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Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. Combination of zigzag and saw chains with 6^3, 3.12^2, 4.8^2, 4.6.12 and $(5^2.8)_2(5.8^2)_1$ nets

Frank C. Hawthorne [1] and Joseph V. Smith

Department of Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

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Nets / Frameworks

Abstract. 4-connected 3-dimensional nets containing zigzag and saw chains may be derived from stacks of parallel congruent 3-connected 2-dimensional nets by linking them together with zigzag or saw chains. Such derivation is governed by the following rules: (1) *every vertex must lie on an infinite h (horizontal) path in the plane of the original 2-dimensional net*; (2) *the number of z (zigzag) edges in any (projected) polygonal circuit in the original 2-dimensional net must be even*; as a consequence of (1) and (2), we have: (3) *z edges must connect infinite h paths of different heights.* Using these rules, all possible translationally and radially symmetric nets derivable from 6^3, 3.12^2, 4.8^2, 4.6.12 and $(5^2.8)_2(5.8^2)_1$ are considered. Of particular interest are the radially symmetric nets, which consist of mirror-related sectors within which there is translational symmetry; such nets can describe sector-twinned crystals.

Introduction

Much crystal structure information has become available over the last twenty years, and an increasing amount of effort is being spent on trying to order and systematize the atomic arrangements that do occur. A fairly fundamental approach to this question considers a structure as a 3-dimen-

[1] *Permanent address*: Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2.

sional net, and systematically enumerates such nets as models for real and possible structures. The pioneering work in this area is that of Wells (1977, 1979, and references therein). More recent work (Smith, 1977, 1978, 1979, 1983; Smith and Bennett, 1981, 1984; Smith and Dytrych, 1984, 1986; Bennett and Smith, 1985; Hawthorne and Smith, 1986; Alberti, 1979; Gottardi and Galli, 1985) has concentrated on the enumeration of 4-connected 3-dimensional nets and their application to tetrahedral framework structures. Such work is also of some practical interest, as these nets may provide models for aluminosilicate and aluminophosphate molecular sieves.

Previous papers in this series have enumerated 4-connected 3-dimensional nets by considering 'out-of-plane' linkages between parallel congruent 3-connected 2-dimensional nets. In this paper, we continue with this procedure and develop some general rules which govern the construction of such nets involving zigzag (z) and sawtooth (s) chains (Smith, 1979).

Enumeration: general relations

In a 3-connected 2-dimensional net, conversion of a single horizontal edge into a zigzag chain converts two vertices from 3-connected to 4-connected. If this process is used to link a stack of parallel congruent 3-connected 2-dimensional nets into a 4-connected 3-dimensional net, then all vertices of the 4-connected net have two h (horizontal) and two z (zigzag) edges incident. Consider a path through the 3-dimensional net, restricted to the plane of an original 2-dimensional net. As there are two h edges incident to each vertex, a path can always approach and leave each vertex once. Consequently, each vertex lies on an infinite horizontal path through the 4-connected 3-dimensional net; note that a circuit (a path that begins and ends at the same vertex) may be considered as an infinite path. Thus 4-connected 3-dimensional nets are constructed from the possible distributions of z linkages over a 3-connected 2-dimensional net, subject to the constraint that: (1) *every vertex must lie on an infinite h path in the plane of the original 2-dimensional net*.

When a horizontal edge of a 3-connected 2-dimensional net is converted into a zigzag chain, the vertices at each end of the z edge are at different heights. For the final 3-dimensional net to be 4-connected, it is necessary for each polygonal circuit of the initial 2-dimensional net to close. This is illustrated in Figure 1, which shows a hexagon into which three z edges have been introduced; the circuit around the hexagon does not close, and hence the initial vertex a is not 4-connected. As each z edge introduces a vertical displacement: (2) *the number of z edges in any polygonal circuit must be even*.

As a corollary of these two rules: (3) *z edges must connect infinite h paths of different heights*. Using these rules, the possible 4-connected 3-

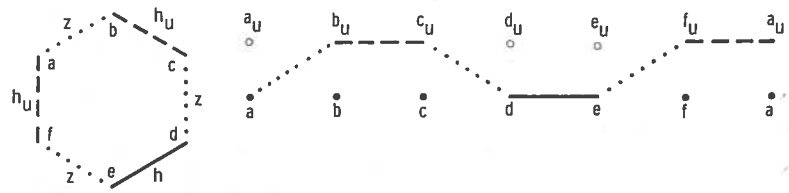


Fig. 1. To the left is a hexagon with vertices a–f; there are three *z* edges (marked by dots) and three *h* edges (marked by full and broken lines); *h* edges in the plane of the original hexagon are marked by full lines, and *h* edges above (h) or below the plane of the original hexagon are marked by broken lines. To the right, the hexagon is opened out and viewed from within the plane of the original hexagon; in this view, the *z* edges are seen as inclined and the *h* edges as horizontal. It is apparent that the odd number of *z* edges in the hexagon means that the polygonal path around the hexagon does not close.

dimensional chains can be rigorously enumerated and retrieved. Nets containing sawtooth chains can be generated from nets based on zigzag chains by sigma-transformations (Shoemaker et al., 1973) in the planes of alternate 2-dimensional nets. The nets are represented by mapping the allowable *h*/*z* configurations on the corresponding 3-connected 2-dimensional net. From a geometrical viewpoint, *h* and *z* edges are of equal length, and thus in projection *h* edges are 1.4 times as long as *z* edges. However, our arguments are topological rather than geometrical, and thus for simplicity, all edges are shown as of equal length in projection. The geometrical feasibility of the derived nets was tested by model building, and from these models the circuit symbols of the nets were derived.

Derivation of *z* chain nets

Combination of zigzag chains with the regular and semi-regular 3-connected 2-dimensional nets 6^3, 3.12^2, 4.8^2 and 4.6.12 was considered by Smith (1979), and all possibilities with translational symmetry for the 6^3 and 3.12^2 nets were evaluated.

The 4.8^2 net: let us consider the application of the above rules to the 4.8^2 net. First, we introduce an octagonal circuit of *h* edges into the net (Fig. 2a). From each vertex on this circuit (1–8), a *z* edge must extend outwards. From rule (2), the fourth edge of each square adjacent to the original octagon must be an *h* edge, and by rule (3), it must be at a different height relative to the *h* edges of the central octagon. The fact that there must be two *h* edges incident to every vertex forces the final arrangement of edges in Figure 2a. There are two possibilities for the next arrangement of edges moving away from the central octagon. The neighbouring octagons (2–5) can have four *z* edges, as in Figure 2b, and this forces the next set of

