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The Geometrical Basis of Crystal Chemistry. VIII

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A study is made of periodic three-dimensional systems of points in which some points are connected to three and some to four others, and examples are given of crystals with structures based on certain of these nets. Radiating nets are briefly discussed, and the basic three-dimensional 3-, (3·4)-, and 4-connected nets are summarized.

In parts I and II (Wells 1954*a*, *b*) an examination was made of some of the simpler 3-connected and 4-connected three-dimensional nets, and further examples of more complex nets were given in parts V, VI, and VII (Wells 1955, 1956; Wells & Sharpe 1963). In particular it was shown that the simplest three-dimensional 3-connected nets (*i.e.* those with the smallest possible value of Z, the number of points in the topological repeat unit) are both systems of decagons (10^3 or 10,3) having $Z=4$. In one of these nets all the links are equivalent (with $y=10$, y being the number of n-gons to which each link is common), and if built with equal links and interbond angles of 120° the net has cubic symmetry and $Z^*=8$, where Z^* is the number of points in the crystallographic unit cell. It is the 3-connected analogue of the diamond net. The latter, the simplest three-dimensional 4-connected net, has the minimum number (2) of points in the topological repeat unit, is a system of puckered 6-gons, and in its most symmetrical configuration (with equal bonds and interbond angles of $109\frac{1}{2}$°) has cubic symmetry and $Z=8$.

Of plane tessellations consisting entirely of 3-gons, 4-gons, or 6-gons there are the special cases: $\varphi_6=1$, $\varphi_4=1$, and $\varphi_3=1$, where φ_p is the fraction of p-connected points. For 5-gons the solution with the lowest values of p is: $\varphi_3=\frac{2}{3}$, $\varphi_4=\frac{1}{3}$, and this corresponds to two nets [Fig. 1(*b*) and (*c*)] having different relative arrangements of the 3- and 4-connected points. Here we consider some of the simpler (3,4)-connected three-dimensional nets which we expect, by analogy with the two-dimensional nets

p	3	3 and 4	4	6
n	6	5	4	3

to fit into a family of basic three-dimensional nets. Before doing so it will be convenient to comment on a question of nomenclature.

Uniform nets

In part I a 3-connected net was described as *uniform* if the shortest circuit starting from any point along any link and returning, along any other link, to the starting point passed through the same total number of links (points). If the shortest circuit was an n-gon the net was described as an n^3 net; we shall prefer the symbol $\{n,p\}$ for a p-connected net in which the shortest circuits are n-gons. As in part VII we shall denote by x the number of n-gons to which a point is common and by y the number of n-gons to which a link is common. In a uniform 3-connected net the minimum value of y is clearly 2 (in contrast to the erroneous statement on p. 543 of part I), and the minimum value of x is therefore 3 since $x/y=p/2$ (part 7, Appendix). The possession of these minimum values of x and y is a necessary but not sufficient condition of uniformity, for there may be several alternative n-gon circuits from a point involving the same two links, in which case x could equal or exceed 3 while the shortest circuits including other pairs of links would not necessarily be n-gons. The condition of uniformity evidently re-

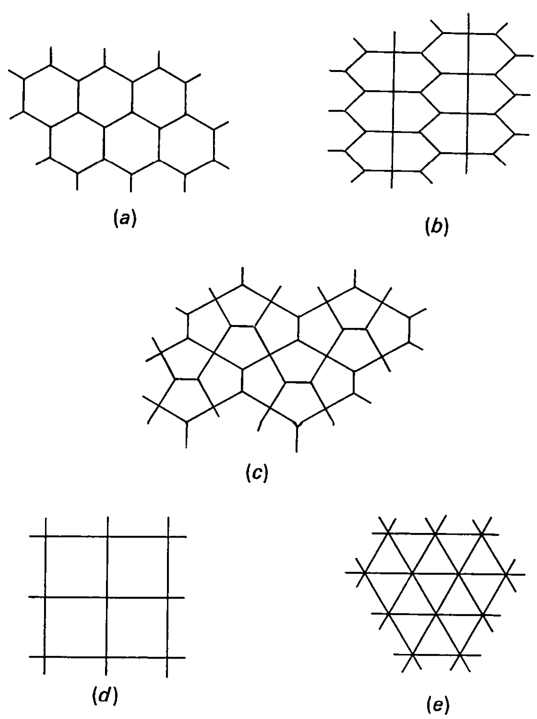


Fig. 1. Plane nets:
(*a*) {6,3}, (*b*) {5,$\frac{3}{4}$}, (*c*) {4,4}, (*d*) {3,6}.

quires that all the three combinations of the links from each point taken two at a time are parts of n-gons. (Note that the net 21 of part I is not a uniform net and should be deleted from Table 3 in that paper. This net should also be excluded from Fig. 6 and the preceding text in part V).

