1\}$ for $i=1,\ldots,n$, where $(v_1,\ldots,v_n)$ are the indices of v and $(v_1',\ldots,v_n')$ the indices of v'. This reflects the fact that in real structures there is no bonding between distant atoms.

3. Symmetry of the silicate graphs

When discussing the symmetry properties of the graphs which are associated with the silicate structures it is more realistic to consider not the graphs S which contain only the tetrahedral vertices, but the graphs S' which contain also the oxygen vertices, since the symmetry of the latter type of graphs is more closely related to the actual isometric symmetry of the structures.

By the symmetry group of a graph we mean its automorphism group. The determination of the automorphism group of a given graph is a problem which we shall not discuss here. We only recall that important results for trees have been obtained by Pólya (1937).

Besides the automorphism group $\Gamma(S')$ of a given graph S' we shall also consider the isometric symmetry group of certain embeddings of S' in euclidean spaces of suitable dimension. The isometric symmetry group of such an embedding is, of course, isomorphic to a subgroup of $\Gamma(S')$, but there are more detailed relations which are of interest:

i. Can S' be embedded in a euclidean space of finite dimension in such a way that the isometric symmetry group of the embedding is isomorphic to the automorphism group $\Gamma(S')$ of S' and, if so, what is the space of lowest dimension having this property?

ii. What are the embeddings of highest symmetry of a graph S' in 2- or 3-dimensional space?

iii. What special properties must a graph S' possess in order that an embedding in 2- or 3-dimensional space can be found with an isometric symmetry group which is isomorphic to the automorphism group $\Gamma(S')$?

ad i: It is well known that any finite simple graph of order n can always be embedded in (n-1)-dimensional euclidean space such that the isometric symmetry group of the embedding and the automorphism group of the graph are isomorphic. For finite graphs S' of order n we thus have n-1 as an upper limit for the dimension of the euclidean space asked for. In the case of 1-, 2- and 3-periodic graphs S' a general answer does not seem possible unless additional properties of the graphs are taken into consideration.

ad ii: An answer to this question is of relevance for determining the highest isometric symmetry which a silicate structure with a given graph S' can possess. No systematic methods of finding highest-symmetrical embeddings of graphs are known to the author.

ad iii: Here we have the

<u>Hypothesis</u>: Each 2-periodic 2-dimensional and 3-connected simple graph can be embedded in the plane in such a way that the isometric symmetry group of the embedding and the automorphism group of the graph are isomorphic. In other words: The automorphism group of such a graph is isomorphic to a 2-dimensional space group.

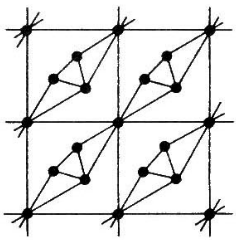


Fig. 5. A 2-periodic 2-dimensional graph whose automorphism group is isomorphic to a 2-dimensional space group cm

The converse of the hypothesis is not true, i. e. there are 2-periodic 2-dimensional simple graphs such as the one in Fig. 5 which are not 3-connected and yet have an automorphism group which is isomorphic to a 2-dimensional space group.

in $\Gamma(S)$. The next step is the partitioning of the set of vertices of S into classes V, W, ... of vertices which are translationally equivalent with respect to a translation in $Y(S)$.

The graphs in $\mathbf{F}$ are finite graphs in which the vertices v^o, w^o, ... stand for the classes V, W, ... of S defined above. Two not necessarily different vertices v^o and w^o are connected by as many edges as a vertex in V has neighbours among the vertices in W. For $Y(S) = T(S)$ the graph S^o is obtained. Note that each absolutely maximal internally stable set in a graph of $\mathbf{F}$ defines an internally stable set in S which is invariant under a translation in $Y(S)$.

The graphs in $\mathbf{H}$ are finite simple graphs in which the vertices v, w, ... are representatives from the classes V, W, ... defined above and in which two vertices v and w are adjacent whenever they are adjacent as vertices in S. In other words, the graphs in $\mathbf{H}$ are induced subgraphs of S which contain exactly one vertex from each class of vertices which are equivalent under a translation in $Y(S)$.

The values of $\alpha(F_i)$ give the highest aluminum concentrations which are compatible with a given periodicity of the aluminum and silicon atoms. The values of $\alpha(H_j)$, on the other hand, give the highest aluminum concentrations which are possible on a local scale, with no guarantee that such a concentration can be realized throughout the structure.

We illustrate the method for the 2-periodic 2-dimensional graph S shown in Fig. 8a. The group $T(S)$ of all translations can be generated by two translations with translation vectors $\underset{\sim}{a}$ and $\underset{\sim}{b}$. Let $Y(S)$ be the subgroup of $T(S)$ which is generated by translations with translation vectors $\underset{\sim}{a}$ and $2\underset{\sim}{b}$. The finite graph $F_k \in \mathbf{F}$ determined by $Y(S)$ is shown in Fig. 8b. The elements of an absolutely maximal internally stable set are marked with circles. Note that $\alpha(F_k) = 3/8$. A finite graph $H_l \in \mathbf{H}$ determined by $Y(S)$ is shown in Fig. 8c. Again the elements of an absolutely maximal internally stable set are marked with circles. Note that $\alpha(H_l) = 3/8$. We therefore have $\alpha(S) = 3/8$. The absolutely maximal internally stable set of S which is uniquely determined by the corresponding set of F_k in Fig. 8b is shown in Fig. 8d.

