bration for each atom is approximately perpendicular to the *bc* plane, which is nearly the plane of the entire molecule. The smallest vibration is for the atom C(7) which is covalently bonded to three heavy atoms. The atom O(9), which is involved only in one hydrogen bond, has larger vibrations than O(8), which is bonded by two hydrogen bonds.

Perdeuteroglycylglycine

Freeman, Paul & Sabine (1967) have just completed a neutron diffraction study of fully deuterated glycylglycine, in its α form. They started their least-squares refinement with our preliminary least-squares parameters. The deuteration has caused an increase in the length of *a* of approximately 0·12 Å. Despite this change the intramolecular bond lengths and angles found for the heavy atoms of the molecule confirm those reported here to within about the sums of the standard deviations. They also find the peptide group to be nonplanar. Their hydrogen (deuterium) bonds are substantially the same as ours with the exception of N(1)···O(8), across layers, which is approximately parallel to **a**. This length has increased from 2·712 to 2·758 Å. There are two of these bonds 'in tandem' in the *a* repeat and the total increase, $2 \times (2{\cdot}758 - 2{\cdot}712) = 0{\cdot}092$ Å, seems to be associated with the 0·12 Å increase in *a*. We leave the interpretation of these interesting deuteration effects to the authors who discovered them. We are grateful to Dr Freeman for a pre-publication report on their results.

One of us (BDS) would like to express gratitude to Professor Robert B. Corey, and all of us to Professor L. Pauling, for their continuing interest and encouragement. Further, we are grateful to Dr Richard E. Marsh for his helpful suggestions and for making available to us his program for the Burroughs 220 digital computer for all the later refinement calculations. This final refinement was carried out in part under a research grant H-2143 from the National Heart Institute, National Institutes of Health, United States Public Health Service. JNW and ABB held Fellowships supported respectively by Shell Development Co. and the Government of India.

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The Geometrical Basis of Crystal Chemistry. IX. Some Properties of Plane Nets

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The solutions of the equations $\Sigma\, n\varphi_n = 6, 4, 3\frac{1}{3}$, and 3 for 3-, 4-, 5-, and 6-connected plane nets respectively represent the permissible proportions of polygons of various kinds. They give no information about the arrangement of the polygons relative one to another. An examination is made of the possible configurations of the 3-connected 5:7, 4:8, 3:9 and 4:7 nets, a family of 4-connected nets, and nets with alternate *p*- and *q*-connected points.

The general aim of these studies (Wells, 1954*a*, *b*, *c*, *d*, 1955, 1956, 1965) is to further our understanding of the reasons for the adoption of a particular crystal structure by a given element or compound. The amount of effort that is being devoted to building up the basic geometrical background to crystal chemistry is surprisingly small compared with that devoted to the actual determination of crystal structures. Consider, for example, the structures of the three polymorphs of phosphorus pentoxide. They present three problems: (1) All are formed from PO_4 groups each sharing 3 corners with other similar groups. The formation of 4 tetrahedral bonds to oxygen is a problem of *chemical bonding*. Granted that the immediate bonding requirements of P and O are satisfied in this way we now have (2) a purely *topological* problem, the investigation of the 3-connected systems, finite and infinite, from which the structures of $(P_2O_5)_n$ must be selected. [For an introduction to 3-connected nets and the derivation of some 3-D nets the reader is referred to part I (Wells, 1954*a*)]. We find that this oxide adopts for one polymorph the simplest possible polyhedral configuration (tetrahedron), for another the simplest 3-connected plane net ($\varphi_6=1$), and for the third a 3-dimensional net. (3) The 3-D net chosen is one of the two simplest ($Z=4$) but it is not the more symmetrical one. It is necessary to distinguish between ordinary (crystallographic) symmetry and topological symmetry. The former is a matter of equality of lengths and angles, *i.e.* it is a metrical property. Topological symmetry is concerned with connectedness and the environment of points and polygons without reference to the actual numerical values of lengths and angles. The two simplest 3-D 3-connected nets (Nets 1 and 2) do in fact have different crystallographic symmetries in their most symmetrical configurations (respectively cubic and tetragonal, $Z=8$), but the basic topological repeat unit in each consists of 4 points, and both nets can be referred to a triclinic cell ($Z=4$). However, regardless of the symmetries of particular configurations of the nets they differ in a more fundamental way. In Net 1 every point is common to 15 10-gons and every link to 10 10-gons ($x=15, y=10$) whereas for Net 2, $x=10$ and $y_{\text{mean}}=6\frac{2}{3}$ (Wells & Sharpe, 1963). Net 1 clearly has higher topological symmetry than Net 2. The reason for the choice of Net 2 rather than Net 1 by the third polymorph of P_2O_5 is presumably a *geometrical* one, that is, a matter of packing and interbond angles; it could equally well be described as a problem in energetics.