The idea of defining uniform nets in the above way arose in connection with 3-connected nets. It is necessary to examine whether the concept can be usefully applied to three-dimensional nets having higher values of p. The condition for uniformity implies that the minimum values of x and y are respectively $p(p-1)/2$ and $(p-1)$. The simplest three-dimensional 6-connected net is the P lattice, for which $x=12$ and $y=4$, so that our criterion, requiring minimum values of 15 and 5, is obviously too rigorous. Of the 15 combinations of 6 bonds three pairs are collinear in the P lattice (and in the I and F lattices 4 and 6 pairs respectively), and circuits involving pairs of collinear bonds in these nets are larger than for the other pairs. A similar complication exists in a net such as that of Fig. 1(d) of part VII with 4 coplanar links from each point. Here only 4 of the 6 combinations of 2 links from any point form parts of 6-gons, the shortest circuits including two collinear bonds being 8-gons. This can be expressed by the symbol $6^4 8^2$ analogous to that for a polyhedron (*e.g.* $3^2 4^2$ for the cuboctahedron). However, the fact that it is possible to have points of the type n^6 with four coplanar links shows that this problem is not simply related to the arrangement of the 4 bonds from a 4-connected point. The net of Fig. 2 has certain similarities to the diamond net, being a system of 6-gons with the same values of x (12) and y (6). The point P is of the type 6^6 but Q is $6^4 8^2$.

Although, therefore, it is not feasible to extend the simple but rigorous condition for uniformity to more highly connected nets we shall retain it here for (3,4)-connected nets and distinguish as uniform $\{n, {}^3_4\}$ nets only those in which the shortest circuit is an n-gon for *any* pair of links from each of the 3-connected and from each of the 4-connected points, *i.e.* the symbol is $(n^3)_a(n^6)_b$ where a and b are the numbers of 3- and 4-connected points in the topological repeat unit.

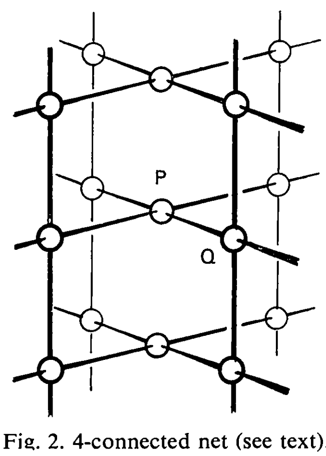


Fig. 2. 4-connected net (see text).

(3,4)-connected nets

For a polyhedron having only 3- and 4-connected vertices the number of the former must be even, and this is also true of the number of 3-connected points in the repeat unit of a periodic network of this kind (two- or three-dimensional). The minimum value of Z is therefore 3. If ψ_n is the fraction of the polygons in a plane net which are n-gons it can be shown that

$$\Sigma n\psi_n = 2(3m+4)/(m+2)$$

where m is the ratio of the numbers of 3-and 4-connected points. For $m=2$, $\Sigma n\psi_n=5$, so that the simplest solution is $\psi_5=1$. As already noted there are two forms of the 5-gon net. The next simplest solutions are: $\psi_4=\psi_6=\frac{1}{2}$; $\psi_3=\psi_7=\frac{1}{2}$. These nets are illustrated in Fig. 3.

For three-dimensional nets the simplest (topological) repeat unit is the linear system of three points intermediate between those for 3-connected and 4-connected nets (Fig. 4). In diagrams of three-dimensional (3,4)-connected nets the 4-connected points are distinguished as shaded circles. The minimum value of Z is here the same as for a two-dimensional net, in contrast to 3-connected and 4-connected nets for which the minimum values of Z for plane and three-dimensional nets are respectively 2 and 4, and 1 and 2.

No attempt has been made to derive the three-dimensional nets systematically. In Table 1 are listed the possible numbers c_3 and c_4 of 3- and 4-connected points in

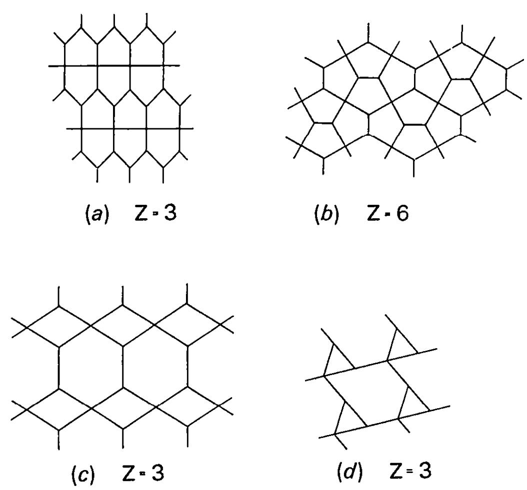


Fig. 3. Plane (3,4)-connected nets.