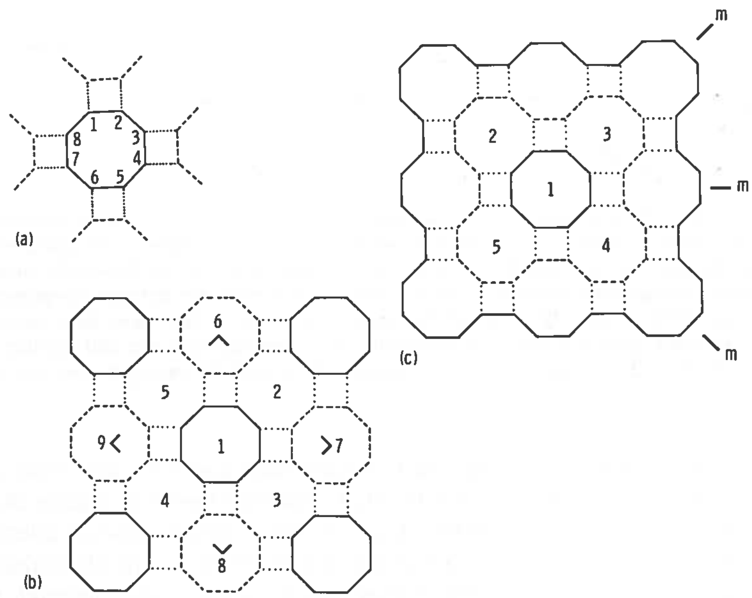


Fig. 2. Octagonal *h* circuits in the 4.8^2 net: (a) an octagonal *h* circuit (vertices 1–8) in the 4.8^2 net; (b) an octagonal *h* circuit (octagon 1) with the neighbouring octagons having four *z* edges; this forces octagons 6–9 to be *h* circuits (at a different level) and eventually produces this translationally symmetric net; (c) an octagonal *h* circuit (octagon 1) with neighbouring octagons (2–5) having two *z* edges; continuation of the two *z* edge arrangement forces this radially symmetric net. L indicate corners of unit cell.

octagons (6–9) to be *h* circuits. Continuation of this process produces a net with translational symmetry, the characteristics of which are listed in Table 1; this is net 93 of Smith (1979). Alternatively, the octagons 2–5 can have two *z* edges, as in Figure 2c. Continuation of this arrangement forces the remainder of the net, which has radial symmetry. Note that this radial net has diagonal mirror symmetry (see Figure 2c), and within each sector of the net there is translational symmetry. Such nets may have application in the study of contact twins and/or sectorial growth mechanisms.

Some *h* circuits may be nested to form larger "building blocks" of concentric *h* circuits that can then form nets with translational symmetry. The simplest net is shown in Figure 3; an octagonal *h* circuit is surrounded by a 24-membered *h* circuit to form a "square" fragment of net that is then repeated to form a net with translational symmetry. There is an infinite family of nets of this sort, with increasingly large fundamental building blocks. The larger nested units may also be combined with simple octagonal *h* circuits or different nested units.

Nets with local translational symmetry can change outwards into nets with radial symmetry. For example, Figure 4 shows a net with a central

Table 1. 3-dimensional 4-connected nets based on addition of zigzag chains to 4.8^2, 4.6.12 and $(5^28)_2(5.8^2)_1$.

Figure number	Arbitrary number	2D net	Z	Circuit symbol	Z	Space group	a (Å)	b (Å)	c (Å)	γ (°)
2b	93z	4.8^2	8	(4^26^38)	16	$I4/mmm$	13	a	5	—
2c	369z	4.8^2	—	Radial	—	$4/mmm$	—	—	5	—
3	370z	4.8^2	32	(4^26^38)	64	$I4/mmm$	26	a	5	—
4	371z	4.8^2	—	Radial	—	$4/mmm$	—	—	5	—
5a	372z	4.8^2	4	(4.6^5)	8	$I4/mmm$	7	a	5	—
5b	373z	4.8^2	8	(4^26^38)	8	$Imcm$	9	11	5	—
5c	374z	4.8^2	16	(4^26^38)	16	$Amam$	16	16	5	—
6a	375z	4.8^2	16	(4^26^38)	32	$Cmmm$	16	32	5	—
6b	376z	4.8^2	48	(4^26^38)	96	$Cmmm$	16	95	5	—
7a	95z	4.6.12	12	(4^26^4)	12	$P6_3/mmc$	13	a	5	—
7b	377z	4.6.12	—	Radial	—	$\bar{6}m2$	—	—	5	—
7c	378z	4.6.12	—	Radial	—	$\bar{6}m2$	—	—	5	—
8a	379z	4.6.12	180	*	180	$P\bar{6}m2$	52	a	5	—
8b	380z	4.6.12	—	Radial	—	$\bar{6}m2$	—	—	5	—
9a	381z	4.6.12	—	Radial	—	$6/mmm$	—	—	5	—
9b	382z	4.6.12	48	$(4^26^4)_1(4^26^38)_1$	48	$P6/mmm$	26	a	5	—
10a	383z	4.6.12	12	$(4^26^4)_1(4^26^38)_2$	24	$Ccmm$	22	15	5	—
10b	384z	4.6.12	24	$(4^26^4)_1(4^26^38)_2$	24	$Pnmm$	12	23	5	—
10c	385z	4.6.12	36	$(4^26^4)_1(4^26^38)_2$	36	$P2_1/m$**	12	30	5	120
11	386z	4.6.12	96	$(4^26^4)_1(4^26^38)_1$	96	$Pmab$	25	44	5	—
14a	243z	$(5^28)_2(5.8^2)_1$	6	$(5^36^3)_1(5^46.8)_1(5^26^38)_1$	12	$A2/m$	8	14	5	108
14b	98c	$(5^28)_2(5.8^2)_1$	6	$(5.6^5)_1(5^46.8)_2$	12	$Ccmm$	15	7	5	—
14c	387z	$(5^28)_2(5.8^2)_1$	12	$(5^36^3)_1(5.6^5)_1(5^46.8)_3(5^26^38)_1$	24	$A2/m$	8	28	5	108
14d	388z	$(5^28)_2(5.8^2)_1$	18	$(5^36^3)_1(5^46.8)_1(5^26^38)_1$	36	$A2/m$	26	14	5	99
14e	389z	$(5^28)_2(5.8^2)_1$	18	$(5^36^3)_2(5.6^5)_1(5^46.8)_4(5^26^38)_2$	18	$P2_1/m$	8	21	5	108
14f	390z	$(5^28)_2(5.8^2)_1$	18	$(5^36^3)_1(5.6^5)_2(5^46.8)_5(5^26^38)_1$	36	$A2/m$	8	42	5	108
14g	391z	$(5^28)_2(5.8^2)_1$	24	$(5^36^3)_1(5.6^5)_1(5^46.8)_3(5^26^38)_1$	24	$P2_1/m$	8	28	5	108
16a	392z	$(5^28)_2(5.8^2)_1$	12	$(5^36^3)_1(5.6^5)_1(5^46.8)_3(5^26^28^2)_1$	24	$A2/m$	9	26	5	90
16b	244z	$(5^28)_2(5.8^2)_1$	12	$(5.6^5)_1(5^46.8)_2$	12	$Pnmm$	9	13	5	—
16c	245z	$(5^28)_2(5.8^2)_1$	12	$(5^36^3)_1(5^46.8)_1(5^26^38)_1$	12	$Pbmm$	9	13	5	—
16d	393z	$(5^28)_2(5.8^2)_1$	36	$(5^36^3)_1(5.6^5)_2(5^46.8)_5(5^26^38)_1$	36	$Pbmm$	9	39	5	—
16e	394z	$(5^28)_2(5.8^2)_1$	36	$(5^36^3)_2(5.6^5)_1(5^46.8)_4(5^26^38)_2$	36	$Pnmm$	9	39	5	—
16f	395z	$(5^28)_2(5.8^2)_1$	24	$(5^36^3)_1(5.6^5)_1(5^46.8)_3(5^26^38)_1$	24	$P2mm$	9	26	5	—