We have chosen this simple example because it illustrates how the problem of accounting for the structures of three polymorphs can be initially broken down into three parts. It would seem that far too little attention is paid to the topological and geometrical aspects [(2) and (3)] of structures as compared with the 'electronic' aspect (1), and that they have much more relevance to crystal chemical discussions than is generally realized. Two general points may be illustrated by simple examples. First, aspects of a structural problem are more easily seen if an analysis of the kind indicated is made. A crystal-field treatment of the $CuCl_4^{2-}$ ion starting from a regular tetrahedral model accounts for the observed interbond angles. There are, however, possible structures for the $CuCl_4^{2-}$ ion other than the finite group, for example, infinite linear or two-dimensional arrangements of octahedral $CuCl_6$ groups sharing edges or corners. Second, failure to classify a problem into the correct category (1), (2), or (3) could lead to discussions of bonding which would be completely irrelevant because of topological or geometrical restrictions. A simple example is provided by the O or S bond angles in CuO or PtS, with a structure in which these angles are necessarily intermediate between 90° and $109\frac{1}{2}$°. [In this connexion it would be useful to know more about the dividing line between the topology and the geometry of connected networks. For example, the diamond net is essentially 'tetrahedral' in that it cannot be constructed with coplanar bonds and conversely the net Fig. 1(*d*) of part VII (Wells & Sharpe, 1963) cannot be made with tetrahedral bonds].

Our main concern in these studies has been with the topological aspect (2) or perhaps, in view of the last remark, we should say with topological and geometrical aspects, (2) and (3). The results of such studies are twofold. First, they aim at deriving, within some specified limits, the structures that can be built from a unit of a particular kind, *e. g.* 3- or 4-connected. It would seem highly desirable to know more about the structures that are geometrically possible, for the conventional crystal chemical treatments tend to discuss structures only in terms of other *known* structures. It is surely relevant to a discussion of the structures of dihalides to know that there is another AX_2 structure in which A and X have the same immediate environments as in the $CdCl_2$ (*C*19) structure and yet there is no dihalide with this structure. Second, it is also important to know which structures are not possible for purely topological or geometrical reasons. An example of a topologically impossible structure was noted in part VI (Wells, 1956), namely, a simple layer structure for a compound A_2X_3 having 6-coordination of A and 4-coordination of X. (Reference is made to this structure later.) The relevance to crystal chemistry of purely geometrical studies such as that of Andreini on space-filling arrangements of polyhedra or the recent work on linear systems of antiprisms (Aurivillius & Lundgren, 1965) is obvious, but it is perhaps less obvious that this subject has a direct bearing on the discussion of radius ratios in simple ionic crystals.

It is preferable to consider the domains of the ions in a crystal A_mX_n rather than the coordination polyhedra, since the problem is then reduced to one of space filling by two (or more) kinds of polyhedron. The number of space-filling arrangements of polyhedra of high symmetry is strictly limited, and therefore the number of simple A_mX_n structures with highly symmetrical domains is also limited for this purely geometrical reason. There is accordingly no reason to expect that the preferred coordination groups will be exhibited by ions in the *simplest* ionic structures, which are subject to the severest geometrical restrictions, but rather that the greater freedom in the mode of packing in a complex structure is more likely to provide the most suitable environments for the ions. The conventional treatment of the structures of the alkali halides does not suggest any simple connexion between radius ratio and structure type, and the cubic coordination of cations in the CsCl and CaF_2 structures should on this view not be regarded as the typical or preferred coordination group but as arising from the geometrical restrictions noted above. (Compare, for example, the coordination of Zr^{4+} in the forms of ZrO_2 with that in complex oxy compounds or that of alkali metal ions in simple and complex halides.)

It would seem that geometrical and topological studies have much to contribute to our understanding of structures. In this paper we examine some properties of plane nets, which have only been considered incidentally in these papers in connexion with the derivation of 3-D nets. Their importance in layer structures needs no emphasis. Numerous structures are based on the simplest 3- and 4-connected plane nets ($p_6=1, p_4=1$ respectively), and a few layers based on more complex nets are known. They include the 3-connected nets (4:8), (4:6:12), and (5:7).

Permitted combinations of polygons in plane nets

If φ_n is the fraction of the total number of polygons which are n-gons then $\Sigma\, n\varphi_n=6$, 4, $3\frac{1}{3}$, and 3 respectively for 3-, 4-, 5-, and 6-connected plane nets. There are the following special solutions corresponding to p-connected nets consisting of polygons of one kind only:

p	n-gons
3	6
4	4
6	3

The missing member of this family, the net consisting of 5-gons, is a net with both 3- and 4-connected points. For such a net having a ratio q of 3- to 4-connected points, $\Sigma\, n\varphi_n=2(3q+4)/(q+2)$, which has the special solution $\varphi_5=1$ for $q=2$.

There is clearly only one 6-connected plane net, and since we shall be concerned chiefly with 3- and 4-connected nets it is convenient to have their equations in expanded form:

$$p=3: 3\varphi_3+4\varphi_4+5\varphi_5+6\varphi_6+7\varphi_7+8\varphi_8+9\varphi_9+\ldots=6 \quad (1)$$

$$p=4: 3\varphi_3+4\varphi_4+5\varphi_5+6\varphi_6+7\varphi_7+8\varphi_8+9\varphi_9+\ldots=4 \quad (2)$$

Solutions of equation (1), other than $\varphi_6=1$, are possible only if some polygons have fewer and others more than 6 sides. For *two* kinds of polygon (satisfying this condition) there is *one* solution for each combination of n_1 and n_2, the simplest being:

$$\varphi_5=\varphi_7=\tfrac{1}{2};\ \varphi_4=\varphi_8=\tfrac{1}{2};\ \text{and}\ \varphi_3=\varphi_9=\tfrac{1}{2}\,.$$

These φ values do not completely define the net, for as we shall see there is an infinite number of ways of arranging the polygons, though the number of arrangements with topologically equivalent polygons of each kind would appear to be strictly limited, a point discussed in relation to the 4:8 net.