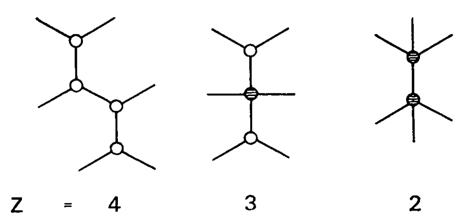


Fig. 4. Repeat units
for 3-, (3,4)-, and 4-connected three-dimensional nets.

repeat units having Z from 3 to 7. There are two nets with $Z=3$ which differ in the arrangement of the 3- and 4-connected points. Of these one is a uniform net, a three-dimensional array of 8-gons which is intermediate between $\{10,3\}$ and $\{6,4\}$. The space-group corresponding to the most symmetrical configuration of this net is $I\bar{4}m2$ with the 4-connected points in $2(d)$, $(0\frac{1}{2}\frac{3}{4})$ *etc.* and the 3-connected points in $4(e)$, $(00z)$ *etc.* It is not possible to have interbond angles of 120° for the 3-connected points *and* $109\frac{1}{2}$° for the 4-connected points, and two possible configurations are:

$$\alpha=120°;\quad z=\tfrac{1}{6};\quad c/a=\sqrt{3};$$

$$\alpha=109\tfrac{1}{2}°;\quad z=\sqrt{3}/(4\sqrt{3}+8);\quad c/a=(\sqrt{3}+2)/\sqrt{2}\,.$$

The former is illustrated in Fig. 5(*a*). Although there are two kinds of non-equivalent link all have $y=8$; for the 3-connected points $x=12$ and for the 4-connected points $x=16$, giving $x_{\text{mean}}=13\frac{1}{3}$.

Table 1. *Some three-dimensional* (3,4)-*connected nets*

Z	c_3	c_4	n-gons	Full symbol	Figure
3	2	1	8*	$(8^3)_2(8^6)$	5(*a*)
			8,10	$(8^3)_2(8^5 10)$	5(*b*)
4	2	2	—	—	—
5	4	1	8*	$(8^3)_4(8^6)$	6
	2	3	7*	$(7^3)_2(7^6)_3$	7(*a*)
7	6	1	9*	$(9^3)_6(9^6)$	7(*b*)
14	8	6	8*	—	8
			6,8	—	9

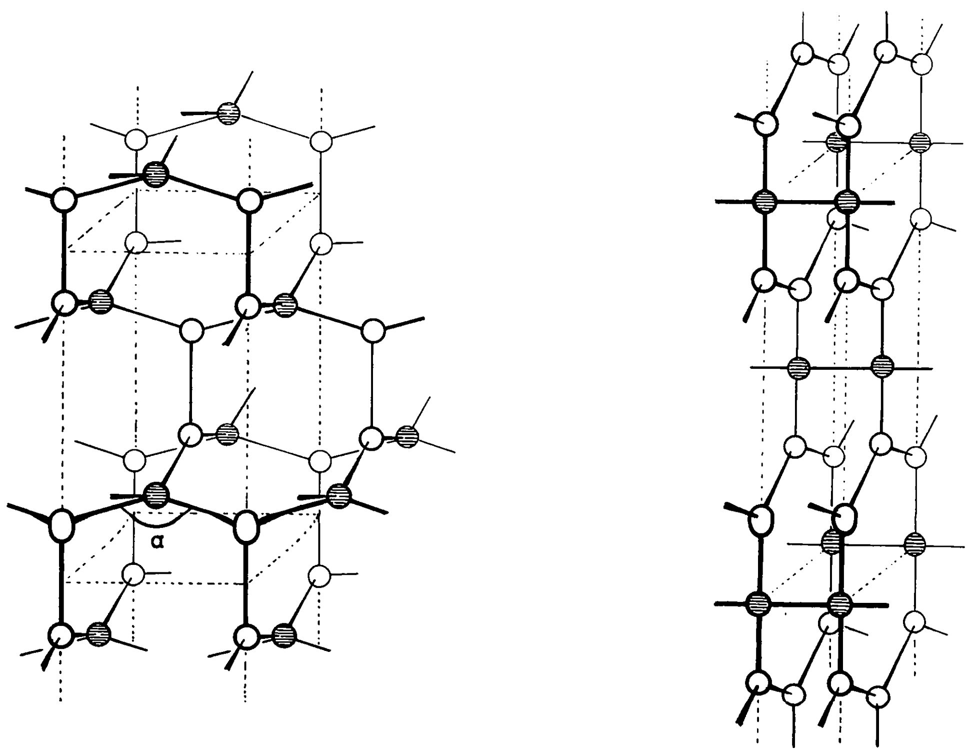
* uniform net

There is a second net with $Z=3$ [Fig. 5(*b*)] differing from that of Fig. 5(*a*) in having the 4-connected points directly connected. In this second net one of the six shortest circuits involving a pair of links from a 4-connected point is a 10-gon; this is accordingly not a uniform net.