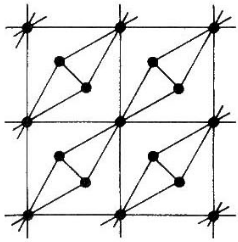


Fig. 6. A 2-periodic 2-dimensional graph whose automorphism group is not isomorphic to a 2-dimensional space group

The hypothesis is not trivial, i. e. there are 2-periodic 2-dimensional simple graphs such as the one in Fig. 6 which are not 3-connected and do have an automorphism group which is not isomorphic to a 2-dimensional space group.

One of the possible extensions of the hypothesis to 3-periodic graphs leads to the (false) conjecture: Each 3-periodic 3-dimensional and 4-connected simple graph has an automorphism group which is isomorphic to a 3-dimensional space group. To this conjecture the 4-regular graph in Fig. 7 provides a counter-example.

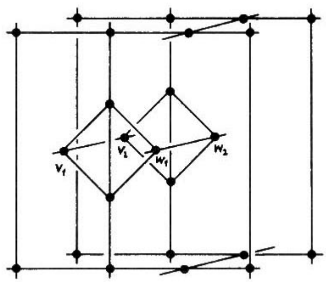


Fig. 7. A 3-periodic 3-dimensional and 4-connected graph whose automorphism group is not isomorphic to a 3-dimensional space group: The permutation ...$(v_1w_1)(v_2w_2)$... is an automorphism of the graph, but cannot be an element of the space group of any embedding of the graph in 3-dimensional space

4. Si/Al-distributions in silicates

There is a rule which is associated with the name of Loewenstein (1954) and also with the names of Goldsmith and Laves (1955). It is based on Pauling's electrostatic valence rule (see Pauling, 1960) and states that in silicate structures two neighbouring TO_4 tetrahedra cannot both be occupied by aluminum atoms. We recall that neighbouring tetrahedra are those with a common vertex. This rule suggests the following question: What is the highest concentration of tetrahedral aluminum atoms that can be realized in a given silicate structure without violation of Loewenstein's rule and what are the corresponding Si/Al-distributions?

Translated into graph-theoretical language Loewenstein's rule states that in a given silicate graph S those tetrahedral vertices which represent the aluminum atoms form an internally stable set (see Hammer and Rudeanu, 1968). The above-mentioned question then leads to the following problem: To find, in the given silicate graph S, all absolutely maximal internally stable sets and to determine what fraction $\alpha(S)$ of the vertices belong to such a set. If $\alpha(S)$ is the only information required, then it is obviously sufficient to construct just one of these sets.

Methods for solving this problem, in the case of finite graphs, can be found in Hammer and Rudeanu (1968). In the case of the 1-, 2- and 3-periodic silicate graphs we may proceed as follows (for details see Klee, 1973): To a given silicate graph S we construct two sets $\mathbb{F} = \{F_1, F_2, \ldots\}$ and $\mathbb{H} = \{H_1, H_2, \ldots\}$ of finite graphs F_i and H_j with the property that $\alpha(F_i) \leqslant \alpha(S) \leqslant \alpha(H_j)$ for all $F_i \in \mathbb{F}$ and $H_j \in \mathbb{H}$, where $\alpha(F_i)$ is the fraction of the vertices in F_i which belong to an absolutely maximal internally stable set and where $\alpha(H_j)$ is defined in an analogous way. A pair $F_k \in \mathbb{F}$ and $H_l \in \mathbb{H}$ can then in general be found such that $\alpha(F_k) = \alpha(S) = \alpha(H_l)$. The graphs in both sets $\mathbb{F}$ and $\mathbb{H}$ depend on the choice of subgroups $Y(S)$ of the group $T(S)$ of all translations in $\Gamma(S)$ and, in addition, the graphs in $\mathbb{H}$ depend on the way in which representatives are chosen from sets of vertices equivalent under translations in $Y(S)$.

The first step in the construction of the graphs in $\mathbb{F}$ and $\mathbb{H}$ is the choice of such a subgroup $Y(S)$ of the group $T(S)$ of all translations

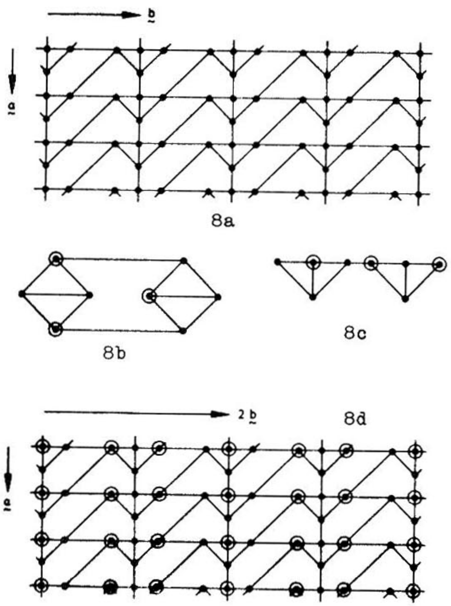


Fig. 8. Construction of an absolutely maximal internally stable set in a 2-periodic 2-dimensional graph. For further explanations see text

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