For *three* (or more) values of n there is an infinite number of solutions having different values of φ_{n1}, φ_{n2}, and φ_{n3}. Similar considerations apply to 4-connected nets. Summarizing:

2 kinds of polygon: one solution for each pair of values of n_1 and n_2 and for each solution an infinite number of relative arrangements of n_1- and n_2-gons.

3 or more kinds of polygon: an infinite number of solutions (different values of φ_{n1}, φ_{n2}, and φ_{n3}) each solution corresponding to an infinite number of arrangements of the polygons.

These arrangements have values of Z (the number of points in the repeat unit) ranging from the smallest permissible value up to infinity. They represent a transition from a conventional crystalline material with small repeat distances to the limiting case where the unit cell includes the whole infinite plane net, and provide one way of looking at the change from crystalline to 'amorphous' solids and glasses.

We examine first the 3-connected nets $\varphi_5=\varphi_7=\frac{1}{2}$, $\varphi_4=\varphi_8=\frac{1}{2}$, and $\varphi_3=\varphi_9=\frac{1}{2}$, then two selected families of 4-connected nets, and finally amplify a point mentioned in part VI (Wells, 1956) concerning nets with two types of point, p- and q-connected.

Configurations of 3-connected plane nets

The net $\varphi_5=\varphi_7=\frac{1}{2}$

Assuming that all the polygons of each kind have the same kinds and arrangements of nearest neighbours, let each 5-gon be surrounded by h 5-gons. Since there are equal numbers of 5-gons and 7-gons their neighbours must be:

$$\text{5-gon}\begin{cases} h\ \text{5-gons} \\ (5-h)\ \text{7-gons}\end{cases};\quad \text{7-gon}\begin{cases}(5-h)\ \text{5-gons} \\ (h+2)\ \text{7-gons}\,.\end{cases}$$

Evidently not all values of h are possible. The case $h=0$ would correspond to a 5:7 net in which each 5-gon is entirely surrounded by 7-gons. This would require that every 7-gon shares edges with 5 5-gons, implying adjacent 5-gons, which is not consistent with $h=0$. The value $h=5$ would correspond to a net composed entirely of 5-gons and may also be eliminated. The values 4 and 3 for h may be eliminated in the following ways:

$h=4$: Let the 5-gon 5a in Fig. 1(a) be surrounded by four 5-gons (and one 7-gon). Since 5b already has one 7-gon neighbour its other neighbours must be 5-gons. Similarly for 5c, when the 7-gon has now two 5-gons neighbours, which is not compatible with $h=4$.

$h=3$: There are two arrangements of three 5-gons around a 5-gon to be considered [Fig. 1(b) and (c)]. If three 5-gons share edges with 5d then the same arrangement of polygons around 5e implies that each 7-gon already has four 5-gon neighbours instead of $5-h=2$ as required. In the alternative arrangement [Fig. 1(c)] let 5f share three adjacent edges with 5g, 5h, and 5j. The sharing of three adjacent edges with 5-gons implies the 5-gon 5k which in turn leads to 5h sharing four edges with 5-gons, which is not permitted.

We conclude that for the 5:7 net the only permissible values of h are 1 and 2. In any net consisting of equal numbers of 5- and 7-gons (or 4- and 8-gons, or 3- and 9-gons), N of each, the total number of edges is $6N$ and the number of points $4N$, so that for an integral number of 5-(or 7-)gons in the unit cell Z is a multiple of 4. For $h=1$ the 5-gons are arranged in pairs with a common edge, and Z is therefore 8 or a multiple of 8. For $h=2$ the 5-gons may be arranged in infinite strings ($Z=8m$) or in groups of three ($Z=12m$) (Fig. 2).

An interesting feature of the net of Fig. 2(a) is that it can be dissected into strips A which are related to one another by a simple translation. If adjacent strips are related by a glide-reflexion line the net (d) is

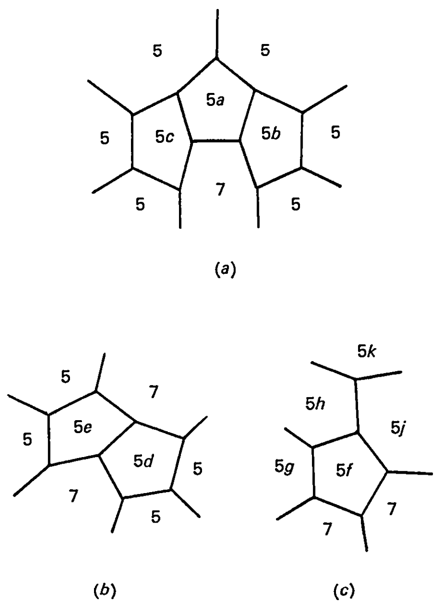


Fig. 1. Derivation of (5:7) nets (see text).