The net of Fig. 6 has $Z=5$ ($c_3=4$, $c_4=1$) and is a uniform 8-gon net. A highly symmetrical configuration with equal links, interbond angles of 120° (c_3) and 90° (c_4) has $Z^*=10$ in the space-group $I4/mmm$ with the 4-connected points in $2(a)$, (000) *etc.* and the 3-connected points in $8(h)$, $(xx0)$ *etc.* with $x=\frac{1}{5}$; $c/a=\sqrt{6/5}$. For all the links in this net $y=6$. For the 3-connected points $x=9$ and for the 4-connected points $x=12$, giving $x_{\text{mean}}=9\frac{3}{5}$. It is interesting to compare with the 8-gon nets of Figs. 5(*a*) and 6 the uniform 3-connected 8-gon nets 5 and 6 of part I:

	x c_3	x c_4	x_{mean}	y	y_{mean}
(3,4)-connected Fig. 5(*a*)	12	16	$13\frac{1}{3}$	8	8
(3,4)-connected Fig. 6	9	12	$9\frac{3}{5}$	6	6
3-connected nets 5 and 6	4	–	4	2 and 3	$2\frac{2}{3}$

A second net with $Z=5$ having $c_3=2$ and $c_4=3$ is a uniform 7-gon net [Fig. 7(*a*)]. For $Z=7$ there are three possible ratios of $c_3:c_4$, and one of the nets is a uniform 9-gon net [Fig. 7(*b*)]. These last two nets are illustrated as topological diagrams since it has not been ascer-



(*a*) (*b*)

Fig. 5. The two simplest three-dimensional (3,4)-connected nets.

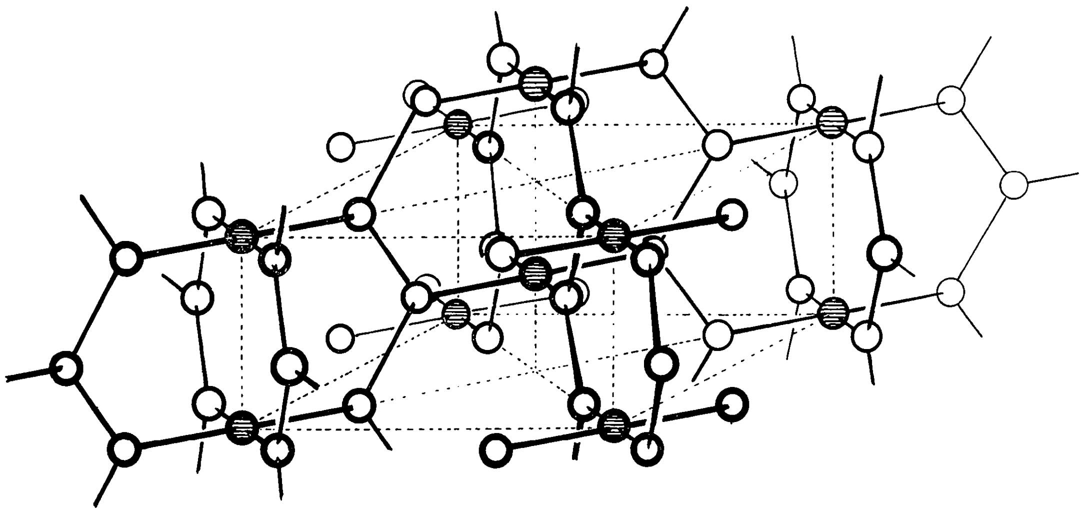
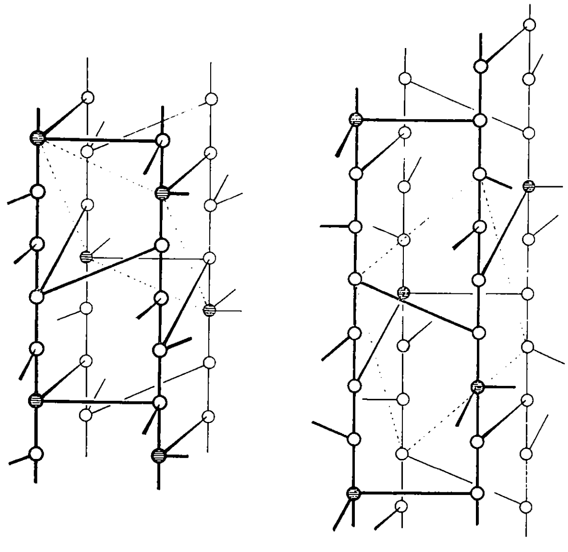


Fig. 6. A uniform (3,4)-connected 8-gon net.

tained whether they have configurations with more symmetrical arrangements of links from the 3- and 4-connected points.