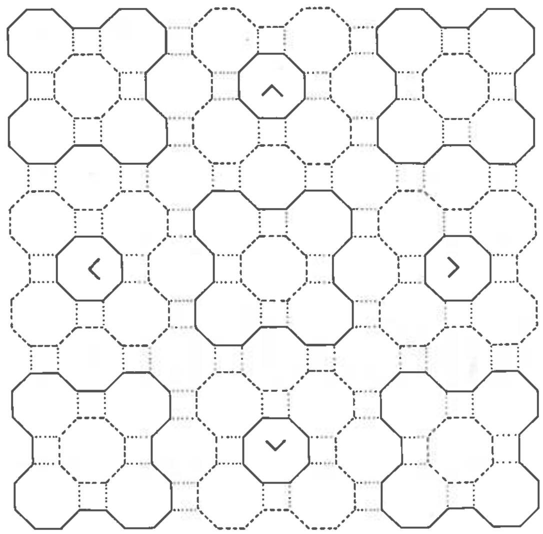


Fig. 3. In 4.8^2, an octagonal *h* circuit has neighbouring octagons with two *z* edges each, forming a 'nested' building block of concentric *h* circuits that by translation generates this net, the simplest of an infinite family of nets based on 'nested' building blocks.

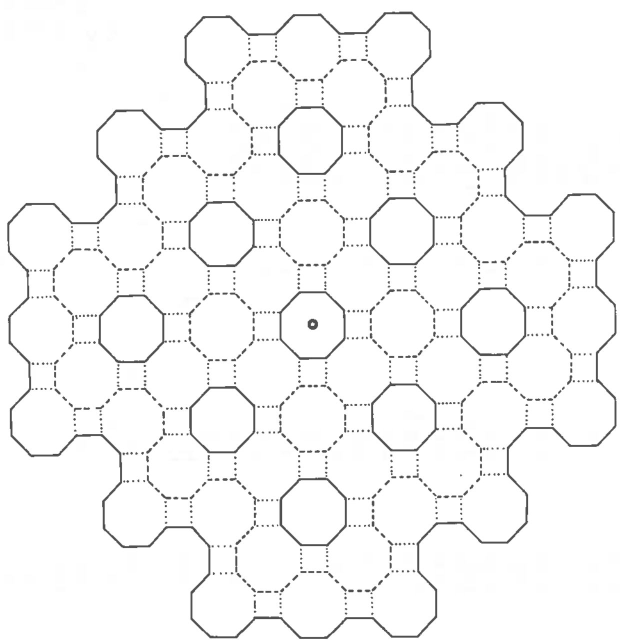


Fig. 4. A core of net 93, grading outwards into a net of radial symmetry; there is an infinite number of nets of this particular type. ☆ indicates origin of radial net.

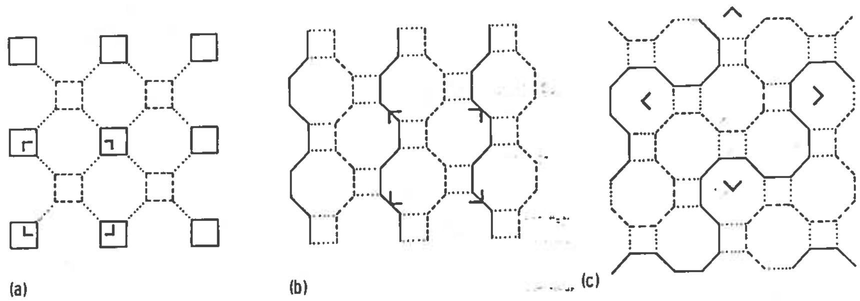


Fig. 5. Square h circuits and infinite linear h paths in the 4.8^2 net: (a) square h circuits completely forces this net; (b) insertion of z edges on two 4.8 edges in a *trans* configuration with regard to the octagons; (c) insertion of z edges on two non-*trans* 4.8 edges.

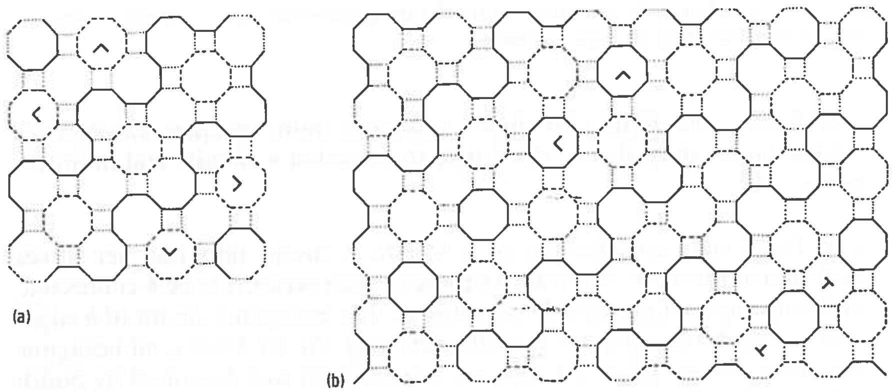


Fig. 6. Combination of octagonal h circuits and infinite h paths in the 4.8^2 net: (a) the simplest member; (b) a more complex member of this infinite family. ⊥ indicates center of unit cell edge.

core of octagonal h circuits with translational symmetry, changing outwards into a net with radial symmetry. There is an infinite family of these nets with different types of translationally symmetric cores. The radial net cannot change outwards into a net with octagonal h circuits and translational symmetry.

Insertion of a square circuit of h edges completely forces the remainder of the net (Fig. 5a). Insertion of z edges on two 4.8 edges in a *trans* configuration with regard to the octagon results in infinite h paths (Fig. 5b). Both of these nets were given by Smith (1979). Insertion of z edges on two 4.8 edges in a non-*trans* configuration forces the net given in Figure 5c; this is a new net.