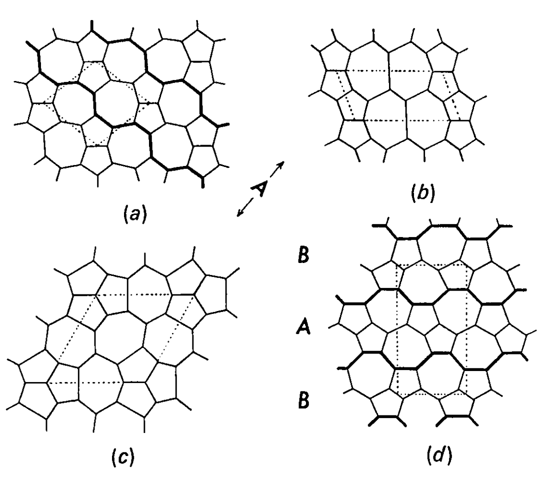


Fig. 2. Configurations of the 3-connected (5:7) net.

formed, and there is obviously an indefinite number of sequences of the two kinds of strip A and B. This family of nets is of interest in connexion with the crystal structure of ScB_2C_2 (Smith, Johnson & Nordine, 1965). Borocarbides MB_2C_2 are formed by a number of $4f$ elements and by Sc. All consist of 3-connected nets of B and C atoms between which lie the metal atoms. In the $4f$ compounds the net is the 4:8 net but in the Sc compound the 5:7 net, the only example at present of this net in a crystal structure. Apart from the fact that the adoption of this net implies pairs of adjacent B and C atoms there is the additional point that the net in ScB_2C_2 is not the simplest 5:7 net with $h=1$ [Fig. 2(a)] but the form (d) with $Z=16$. Fig. 3 shows the close correspondence between layers of types (a) and (d) of Fig. 2. From aa to bb they correspond exactly, from bb to $a'a'$ only partially, and at $a'a'$ they again superpose exactly. It would be interesting to know the reasons for the adoption of the ScB_2C_2 structure.

As a matter of interest it may be noted that attempts to make $h>2$ in the 5:7 net lead to nets of other kinds, such as the infinite linear arrangement $\varphi_5=\frac{2}{3}$; $\varphi_7=\frac{1}{3}$ [Fig. 4(a)], or the two-dimensional nets:

$$\varphi_5=\tfrac{4}{5};\ \varphi_{10}=\tfrac{1}{5},\ \text{[Fig. 4}(b)\text{]}$$

and $$\varphi_5=\tfrac{6}{7};\ \varphi_{12}=\tfrac{1}{7},\ \text{[Fig. 4}(c)\text{]}\,.$$

The net $\varphi_4=\varphi_8=\frac{1}{2}$

Assuming that all polygons of each kind have the same immediate environment let the (edge-sharing) neighbours of a 4-gon and 8-gon be:

$$\text{4-gon}\begin{cases} h \text{ 4-gons} \\ 4-h \text{ 8-gons}\end{cases} \quad \text{8-gon}\begin{cases} 4-h \text{ 4-gons} \\ 4+h \text{ 8-gons}\,.\end{cases}$$

Here the case $h=0$ is possible because four 4-gons may be placed around an 8-gon without 4-gons sharing edges one with another. The unique solution for $h=0$ arises by placing the unit (a) of Fig. 5 at the points of

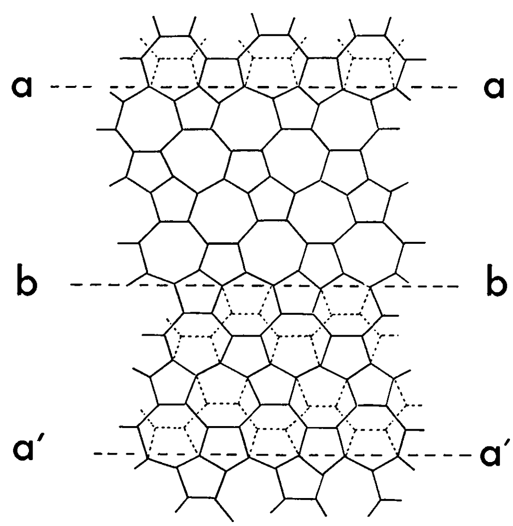


Fig. 3. Correspondence between the nets of Fig. 2(a) and (d).

the simplest 4-connected plane net [Fig. 6(*a*)]. Nets having $h=1$ and $h=2$ arise by placing the unit (*b*) of Fig. 5 at the 4-connected points of the appropriate (3,4)-connected net and the unit (*c*) at the points of the simplest 3-connected plane net. (The sharing of a pair of opposite edges between 4-gons, for $h=2$, does not lead to a plane 4:8 net.) The resulting 4:8 nets are shown in Fig. 6(*b*), (*c*) and (*d*). If the orientations of the added 4-gon units in Fig. 6(*b*) are different in successive horizontal rows – they must all be similarly oriented in a given row – an indefinite number of nets can be formed, all having $h=1$ and progressively larger unit cells. There is also an indefinite number of nets of type (*d*) with mixed orientations of the portion enclosed within the heavy lines. If we relax the condition that all polygons of each kind have the same arrangement of nearest neighbours then infinite families of nets arise having, for example, all 4-gons equivalent but two or more types of 8-gon [Fig. 6(*e*)] or two or more types of both 4- and 8-gon [Fig. 6(*f*)].