Nets in which the 3-connected points are linked only to 4-connected points and *vice versa*

Special interest attaches to nets of this type. It is possible only if Z is a multiple of 7 and the ratio $c_3:c_4=4:3$. No example of a net of this kind with $Z=7$ has been found but two are known with $Z=Z^*=14$. The Pt and O atoms in $NaPt_3O_4$ (Waser & McClanahan, 1951) form a (3,4)-connected net (Fig. 8) in which the Pt atoms form four bonds to O and the O atoms three to Pt. (In this description we omit the weak additional Pt–Pt bonds.) The space-group is $Pm3n$ with Pt in $6(c)$, $\pm(\frac{1}{4}0\frac{1}{2})$, and O in $8(e)$, $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})\pm(\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4})$ *etc.* In contrast to this structure in which there is square planar bonding by Pt, the phenacite (Ge_3N_4) structure (Fig. 9) has tetrahedral coordination of the 4-connected atoms. (The bonds from the 3-connected atoms are approximately coplanar in both structures). The net of Fig. 9 represents the idealized structure of Ge_3N_4 and a number of complex oxides and fluorides of the type A_2BX_4 in which both A and B are tetrahedrally coordinated, including Be_2GeO_4 and Be_2SiO_4 (phenacite), Zn_2SiO_4, Li_2MoO_4, Li_2WO_4, and Li_2BeF_4.



(a) (b)

Fig. 7. Topological diagrams of uniform (3,4)-connected 7-gon and 9-gon nets.

Three-dimensional borate ions

Networks built of 3- and 4-connected points are suitable for borates since by placing an O atom along each link we may have planar BO_3 and tetrahedral BO_4 groups joined by sharing O atoms. If L is the number of links in the repeat unit, $L=\frac{1}{2}(3c_3+4c_4)$, and the formula of such a three-dimensional borate ion would be B_ZO_L,

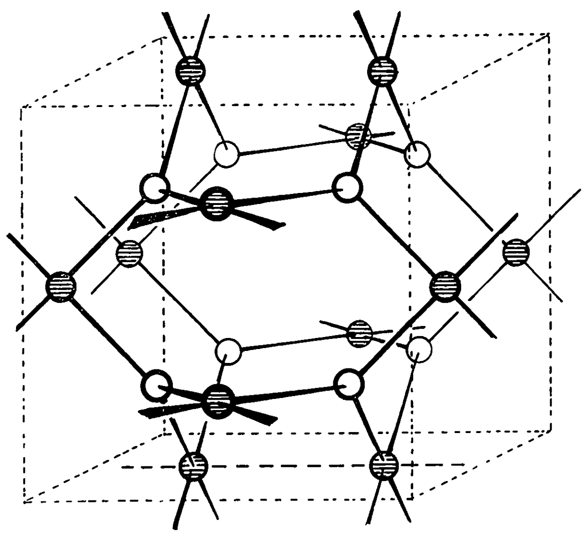


Fig. 8. The (3,4)-connected net representing the arrangement of O and Pt atoms in $NaPt_3O_4$. (Shaded circles represent Pt atoms; Na atoms at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ omitted.)

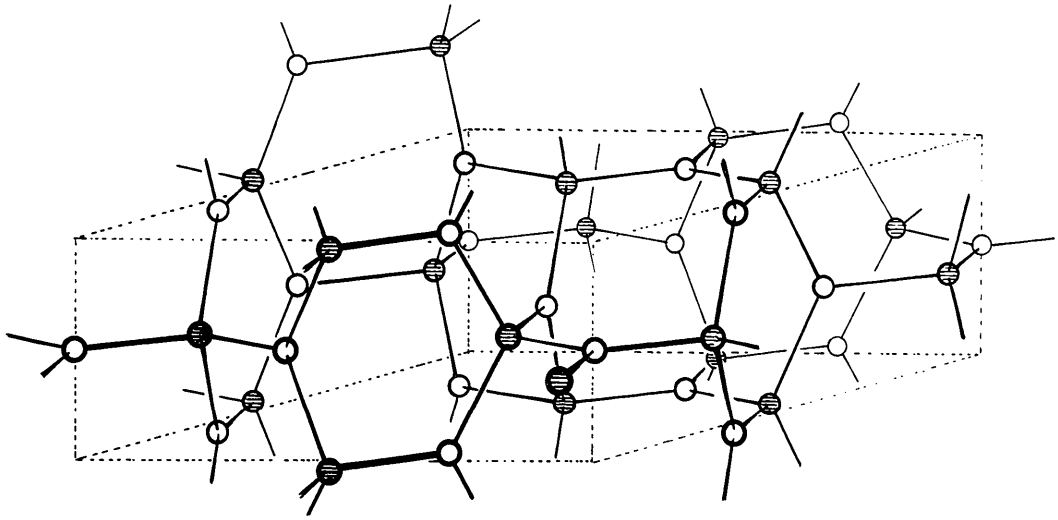


Fig. 9. The (3,4)-connected net representing the structure of Ge_3N_4 (or phenacite). Shaded circles represent N atoms.