Octagonal h circuits can be combined with infinite h paths to produce another infinite family of nets; Figure 6a shows the simplest member of

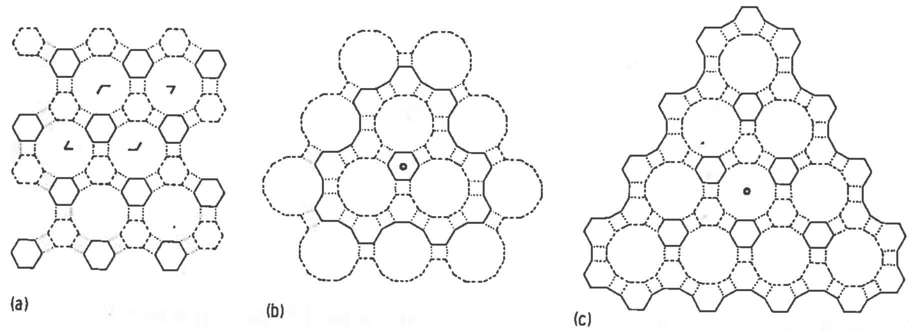


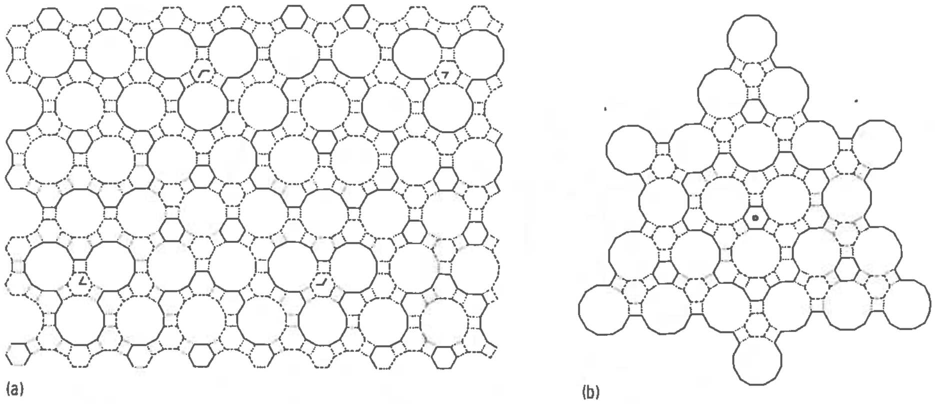
Fig. 7. Insertion of hexagonal h circuits into the 4.6.12 net: (a) all hexagons are h circuits; (b) the hexagons nearest to the original hexagonal h circuit have two z edges; this immediately produces a nested arrangement which can be continued to form this radial net; (c) a translationally symmetric core, changing outwards into a radially symmetric net; an infinite family of these is possible.

this family, and Figure 6b shows a slightly more complex example. A similar family may also be developed from nested h circuits and infinite h paths.

The 4.6.12 net: introduction of a square h circuit into this net forces violation of rule (1) in the nearest squares if each vertex is to be 4-connected, and thus this configuration is not allowed. If a hexagonal circuit of h edges is introduced, there are two possible nets (Fig. 7a, b). Firstly, all hexagons may be h circuits (Fig. 7a); this net (number 95) was described by Smith (1979) and is the basis of the cancrinite structure. In the second net, the hexagons nearest to the central h circuit are allowed to have two z edges; continuation of this restriction out from the centre produces the radial net of Figure 7b. The hexagonal h circuits of Figure 7a can combine with the radial net of Figure 7b to produce an infinite family of radial nets, an example of which is given in Figure 7c. Nested h circuits can also combine with simple hexagonal h circuits to form an infinite family of translationally symmetric nets (e.g. Fig. 8a) and an infinite family of radial nets (Fig. 8b).

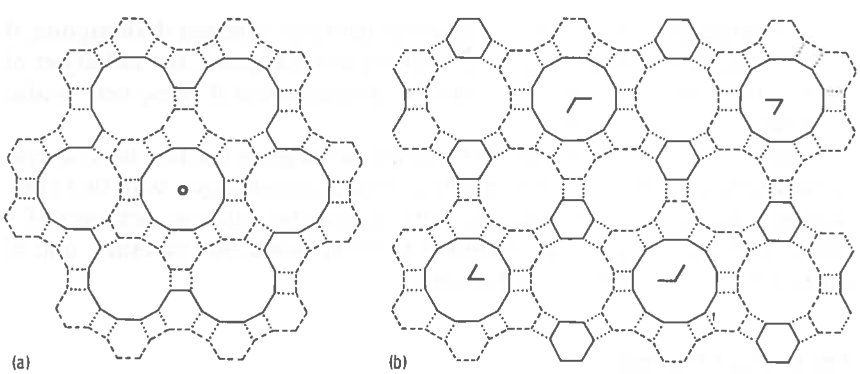
Consider the insertion of a dodecagonal circuit of h edges in the 4.6.12 net. Application of rules (1) and (2) to the adjacent squares and hexagons forces a nested arrangement of h circuits that, if continued, results in the radial net of Figure 9a. Finite nested arrangements of h circuits can combine with single h circuits (e.g. Fig. 9b) to form an infinite family of translationally symmetric nets and an infinite family of radially symmetric nets.

Consider the insertion of two z edges into a dodecagon. If they are *trans*, the net in Figure 10a results, with infinite h paths. If they are not *trans* (and not *cis*), the net in Figure 10b results (again with infinite h paths)



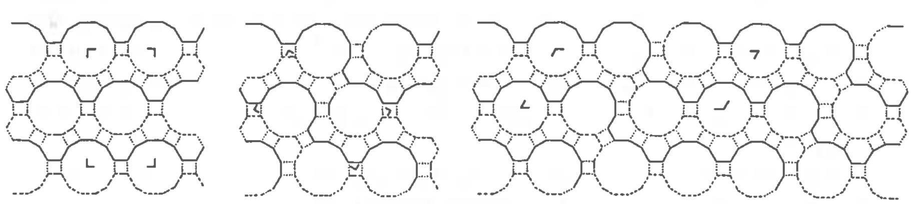
(a) (b)

Fig. 8. Combination of nested *h* circuits and simple hexagonal *h* circuits in 4.6.12 to form (a) a net with translational symmetry; (b) a net with radial symmetry. An infinite family of these nets is also possible.



(a) (b)

Fig. 9. Insertion of dodecagonal *h* circuits into 4.6.12: (a) a simple radial net centered on the initial *h* circuit; (b) combination of nested octagonal and simple hexagonal *h* circuits to form a net with translational symmetry; infinite families of both radial and translationally symmetric nets of these types are possible.



(a) (b) (c)

Fig. 10. Nets with infinite *h* paths in 4.6.12: (a) introduction of two *z* edges on *trans* 4.12 edges of dodecagons; (b) introduction of two *z* edges on 4.12 edges of dodecagons with the *z* arrangement staggered in adjacent dodecagons; (c) the simplest combination of (a) and (b); an infinite family of these are possible.