The net $\varphi_3=\varphi_9=\frac{1}{2}$

Proceeding as before the cases $h=2$ or 3 may be eliminated by arguments similar to those already used. Fig. 7 shows three nets with $h=0$ and one, (*d*), with $h=1$, of which the last gives an infinite series of nets having different orientations of the portion enclosed within the heavy lines.

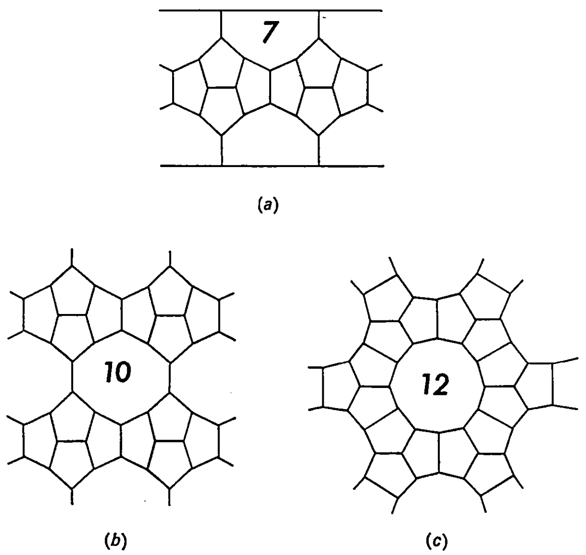
Summarizing, the permissible values of h for the nets discussed are:

Net	h		
5:7		1	2
4:8	0	1	2
3:9	0	1	

Of the 11 nets illustrated in Figs. 2, 6, and 7 [excluding 2(*d*); 6(*e*) and (*f*)] four give rise to infinite families of nets in all of which each type of polygon retains the same arrangement of nearest neighbours as in the basic net.

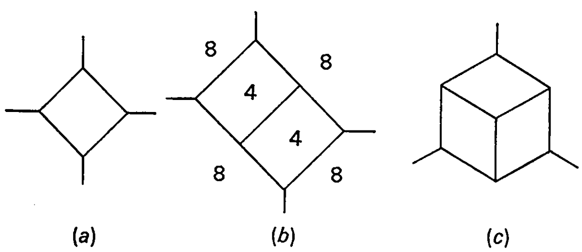
The 3-connected 4:7 and 4:8 plane nets

There is an infinite family of 3-connected plane nets composed of 4-gons and only one other kind of polygon, of which the first four members are:



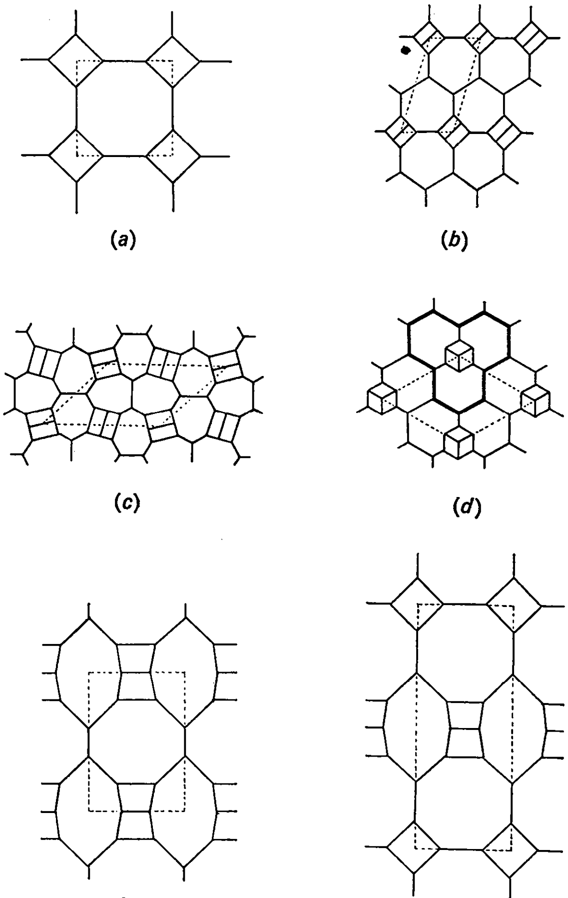
(*a*) (*b*) (*c*)

Fig. 4. Some 3-connected nets containing pentagons (see text).



(*a*) (*b*) (*c*)

Fig. 5. Derivation of (4:8) nets with $h=0$, 1, and 2.



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Fig. 6. Configurations of the 3-connected (4:8) net.

φ_4	φ_7	φ_8	φ_9	φ_{10}
$\frac{1}{3}$	$\frac{2}{3}$			
$\frac{1}{2}$		$\frac{1}{2}$		
$\frac{3}{5}$			$\frac{2}{5}$	
$\frac{2}{3}$				$\frac{1}{3}$

etc.