i.e. B_3O_5, B_4O_7, B_5O_8, B_5O_9, B_5O_{11}, *etc.* (The charge on the ion is the value of c_4). Borates of this kind can be prepared and the structures of compounds of the first three types have been determined, namely, CsB_3O_5, $Li_2B_4O_7$, and KB_5O_8. They do not, however, correspond to any of the networks of Table 1. We have been interested here in finding the nets with the largest circuits; the borates are built from sub-units containing the smallest, most compact, ring systems. In Fig. 10 the O atoms along each link are omitted. Each unit has four free links and can form a net of the diamond type in which the repeat unit necessarily consists of two of the units of Fig. 10, so that $Z=6$, 8, and 10 respectively. A further point of interest is that whereas in CsB_3O_5 the structure consists of one three-dimensional framework ion (with the Cs^+ ions in the interstices) in the other two salts there are two interpenetrating frameworks as, for example, in Cu_2O.

Summary of basic nets

Since the repeat unit of a three-dimensional net need possess only six free links we may recognize the following set of basic nets:

	Z	p	n		n
Cubic {10, 3}	4	3	10	compare the	6
Fig. 5(*a*)	3	3,4	8	plane nets	5
Diamond	2	4	6		4
P lattice	1	6	4		3

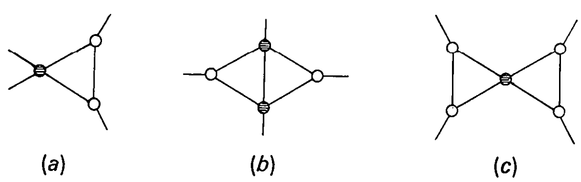


Fig. 10. Structural units in polyborate ions: (*a*) $(B_3O_5)_n^{n-}$, (*b*) $(B_4O_7)_n^{2n-}$, (*c*) $(B_5O_8)_n^{n-}$.

More highly connected nets possess more than the essential number of free links from their repeat units. The most symmetrical forms of 8-connected and 12-connected nets are the cubic *I* and *F* lattices with $Z^*=2$ and 4 and $n=4$ and 3 respectively; they may be formed from 2 and 4 interpenetrating *P* lattices respectively.

Between {10,3} and the plane {6,3} are the {7,3}, {8,3}, and {9,3} nets derived in parts I and VI, and intermediate between {10,3} and {6,4} lie the (3,4)-connected nets with 7-, 8-, and 9-gon circuits. The two remaining gaps in Table 2, $R_{3,4}$ and R_5, are filled by infinite three-dimensional radiating (*i.e.* non-periodic) nets, which we now consider.

Table 2. *Some basic nets*

n \ p	3	3 and 4	4	6
3				Plane {3,6}
4			Plane {4,4}	*P* lattice 1
5		Plane {5,$\frac{3}{4}$}	Fig. 14 R_5	
6	Plane {6,3}	Fig. 15 $R_{3,4}$	Diamond 2	
7	{7,3}	Fig. 7(*a*)		
8	{8,3}	Fig. 5(*a*) 3		
9	{9,3}	Fig. 7(*b*)		
10	Cubic {10,3} 4			

Radiating nets

In this series of papers we have been concerned solely with periodic nets or surface tessellations. Since the amount of information obtainable by normal X-ray studies is largely determined by the extent to which a system approximates to a regular diffraction grating, crystallographers are usually interested in regular repeating patterns having long-distance order. However, other types of structure can be envisaged which may be important in, for example, crystallizing polymers or glasses. Ordering might start at a point and lead to some sort of structure which cannot extend indefinitely for purely topological or geometrical reasons. In a covalent structure or glass a system of 5-rings might be formed which is not part of any possible three-dimensional network; in a sphere packing transition to a more close-packed lattice packing may be possible, as for the icosahedral sphere packing (MacKay, 1962). Systems which, like the icosahedral sphere packing, radiate from a unique central point are obviously of interest in this connexion. The following note shows the relation of certain radiating systems to the three-dimensional polyhedra of part VII and to the basic nets of Table 2.