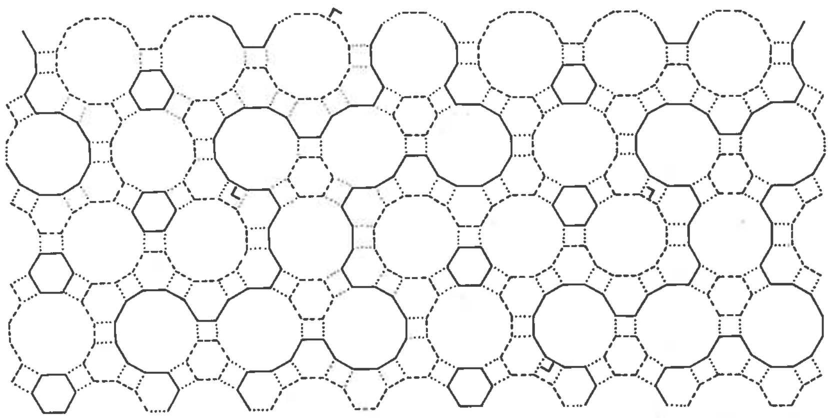


Fig. 11. Combination of *h* circuits with infinite *h* paths; an infinite family is possible, of which this complex net is one of the simpler examples.

if the arrangement of *z* edges is staggered between adjacent dodecagons; if the arrangement in alternate dodecagons is not staggered, the radial net of Figure 9a results. An infinite family of combinations if these nets is also possible (e.g. Figure 10c).

Combinations of *h* circuits with infinite paths gives rise to a very diverse infinite family of nets. As an example, consider a dodecagon with two next-nearest-edges as *z* edges (Fig. 11). This forces the adjacent hexagon of *h* edges, and the net may be continued to form numerous variants; one of the simpler forms is shown in Figure 11.

The $(5^2.8)_2(5.8^2)_1$ net

There are three nets of this type, the centered net, the oblique net and the zigzag net (Smith and Bennett, 1984). The oblique net is a geometric distortion of the centered net, and the two are topologically identical. The zigzag net is topologically distinct, and thus there are two distinct $(5^2.8)_2(5.8^2)_1$ nets to be considered. A prominent feature of these nets is the infinite chains of edge-sharing pentagons. Any path that crosses one of these chains must touch at least two pentagons, and thus a consideration of the allowed *h* and *z* configurations for pentagonal dimers is a useful way to proceed.

According to rules (1), (2) and (3), there are three possible arrangements of *h* and *z* edges over an edge-sharing pentagonal dimer, labelled types *a*, *b* and *c* in Figure 12. Consideration of the ways in which these configurations 'fit' the various varieties of $(5^2.8)_2(5.8^2)_1$ net will lead to the enumeration of the possible 4-connected 3-dimensional nets of this type. Another useful fact when considering *h* and *z* edges in these nets is that

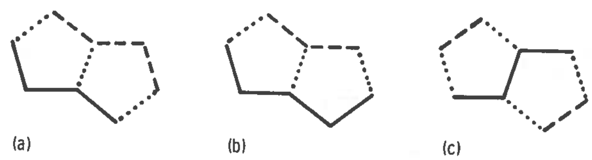


Fig. 12. The three possible arrangements of *h* and *z* over an edge-sharing pentagonal dimer.

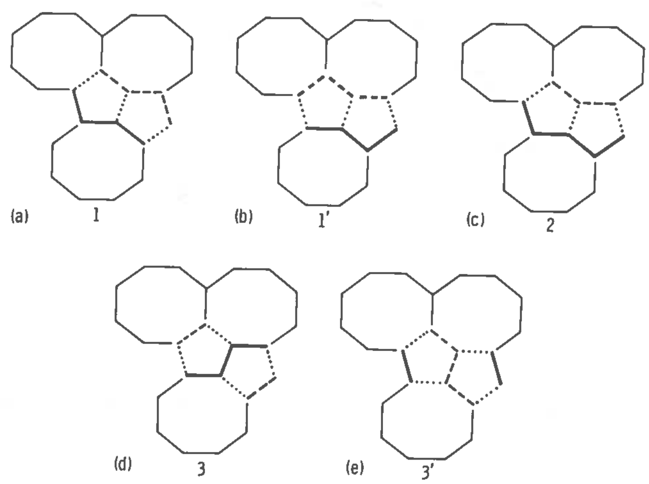


Fig. 13. The ways in which the dimeric configurations of Figure 12 will fit into the centered $(5^2.8)_2(5.8^2)_1$ net.

pentagonal and/or dodecagonal rings of *h* edges always lead to a linkage violation, and hence are forbidden.

Centered $(5^2.8)_2(5.8^2)_1$ *net*: the type *a* dimeric configuration will fit into the centered net in two distinct ways (Fig. 13a, b), labelled types 1 and 1′. Type *b* will fit into the net in only one way (Fig. 13c, type 2); altering the orientation of this dimer merely produces a symmetrically equivalent arrangement. Type *c* will fit into the net in only one way (Fig. 13d, type 3). Another orientation of type *c* in the net is distinct (Fig. 13e), but forces *h* edges around three adjacent sides of an adjacent pentagon; by rules (1) and (2), this forces a pentagonal *h* circuit, and it is easily shown that a pentagonal *h* circuit is not possible in any of the $(5^2.8)_2(5.8^2)_1$ nets.

All nets may be retrieved by considering possible combinations of types 1, 1′, 2 and 3. Of course, not all combinations are allowed as the dimers must be able to link together to form the linear pentagonal chains characteristic of the parent 2-dimensional net; for example, types 1 and 1′

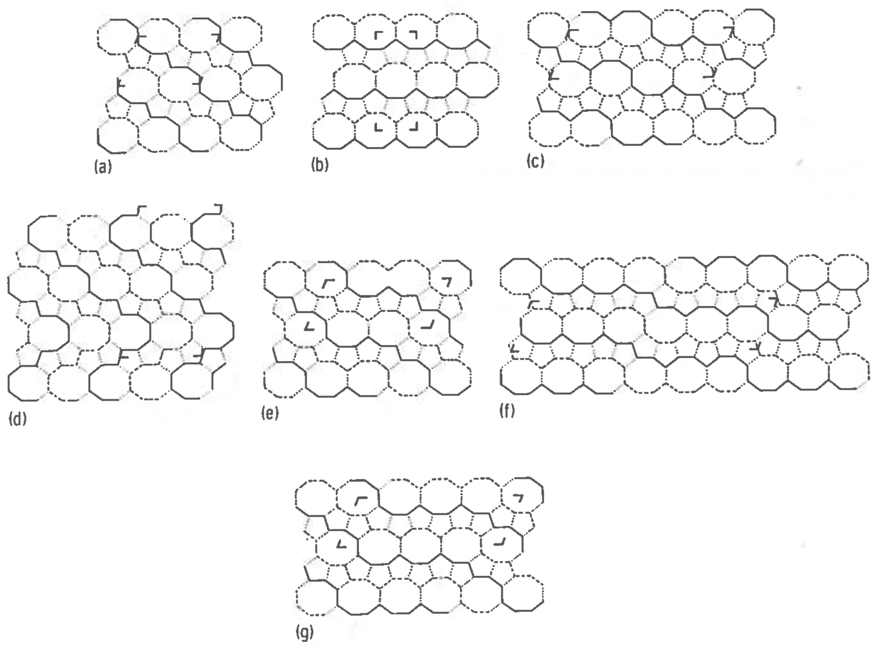


Fig. 14. Nets derived from the centered $(5^2.8)_2(5.8^2)_1$ net by insertion of *h* and *z* edges; see text for details.

cannot combine (without the presence of type 2) as type 1 has only *h* edges in the edge-sharing positions whereas type 2 has only *z* edges at these positions.