By adding a point above and below the centre of a 4-gon in the plane 4:8 net an octahedron is formed. These points may then be connected by further links to the corresponding points of layers above and below to give a three-dimensional 5-connected net consisting of octahedra joined as in the B framework of CaB_6. It is of interest to know which other structures of this type are possible. A section through a net of this kind

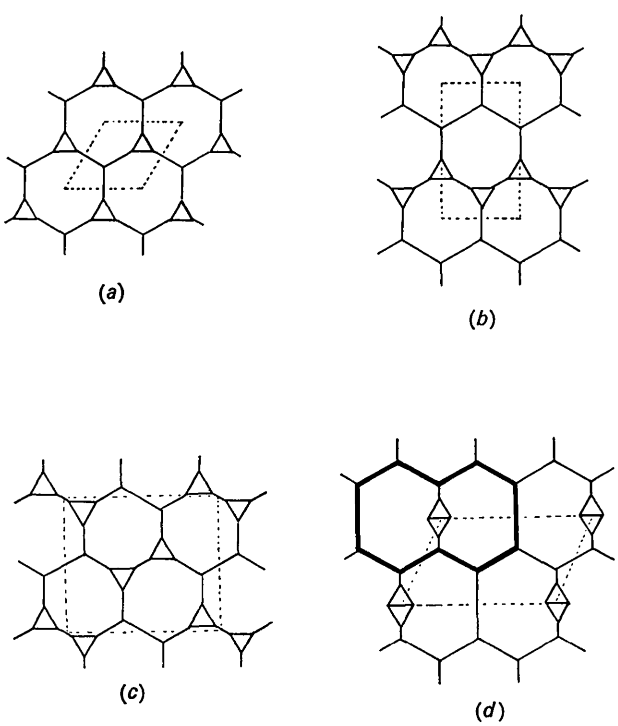


Fig. 7. Configurations of the 3-connected (3:9) net.

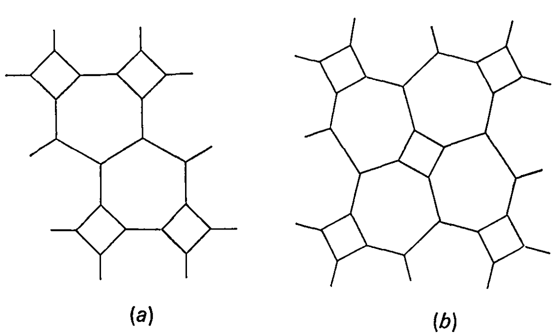


Fig. 8. Two configurations of the 3-connected (4:7) net.

is a 3-connected net containing 4-gons which do not share edges or vertices with other 4-gons. It can be shown that:

Of the family of 3-connected nets composed of 4-gons and only one other type of polygon only the 4:7 and 4:8 nets can be realized with discrete 4-gons.

If a 4-gon is to be surrounded entirely by n-gons in a net having a ratio α of 4-gons to n-gons, then the number of 4-gons surrounding an n-gon must be 4α, assuming all polygons of a given kind to be topologically equivalent. To avoid adjacent (edge-sharing) 4-gons 4α must not exceed $n/2$, a limit reached at $n=8$. Supposing the n-gons not to be topologically equivalent then on average they must share edges with 4α 4-gons, and if some have fewer others must have more than 4α 4-gon neighbours, which would imply the sharing of edges between 4-gons. The only nets satisfying the condition are therefore the 4:7 and 4:8 nets.

It is of interest that the form of the 4:7 net on which the structure of UB_4 is based is not the simplest one [Fig. 8(*a*)] but the variant (*b*) which has a more uniform distribution of 4-gons around a 7-gon.

A family of 4-connected plane nets

Certain structures formed from octahedral groups linked to six others through their vertices can be dissected into slices one octahedron thick which then stack vertically above one another. The equatorial edges of the octahedra in one slice form a 4-connected net, but it is simpler to work with the net, also 4-connected, which results from joining together the M atoms at the centres of the octahedra. Fig. 9 shows the octahedral framework of $NaNb_6O_{15}F$ illustrated in this way. The net derived in this way from the ReO_3 (cubic bronze) structure is the simplest plane 4-connected net, $\varphi_4=1$, that from the hexagonal bronze structure is the net, $\varphi_3=\frac{2}{3}$, $\varphi_6=\frac{1}{3}$, and from the tetragonal bronze structure, $\varphi_3=\frac{2}{5}$, $\varphi_4=\frac{1}{5}$, $\varphi_5=\frac{2}{5}$. The structures of $NaNb_6O_{15}F$ and $LiNb_6O_{15}F$ may also be represented in this way if the atoms at the centres of the pentagons are omitted.

4-connected nets consisting of 3-, 4-, and 5-gons have fractions φ_k of k-gons given by:

$$3\varphi_3+4\varphi_4+5\varphi_5=4\ ,$$

the solutions of which are $\varphi_3=\varphi_5=a/m$, $\varphi_4=(m-2a)/m$, where a, b and m are integers $(m>2)$. Of the infinite set of solutions the simplest are:

$$\begin{array}{ll} \varphi_3 & \frac{1}{3},\ \frac{1}{4},\ \frac{1}{5},\ \frac{2}{5},\ \frac{1}{6}, \\ \varphi_4 & \frac{1}{3},\ \frac{1}{2},\ \frac{3}{5},\ \frac{1}{5},\ \frac{2}{3},\ \textit{etc.} \\ \varphi_5 & \frac{1}{3},\ \frac{1}{4},\ \frac{1}{5},\ \frac{2}{5},\ \frac{1}{6}, \end{array}$$

The facts that the Li and Na compounds mentioned above are based on different nets (*i.e.* different solutions of $\Sigma\, n\varphi_n=4$) and that in the Li compound there are topologically non-equivalent 4-gons show that these compounds present a formidable problem:

	φ_3	φ_4	φ_5
Tetragonal bronze, $NaNb_6O_{15}F$	$\frac{2}{5}$	$\frac{1}{5}$	$\frac{2}{5}$
$LiNb_6O_{15}F$	$\frac{1}{5}$	$\frac{3}{5}$	$\frac{1}{5}$

The following note, confined to a study of only one of these nets, may be of interest rather as illustrating the complexity of the problem than throwing much light on the reasons for the choice of structure in this group of compounds.