Plane radiating nets

(1) Any $\{n, p\}$ may be drawn as a plane radiating net. Rather than drawing the edges of the polygons as straight lines it is convenient to draw these nets as series of points on concentric circles.
(2) For {3,3}, {3,4}, {3,5},{4,3}, and {5,3} the nets are finite, being simply the Schlegel diagrams of the five Platonic solids [Fig. 11, (*a*)–(*e*)].
(3) For {3,6}, {4,4}, and {6,3} the radiating net is identical with the periodic plane net. Since these are the only regular periodic plane nets (*i.e.* with all polygons *n*-gons and all points *p*-connected) all higher members of these series, namely, $\{3,p\}, p > 6$, $\{4,p\}$, $p > 4$, and $\{6,p\}$, $p > 3$, and their reciprocals can be realized (*on the Euclidean plane*) only as radiating nets. (Part VII was concerned with showing that they can also be drawn on certain types of three-dimensional periodic surfaces.) If drawn in the most symmetrical way the highest axial symmetry is *n* or *p* according to whether the centre of a polygon or a point is taken as origin. Fig. 12 shows the central portions of {7,3} drawn in these two ways.

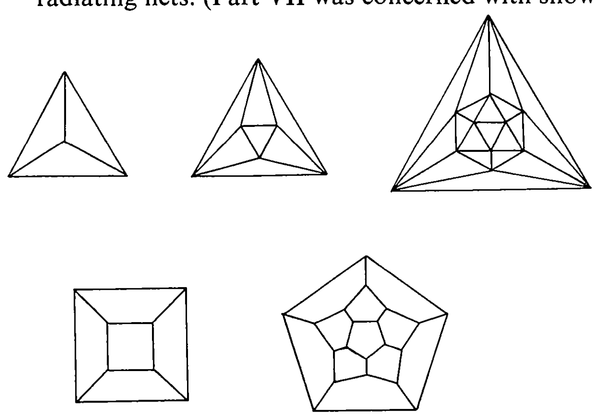


Fig. 11. Schlegel diagrams of the Platonic solids.

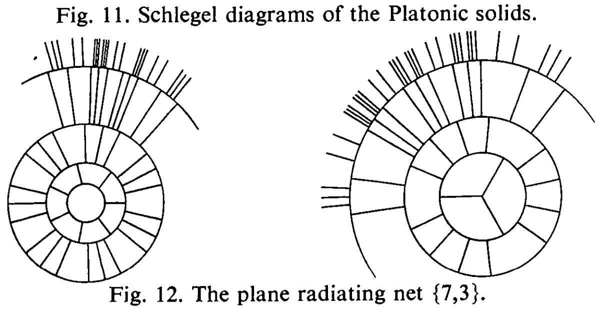


Fig. 12. The plane radiating net {7,3}.

Three-dimensional radiating systems

For arrangements of links which are symmetrically disposed in three dimensions we may expect to find three-dimensional radiating systems. We are particularly interested in the possibility of nets corresponding to the spaces marked *R* in Table 2, and we consider first systems of the type n^6 involving four tetrahedral bonds. For $n=3$ the system consists of a central point connected to the vertices of a tetrahedron, or the topologically equivalent case where the central point is projected through the base of the tetrahedron to form a bipyramid [Fig. 13(*a*) and (*b*)]. For $n=4$ each vertex of a cube is connected to one of the vertices of a circumscribing cube [Fig. 13(*c*)]. In contrast to the finite 3^6 or 4^6 the system 5^6 is an infinite radiating net which starts from a central pentagonal dodecahedron (Fig. 14). This is surrounded by a shell of 12 dodecahedra which is succeeded by further shells of dodecahedra. This radiating 5^6 is the net R_5 of Table 2. For all of these systems $y=3$. The radiating 6^6 is found to be identical with the diamond net ($y=6$), *i.e.* it is also periodic (compare the plane nets {3,6}, {4,4}, and {6,3}).

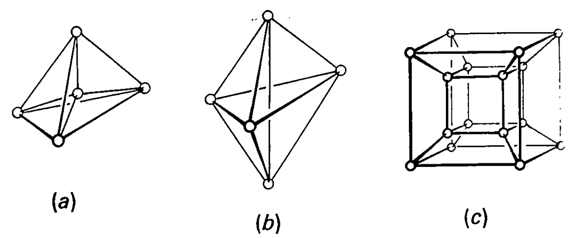


Fig. 13. Finite radiating nets:
(*a*) and (*b*) {3,4} or 3^6, (*c*) {4,4} or 4^6.