Consider first all combinations of a single type configuration. All combinations are allowed, and are shown in Fig. 14a–d. For type 1, only the straight pentagonal chain is forced; this chain can be combined with itself (as is the case in Fig. 14a) or with any other chain which has a comparable interchain linkage; the net in Fig. 14a is number 243 of Smith and Bennett (1984). For type 1′, the whole net is forced (Fig. 14b) and is number 98c of Smith and Bennett (1984). Type 2 also forces the complete net (Fig. 14c) and is a new net. Type 3 is equivalent to type 1, but as the orientation is different, an infinite series of 4-connected 3-dimensional nets may be developed by cross-linking type 1 chains and type 3 chains in various ratios; the simplest is net 242 of Smith and Bennett (1984), which has a type 1 : type 3 ratio of 1 : 1; a slightly more complex example, which a type 1 : type 3 ratio of 2 : 1 is shown in Fig. 14d.

We will now consider all combinations of two types of dimeric configurations. As shown above, types 1 and 1′ alone cannot combine. Combination of types 1 and 2 forms an infinite series of nets, of which that

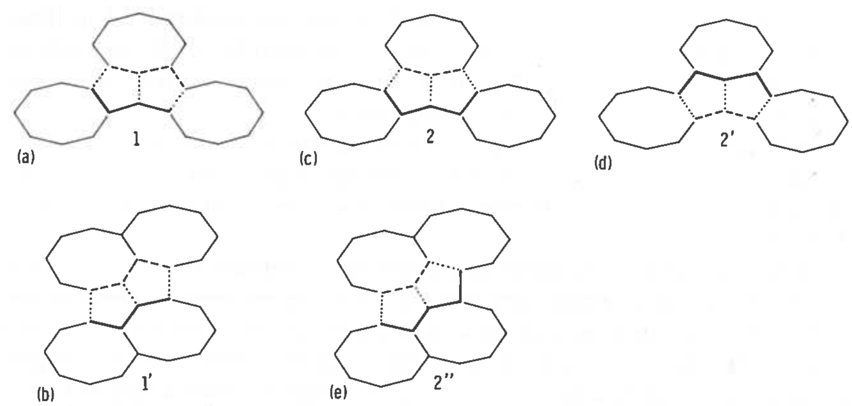


Fig. 15. The way in which the dimeric configurations of Figure 12 will fit into the zigzag $(5^2.8)_2(5.8^2)_1$ net.

in Fig. 14e is the simplest; the linear configuration $2 \cdot 2$ is forced, but then may combine with type 1 dimers in any proportion. Type 1 and 3 cannot combine. Types 1′ and 2 can combine to form an infinite family of nets, subject to the condition that the type 2 dimers link in pairs across a common *h* edge; the simplest member $(1' \cdot 2 \cdot 2)^{\circ}$ is shown in Figure 14f. Types 1′ and 3 both have only *z* edges as the linking pentagonal edges, and thus can combine in any ratio and order to form another infinite family. The alternating sequence $(1' \cdot 3)^{\circ}$ is the simplest arrangement, and this is the same as the simple $(2)^{\circ}$ net (Fig. 14c); $(1' \cdot 3 \cdot 3)^{\circ}$ is the next member of the series, and is equivalent to $(1 \cdot 2 \cdot 2)^{\circ}$ (Fig. 14e), and $(1' \cdot 1' \cdot 3)^{\circ}$ is equivalent to $(1^1 \cdot 2 \cdot 2)^{\circ}$ (Fig. 14f). Attempts to combine types 2 and 3 always seem to lead to linkage violations in or across adjacent pentagonal chains.

There are four possible combinations of the three types of dimeric configurations: 11′2, 11′3, 123 and 1′23. Of these, the pentagonal chain linking edges of type 1 are both *h*, whereas the analogous edges in types 1′ and 3 are both *z*, therefore combinations involving 11′3 cannot form. For the combination 11′2, these form an infinite series subject to the restriction that type 1 cannot link to type 1′; the simplest net is shown in Figure 14g. Attempts to make nets from types combinations 123 and 1′23 always lead to linkage violations in neighbouring chains.

Attempts to construct nets out of all four types of dimeric configurations always lead to linkage violations in nearest or next-nearest neighbouring pentagonal chains, although we cannot discount the possibility that some extremely complex nets do exist.

Zigzag $(5^2.8)_2(5.8^2)_1$ *net*: the type *a* dimeric configuration (Fig. 12) will fit into the centered net in two distinct ways (Fig. 15a, b), labelled 1 and

1′. The type *b* dimeric configuration will fit into the centered net in three distinct ways (Fig. 15c–e), but type 2″ inevitably leads to linkage violations. The type *c* configuration also leads to linkage violations, leaving types 1, 1′, 2 and 2′ as allowable arrangements.

All single combinations of these arrangements are valid, and are shown in Fig. 16a–c. The simple type 1 is a new net, type 2 and type 2′ are nets 244 and 245 of Smith and Bennett (1984), and type 1′ is identical to type 2 (Fig. 16b).

When considering multiple combinations of configurations 1, 1′, 2 and 2′, type 1′ cannot combine with the rest as it cannot mate to them in the $(5^2.8)_2(5.8^2)_1$ net, and permissible combinations involve only types 1, 2 and 2′. Consider the 1 · 2 combinations; type 2 can only link through *z* edges, whereas type 1 can link through both *h* and *z* edges. Consequently all type 1 arrangements must occur in pairs linked through their *h* edge (i.e. 1 · 1). These can then link to type 2 arrangements to form an infinite series of nets, the simplest of which is shown in Fig. 16d. For 1 · 2′ combinations, a similar situation occurs, except that 2′ links solely through *h* edges and thus the type 1 arrangements must pair by linking through their *z* edges. Again an infinite series results, the simplest one being shown in Fig. 16e. Obviously types 2 and 2′ cannot pair together.

For the combination of all three types, the only restriction is that types 2 and 2′ cannot link, and within this constraint an infinite series of nets results. The simplest is shown in Fig. 16f.

Radial nets: a radial net must involve concentric *h* circuits, and hence must be centered either on a pentagonal or an octagonal *h* circuit. In both the centered and zigzag nets, insertion of a pentagonal *h* circuit forces a linkage error. For the zigzag net, an octagonal *h* circuit forces linkage errors, but for the centered net there are no errors and a radial net is completely defined (Fig. 17). This net has *mm* plane point symmetry at the origin, and has translational symmetry within each asymmetric part of the net.