The 4-connected plane net: $\varphi_3=\frac{2}{5}$, $\varphi_4=\frac{1}{5}$, $\varphi_5=\frac{2}{5}$

We assume all polygons of a given kind to be topologically equivalent and describe the configurations of the net in terms of the 'coordination' (edge-sharing) of one polygon by neighbouring polygons. These coordination numbers are related to the values of φ_n. For example, if a 3-gon has k 4-gon (edge-sharing) neighbours then a 4-gon must have $2k$ 3-gon neighbours because $\varphi_3=2\varphi_4$. Three parameters are required to define a net:

$$\text{3-gon}\begin{cases} h & \text{3-gons} \\ k & \text{4-gons} \\ 3-h-k & \text{5-gons}\end{cases} \qquad \text{4-gon}\begin{cases} 2k & \text{3-gons} \\ l & \text{4-gons} \\ 4-2k-l & \text{5-gons}\end{cases}$$

$$\text{5-gon}\begin{cases} 3-h-k & \text{3-gons} \\ 2-k-\frac{1}{2}l & \text{4-gons} \\ h+2k+\frac{1}{2}l & \text{5-gons}\end{cases}$$

where h and k must lie between 0 and 3 and l between 0 and 4 inclusive.

Certain restrictions on the values of h, k, and l follow from arguments such as the following. From the coordination of a 5-gon, it follows that l is even. The value $l=4$ may be excluded since it would imply that a 4-gon is surrounded entirely by 4-gons (*i.e.* plane 4-gon net). Therefore the possible values of l are 0 or 2 only. The value 3 for h can be excluded by a similar argument, and the impossibility of surrounding a 4-gon by more than 4 3-gons eliminates $k=3$. It is then necessary to study each of the combinations of the remaining values of h, k, and l, namely, h and $k=0$, 1, or 2 for $l=0$ and for $l=2$. Since the maximum value of $h+k$ is clearly 3, the combination $h=k=2$ is inadmissible, so that there are 16 combinations of h, k, and l to investigate. The procedure is to start to construct the net and to show either that a periodic net with the specified values of h, k, and l arises, or that at some stage it becomes impossible to proceed further while maintaining these values and the topological equivalence of the polygons of each kind.

The solutions found are shown in Fig. 10. Note that the values of h, k, and l do not necessarily uniquely characterize the net. There are, for example, two solutions, (a) and (b) for $h=k=l=0$. For the structures under discussion only solutions with $h=0$ are relevant, for solutions with $h>0$ involve the sharing of edges between triangles. This is geometrically impossible if the 4-gons approximate to squares (Fig. 11).

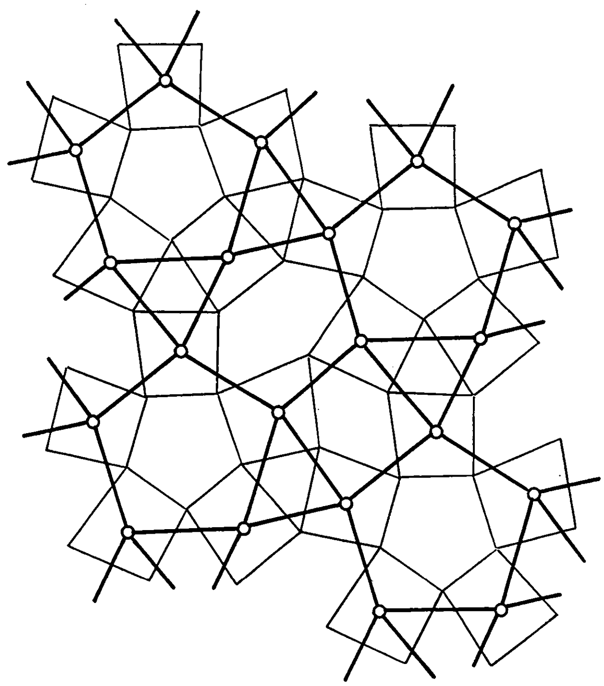


Fig. 9. Plan of $NaNb_6O_{15}F$ showing (thin lines) equatorial edges of octahedral coordination groups and (thick lines) the 4-connected net formed by joining atoms at centres of metal–oxygen octahedra.