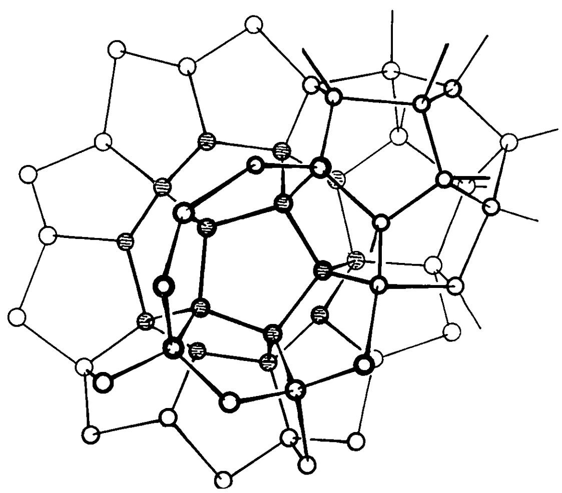


Fig. 14. The radiating dodecahedral net {5,4} or 5^6.

The existence of the radiating system 5^6 suggested the possibility of a radiating (3,4)-connected net formed of hexagons which would fill the gap between the plane 5-gon net and the 7-gon, 8-gon, and 9-gon periodic nets. There is in fact a net of this kind (Fig. 15) which consists of an infinite set of concentric tetrahedra linked alternately by lines joining vertices and mid-points of edges. Apart from the central group of 10 3-connected points each successive tetrahedral shell contains 6 3-connected and 4 4-connected points so that for the infinite system $c_3:c_4=3:2$. This net, $R_{3,4}$, completes the family of fundamental nets of Table 2.

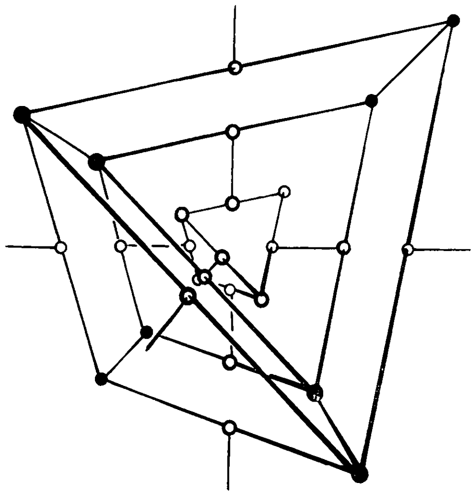


Fig. 15. The radiating net $\{6,\frac{3}{4}\}$.

The relation of the radiating systems and the surface tessellations of part VII to other 4-connected systems is shown below.

Regular and uniform 4-*connected systems*

$y=2$ These include the following:

- $n=3$ octahedron, {3,4}
- $n=4$ plane net, {4,4}
- $n\geq 5$ (*a*) infinite plane radiating nets,
  - (*b*) the infinite three-dimensional surface tessellations of part VII, {5,4}, {6,4}, and {7,4}; others have $2\langle y\rangle 3$. (The *y* values for these nets were not given, and {7,4} was not illustrated; it is the reciprocal of Fig. 22(*c*) of part VII).

$y=3$

- $n=3$ finite radiating 3^6 [Fig. 13, (*a*) and (*b*)]
- $n=4$ finite radiating 4^6 [Fig. 13(*c*)]
- $n=5$ infinite radiating 5^6 (Fig. 14)

$y=6$

- $n=6$ diamond net, 6^6 or (6,4).

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A Ternary Alloy with $PbCl_2$-type Structure: TiNiSi(*E*)*

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Beck and coworkers have found *E* phases in several ternary systems of transition elements with either silicon or germanium at the composition 1:1:1. The crystal structure of TiNiSi(*E*) has been determined and refined by least squares with (limited) three-dimensional single-crystal data to a final *R* value of 0·086 (excluding 002 due to apparent extinction, and all non-observed reflexions). The lattice parameters for the primitive orthorhombic cell are:

$$a_0=6\cdot1484\pm0\cdot0012,\ b_0=7\cdot0173\pm0\cdot0014,\ c_0=3\cdot6698\pm0\cdot0007\ \text{Å}\,.$$

The *E* phase is isotypic with $PbCl_2$(*C*23), space group *Pnam*. All near-neighbor distances are within 0·06 Å of the following average values: Ti–Ti 3·18, Ti–Ni 2·83, Ti–Si 2·61, Ni–Ni 2·67, Ni–Si 2·33 Å The numbers of near-neighbors are compared with those in Co_2Si, $\theta-Ni_2Si$ and U_3Si_2.

Introduction

The *E* phase was first identified by Westbrook, DiCerbo & Peat (1958) in the titanium-nickel-silicon system at the composition TiNiSi. Subsequently Spiegel, Bardos & Beck (1963) concluded from the powder X-ray diffraction diagrams that twenty-one additional phases in other ternary systems of transition elements with either silicon or germanium are isomorphous with TiNiSi(*E*) and they indexed the powder patterns on large orthorhombic cells. They found

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