Derivation of *s* chain nets

A *z* chain may be converted to an *s* chain by a σ-transformation (Shoemaker et al., 1973) through alternate vertices, and to a *c* (crankshaft) chain by applying the transformation through each vertex. Thus the 3-dimensional 4-connected *z* chain nets considered above may be transformed into *s* chain nets by applying σ-transformations through alternate vertices. The simplest way in which this may be done is to apply the transformation through alternate prototype 2-dimensional nets, and this is the only procedure considered in detail here. It is also possible to apply the transformation at different heights in adjacent prototype *z* chains; if it becomes necessary to

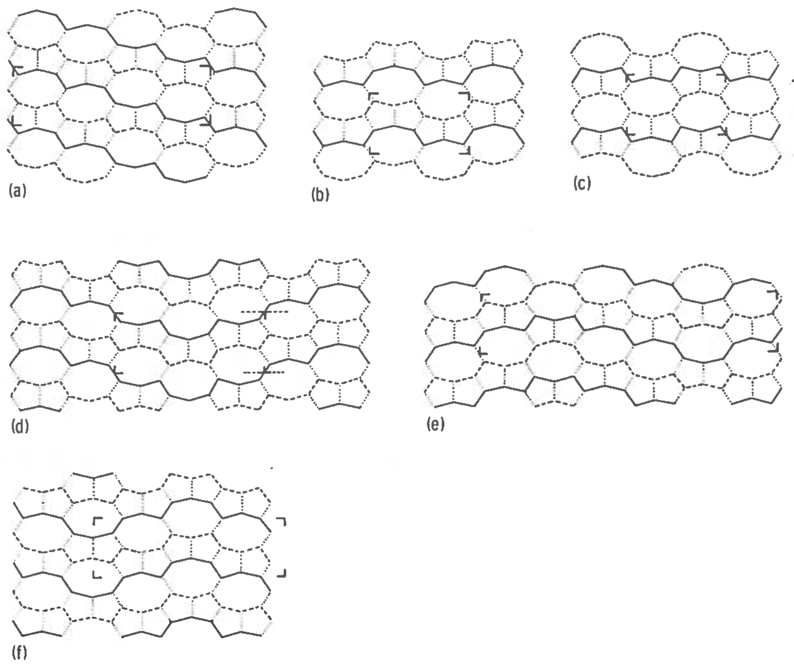


Fig. 16. Nets derived from the zigzag $(5^2.8)_2(5.8^2)_1$ net by insertion of *h* and *z* edges; see text for details.

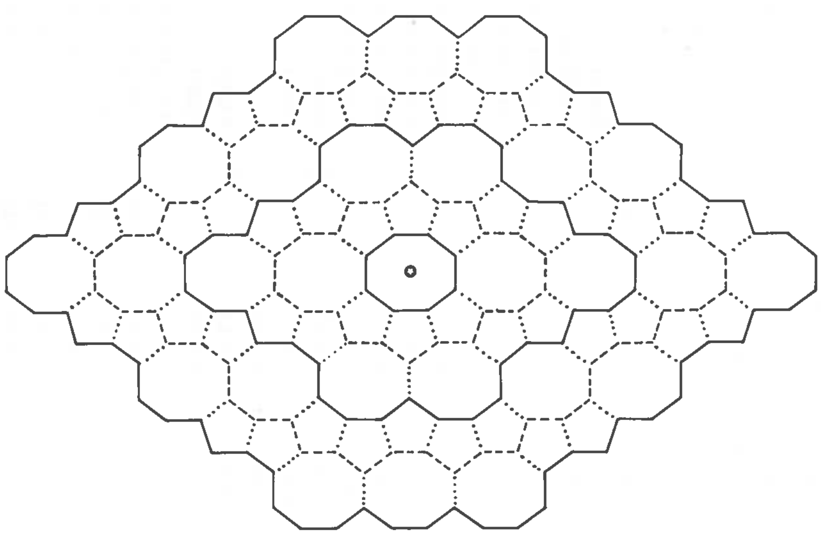


Fig. 17. The radial net centered on an octagonal *h* circuit in the centered $(5^2.8)_2(5.8^2)_1$ net.

Table 2. 3-dimensional 4-connected nets based on addition of sawtooth chains to 4.8^2, 4.6.12 and $(5^2.8)_2(5.8^2)_1$.

Figure number	Arbitrary number	2D net	Z	Circuit symbol	Z	Space group	a (Å)	b (Å)	c (Å)	γ (°)
2b	93s	4.8^2	12	$(4^3.6^3)_2(4^2.6.8^3)_1$	24	*P4/mmm*	13		7	—
2c	369s	4.8^2	—	Radial	—	*4/mmm*	—	—	7	—
3	370s	4.8^2	48	$(4^3.6^3)_2(4^2.6.8^3)_1$	96	*P4/mmm*	26	a	7	—
4	371s	4.8^2	—	Radial	—	*4/mmm*	—	—	7	—
5a	372s	4.8^2	6	$(4^3.6^2.8)_2(4.6.8^4)_1$	12	*P4/mmm*	7	a	7	—
5b	373s	4.8^2	12	$(4^3.6^3)_2(4^2.6.8^3)_1$	12	*Pmam*	9	11	7	—
5c	374s	4.8^2	24	$(4^3.6^3)_2(4^2.6.8^3)_1$	24	*Pmam*	16	16	7	—
6a	375s	4.8^2	24	$(4^3.6^3)_2(4^2.6.8^3)_1$	48	*Cmmm*	16	32	7	—
6a	375s′	4.8^2	24	$(4^3.6^3)_2(4^2.6.8^3)_1$	48	*Cmmm*	16	32	7	—
6b	376s	4.8^2	72	$(4^3.6^3)_2(4^2.6.8^3)_1$	144	*Cmmm*	16	95	7	—
6b	376s′	4.8^2	72	$(4^3.6^3)_2(4^2.6.8^3)_1$	144	*Cmmm*	16	95	7	—
7a	95s	4.6.12	18	$(4^3.6^3)_2(4^2.6^2.8^2)_1$	18	*P3m1*	12	a	7	—
7b	377s	4.6.12	—	Radial	—	$\bar{6}m2$	—	—	7	—
7c	378s	4.6.12	—	Radial	—	$\bar{6}m2$	—	—	7	—
8a	379s	4.6.12	270	*	270	$P\bar{6}m2$	52	a	7	—
8b	380s	4.6.12	—	Radial	—	$\bar{6}m2$	—	—	7	—
9a	381s	4.6.12	—	Radial	—	*6/mmm*	—	—	7	—
9b	382s	4.6.12	72	$(4^3.6^3)_4(4^2.6^2.8^2)_1(4^2.6^3.8)_1$	72	*P6/mmm*	26	a	7	—
9b	382s′	4.6.12	72	$(4^3.6^3)_4(4^2.6^2.8^2)_1(4^2.6^3.8)_1$	72	*P6/mmm*	26	a	7	—
10a	383s	4.6.12	18	$(4^3.6^3)_6(4^2.6^3.8)_2(4^2.6^2.8^2)_1$	36	*Ccmm*	22	15	7	—
10b	384s	4.6.12	36	$(4^3.6^3)_6(4^2.6^3.8)_2(4^2.6^2.8^2)_1$	36	*Pnmm*	12	23	7	—
10c	385s	4.6.12	54	$(4^3.6^3)_6(4^2.6^3.8)_2(4^2.6^2.8^2)_1$	54	$P2_1/m$**	12	30	7	120
11	386s	4.6.12	144	$(4^3.6^3)_4(4^2.6^3.8)_1(4^2.6^2.8^2)_1$	144	$P2_1/m$	25	44	7	—
14a	243s	$(5^2.8)_2(5.8^2)_1$	18	$(4^2.5^2.6.7)_4(4^2.5.6^2.7)_2(5^6.4.8)_2$ $(5^3.6.8^2)_1(5^2.6.8^3)_1$	18	*P2/m*	8	14	7	108