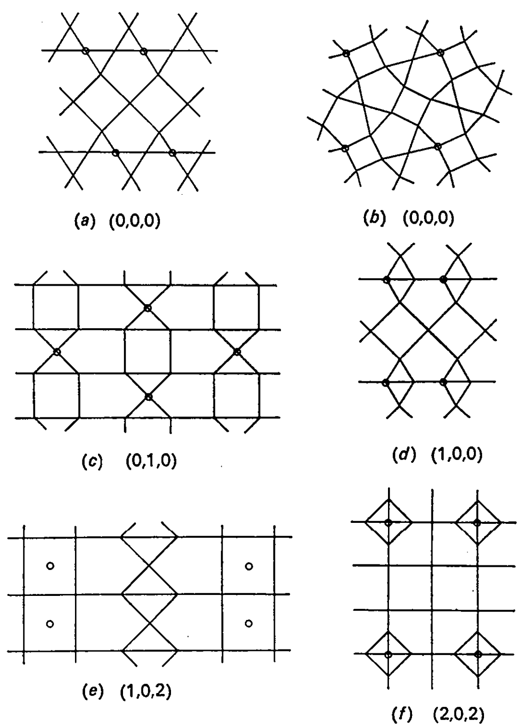


Fig. 10. Configurations of the 4-connected plane net, $\varphi_3=\frac{2}{5}$, $\varphi_4=\frac{1}{5}$, $\varphi_5=\frac{2}{5}$. Small circles mark corners of repeat unit. Figures in parentheses are values of h, k and l.

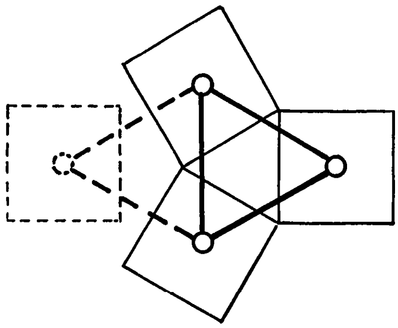
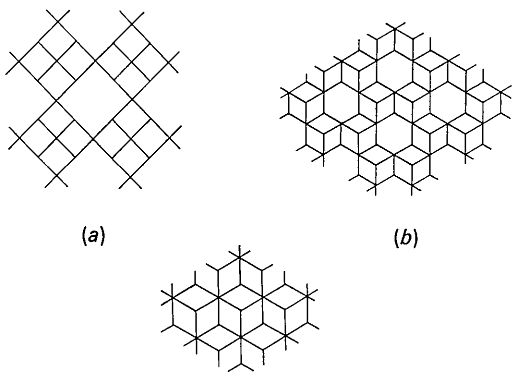


Fig. 11. The case $h>0$ in certain 4-connected nets (see text).



(c)

Fig. 12. The three plane nets with alternating p- and q-connected points.

Of the three nets with $h=0$, Fig. 10 (a), (b) and (c), two are known to represent actual crystal structures, namely (b), tetragonal bronzes, and (c), $NaNb_6O_{15}F$.

Plane nets with alternating p- and q-connected points

Nets in which points of two kinds (p- and q-connected) alternate are of special interest in connexion with the structures of compounds A_mX_n in which the coordination numbers of both A and X are 3 or more. The simple layer structure of $Mg(OH)_2$ may be represented as a plane (6,3)-connected net and the Ge_3N_4 structure as a three-dimensional (4,3)-connected net. Incidental to the derivation of three-dimensional nets in part 6 (Wells, 1956) it was noted that a simple layer structure is not possible for a compound A_2X_3 if A is to be 6- and X 4-coordinated. The following is a more complete treatment of this problem.

The only possible plane nets composed of alternate points of two kinds c_p and c_q are the $c_3:c_4$, $c_3:c_5$, and *$c_3:c_6$* nets

If p- and q-connected points alternate all the polygons must have even numbers of edges, in which case the maximum attainable ratio of links to points is reached when the number of edges of each polygon is the smallest possible, namely 4. We first show that for any plane net composed of 4-gons the ratio of links to points is 2 regardless of the connectedness of the points. In the reciprocal net all points are 4-connected and their number is that of original 4-gons (say, N). The number of links in the reciprocal net is equal to the number of links in the original net. This number is $2N$ since every 4-gon has 4 edges and each edge is common to two 4-gons. We require to find the number of polygons (N^*) in the reciprocal net, which is equal to the number of *points* in the original net. The number of points (N) in the reciprocal net is equal to $N^* \, \Sigma \, n\varphi_n/4$ where φ_n is the fraction of n-gons. But for a 4-connected net $\Sigma \, n\varphi_n=4$ whence $N=N^*$. The number of polygons in the reciprocal net and of points in the original net is therefore N, and the ratio of links to points is 2.

For a periodic net consisting of alternate p- and q-connected points the fractions of these points are $q/(p+q)$ and $p/(p+q)$ respectively and therefore the number of links is $pqN/(p+q)$, whence the ratio of links to points is $pq/(p+q)$. The only combinations of (different values of) p and q (≥ 3) giving $pq/(p+q) \lesssim 2$ are 3 and 4, 3 and 5, and 3 and 6. The corresponding nets are shown in Fig. 12.

$$\begin{aligned}
&(a)\ c_3=\tfrac{4}{7} \quad c_4=\tfrac{3}{7} \\ &\ f_4=\tfrac{4}{5} \quad f_8=\tfrac{1}{5}
\end{aligned}\Bigg\}\ Z=7$$

$$\begin{aligned}
&(b)\ c_3=\tfrac{5}{8} \quad c_5=\tfrac{3}{8} \\ &\ f_4=\tfrac{6}{7} \quad f_6=\tfrac{1}{7}
\end{aligned}\Bigg\}\ Z=8$$

$$\begin{aligned}
&(c)\ c_3=\tfrac{2}{3} \quad c_6=\tfrac{1}{3} \\ &\ f_4=1
\end{aligned}\Bigg\}\ Z=3\,.$$

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