14b	98cs	$(5^2.8)_2(5.8^2)_1$	18	$(4^2.5^2.6.7)_4(4^2.5.6^2.8)_2(5^4.6.8)_2(5.6.8^4)_1$	18	*C2mm*	15	7	7	–
14c	387s	$(5^2.8)_2(5.8^2)_1$	36	$(4^2.5^2.6.7)_8(4^2.5.6.7)_2(4^2.5.6^2.8)_2$ $(5^4.6.8)_3(5^3.6.8^2)_1(5^2.6.8^3)_1(5.6.8^4)_1$	36	*P2/m*	8	28	7	108
14d	388s	$(5^2.8)_2(5.8^2)_1$	48	$(4^2.5^2.6.7)_4(4^2.5.6^2.7)_2(5^4.6.8)_1$ $(5^3.6.8^2)_1(5^2.6.8^3)_1$	48	*P2/m*	26	14	7	99
14e	389s	$(5^2.8)_2(5.8^2)_1$	27	$(4^2.5^2.6.7)_8(4^2.5.6^2.7)_8(4^2.5.6^2.8)_2$ $(5^4.6.8)_4(5^3.6.8^2)_2(5^2.6.8^3)_2(5.6.8^4)_1$	27	*Pm*	8	21	7	108
14f	390s	$(5^2.8)_2(5.8^2)_1$	54	$(4^2.5^2.6.7)_{12}(4^2.5.6^2.7)_2(4^2.5.6^2.8)_4$ $(5^4.6.8)_5(5^3.6.8^2)_1(5^2.6.8^3)_1(5.6.8^4)_2$	54	*P2/m*	8	42	7	108
14g	391s	$(5^2.8)_2(5.8^2)_1$	36	$(4^2.5^2.6.7)_6(4^2.5.6^2.7)_4(4^2.5.6^2.8)_2$ $(5^4.6.8)_3(5^3.6.8^2)_2(5.6.8^4)_1$	36	*Pm*	8	28	7	108
16a	392s	$(5^2.8)_2(5.8^2)_1$	18	$(4^2.5^2.6.7)_8(4^2.5.6^2.7)_2(4^2.5.6^2.8)_2$ $(5^4.6.8)_3(5^3.6.8^2)_1(5^2.6.8^3)_1(5.6.8^4)_1$	36	*P2/m*	9	26	7	90
16b	244s	$(5^2.8)_2(5.8^2)_1$	18	$(4^2.5^2.6.7)_4(4^2.5.6^2.8)_2(5^4.6.8)_2(5.6.8^4)_1$	18	*P2mm*	9	13	7	–
16c	245s	$(5^2.8)_2(5.8^2)_1$	18	$(4^2.5^2.6.7)_2(4^2.5.6^2.7)_4(5^4.6.8)_1(5^2.6.8^3)_2$	18	*Pbmm*	9	13	7	–
16c	245s′	$(5^2.8)_2(5.8^2)_1$	18	$(4^2.5^2.6.7)_2(4^2.5.6^2.7)_4(5^4.6.8)_1(5^2.6.8^3)_2$	18	*Pbmm*	9	13	7	–
16d	393s	$(5^2.8)_2(5.8^2)_1$	54	$(4^2.5^2.6.7)_6(4^2.5.6^2.7)_2(4^2.5.6^2.8)_2$ $(5^4.6.8)_3(5^3.6.8^2)_1(5.6.8^4)_1$	54	*Pbmm*	9	39	7	–
16d	393s′	$(5^2.8)_2(5.8^2)_1$	54	$(4^2.5^2.6.7)_8(4^2.5.6^2.8)_2(5^4.6.8)_3$ $(5^2.6.8^3)_1(5.6.8^4)_1$	54	*Pbmm*	9	39	7	–
16e	394s	$(5^2.8)_2(5.8^2)_1$	54	$(4^2.5^2.6.7)_{10}(5^4.6.8)_2(5^2.6.8^3)_2(5.6.8^4)_1$	54	*P2mm*	9	39	7	–
16f	395s	$(5^2.8)_2(5.8^2)_1$	36	$(4^2.5^2.6.7)_6(4^2.5.6^2.7)_4(4^2.5.6^2.8)_2$ $(5^4.6.8)_3(5^3.6.8^2)_2(5.6.8^4)_1$	36	*2Pbmm*	9	26	7	–
16f	395s′	$(5^2.8)_2(5.8^2)_1$	36	$(4^2.5^2.6.7)_{10}(4^2.5.6^2.8)_2(5^4.6.8)_3$ $(5^2.6.8^3)_2(5.6.8^4)_1$	36	*P2mm*	9	26	7	–

* not constructed in this study.
** first setting used for monoclinic space groups.

consider such nets, they may be derived by extension of the reasoning used here.

For those *z* chain nets which the *h* edges at different heights have the same arrangements (e.g. Fig. 2b), it is immaterial at which height the σ-transformation occurs. For *z* chain nets in which the *h* edges have different arrangements at different heights (e.g. Fig. 6a), two *s* chain nets are derived (Table 2) depending on the height at which the σ-transformation is done; each of these nets will have the teeth of the saw chains pointing in different directions. Such nets occur for the illustrations of Figures 6a, b, 9b, 16c, d, f and are designated by the unprimed and primed *s* nets of Table 2.

Discussion

This work completes the enumeration of 4-connected 3-dimensional nets based on simple zigzag and saw chain linkages of the 6^3, 3.12^2, 4.8^2, 4.6.12 and $(5^2.8)_2(5.8^2)_1$ net. Representative structures have been described by Smith (1979) and Smith and Bennett (1984), and none of the additional nets derived here are known as structures as yet. However, the radial nets are of particular interest and may have application to twinning and sectorial growth mechanisms. The radially symmetric nets of Figures 3c, 7b, 8b, 9a, etc. all consist of sectors within which the net has translational symmetry; however, there is not translational symmetry between sectors, which are related by mirror planes. Thus crystals in which such 'sector twins' occur may actually be represented by a single continuous net with radial symmetry, rather than a series of discrete nets with different orientations. In terms of crystal growth, it would seem more reasonable to consider growth of a single radially symmetry phase rather than growth of several different crystals in a particular angular relationship. In the same vein, the nets of Figures 4 and 7c are of interest, containing a core that has translational symmetry, changing outwards into radially symmetric nets that consist of sectors with internal translational symmetry but externally related by mirror operations. Such nets would seem to be of use in zoned crystals which consist of a core of continuous single-phase material surrounded by 'sector twins'. Again this complex situation can be described by a single albeit complex net.

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