atom positions in the ordered layers together with that of the superstructure of the $2H$ type. In the first ordered layer, the positions indicated by circles with the letter L are occupied by Ti atoms and the sites indicated by other circles are vacant. The second ordered layer consists of the positions indicated by squares for $12R$-$TC\sqrt{3}a\sqrt{3}ac$, $4H$-$M\sqrt{3}a\sqrt{3}b2c$ and $4H$-$M\sqrt{3}b\sqrt{3}a3c$ and by triangles for $6R$-$M\sqrt{3}a\sqrt{3}b2c$, and the sites with the letter M are occupied by Ti atoms. In this manner, the stacking sequences are represented by $LMNPLMNP\cdots$ for $4H$-$M\sqrt{3}a\sqrt{3}b2c$ and $LMNPQRLMNPQR\cdots$ for $12R$-$TC\sqrt{3}a\sqrt{3}ac$, $6R$-$M\sqrt{3}a\sqrt{3}b2c$ and $4H$-$M\sqrt{3}b\sqrt{3}a3c$, respectively.

It has been revealed that short-range order exists in a crystal of $12R$ near $Ti_{1.25}S_2$. The crystal as grown at 873 K by a chemical-transport process has three-dimensional short-range order, *i.e.* $12R$-(SRO)(SRO)(SRO). A crystal annealed at 723 K has two-dimensional long-range order and one-dimensional short-range order, *i.e.* $12R$-$H2a2a$(SRO). The supercell dimension suggests that the arrangement model in an ordered layer of $12R$-$H2a2a$(SRO) is as follows: one quarter of the sites are occupied by Ti atoms and three quarters are regularly vacant. This arrangement has been known as an ordered layer in $2H$-$M2b2a2c$ (Bando *et al.*, 1980), the composition of which is very similar to that of $12R$-$H2a2a$(SRO).

Once formed, polytypes such as $12R$ or $4H$ can exist over a large composition range (Saeki & Onoda, 1982*a*,*c*). As described in this paper, each polytype has a tendency to generate the superstructure according to the composition. The arrangement model in an ordered layer is dependent on the composition of the specimen, while the periodicity along the c axis arises from the definite stacking sequence of the ordered layers.

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Tetrahedral AX_2 Structures

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Abstract

Structures built from tetrahedral AX_4 groups sharing some or all of their X atoms may be classified according to the numbers of tetrahedra to which the X atoms belong. This survey is restricted to structures of composition AX_2 in which all AX_4 groups share their X atoms in the same way, and it is concerned with the topology rather than the geometry of the structures. If v_x is the number of X atoms of each AX_4 group common to x such groups (that is, x is the coordination number of X) then $\sum v_x = 4$ and $\sum v_x/x = 2$. A study is made of the types of structure, finite, one-, two-, or three-dimensional, which are possible in the three classes, I ($v_2 = 4$), II ($v_1 = 1$, $v_3 = 3$), and III ($v_1 = 1$, $v_2 = 1$, $v_4 = 2$).

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Introduction

Since the number of structures that can be built from tetrahedral coordination groups AX_4 is indefinitely large we shall simplify the problem by introducing a number of restrictions, of which the first two may be described as topological and the others as geometrical: (i) All AX_4 groups share their X atoms in the same way with other similar groups, that is, they are *topologically* equivalent; differences in symmetry leading to *crystallographically* non-equivalent A atoms will be disregarded. (ii) The primary classification will be based on the coordination numbers of the X atoms, but only the values 1, 2, 3, 4, 6, and 8 will be considered. The values 5 and 7 are excluded on the grounds that they are unlikely to be found in realizable structures, and values greater than 8 are not consistent with (iii) and (iv). (iii) It must be possible to build a structure with *regular* tetrahedra. (iv) The distance between any pair of X atoms belonging to *different* tetrahedra must not be less than the distance X–X within a tetrahedron, that is, the edge length. (v) The sharing of *faces* between tetrahedra is excluded because it leads to unreasonably small distances between A atoms.

Table 1. *Tetrahedral structures classified according to numbers (v_x) of x-connected vertices*

Formula	v_1	v_2	v_3	v_4	v_6	v_8	Examples
AX_4	4						XeO_4
A_2X_7	3	1					Cl_2O_7
AX_3	2	2					SO_3
A_2X_5	1	3					P_2O_5
	2			2			–
AX_2		4					SiO_2, HgI_2, $(GaP)S_4$
	1		3				AlOCl
	1	1		2			–
A_2X_3		2		2			–
		1	3				Si_2N_2O
	1				3		–
A_3X_4			4				Si_3N_4
		2			2		–
AX				4			ZnS, LiOH
			2		2		–
		1			3		–
A_3X_2					4		Be_3N_2
A_2X						4	Li_2O

In a tetrahedral structure A_mX_n in which all AX_4 groups share their X atoms in the same way let v_x be the number of X atoms of each AX_4 group which are common to x such groups, that is, x is the coordination number of X. The value of x may, of course, be different for different X atoms of the same AX_4 group. Then $\sum v_x = 4$ and $\sum v_x/x = n/m$. Table 1 lists solutions of these equations for a number of simple formulae A_mX_n, the portion enclosed by the heavy lines indicating the field covered in the present study. To derive the structures corresponding to the solutions of Table 1 we adopt a topological approach. If x is not greater than 2 for any X atom (as in class I) it is sufficient to consider the number of tetrahedra to which each is joined (by sharing X atoms) and to describe the structure in terms of the basic net of A atoms. However, if there are X atoms with values of $x \geq 3$ these, together with the A atoms, must be included in the description of the topology of the structure, as in class II.

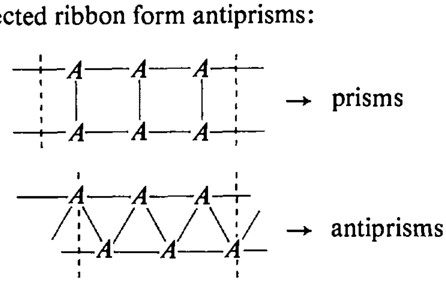
First we remind the reader of the types of connected system which are possible if each point is connected to some number (p) of similarly connected points. The points in the basic connected systems so derived may be replaced by any object (*e.g.* a tetrahedron) capable of forming the appropriate number of connections. For $p = 1$ the only possible structure is a pair of connected points, and for $p = 2$ the only possibilities are rings or an infinite chain. However, for $p \geq 3$ structures of all four major types can be formed, finite (*e.g.* polyhedra), or systems extending indefinitely in one, two, or three dimensions (1D, 2D, or 3D nets). Thus for three connections from each point the possible structures include all polyhedra having three edges meeting at each vertex [of which the simplest are three of the regular solids, tetrahedron (3^3), cube (4^3), and pentagonal dodecahedron (5^3), seven of the Archimedean solids (Table 2), and the infinite family of prisms ($4^2.m$)], the simple (1D) ladder, planar 3-connected nets [of which the simplest is the tessellation of hexagons (6^3)], and 3D nets (of which the most symmetrical are the 'uniform' nets, 7^3, 8^3, 9^3, 10^3, and 12^3). An introduction to 3D nets is available (Wells, 1975) and also more detailed treatments (Wells, 1977, 1979). The

Table 2. *The Archimedean semi-regular polyhedra*

	Symbol	Number of vertices		Symbol	Number of vertices
3-connected			4-connected		
Truncated tetrahedron	3.6^2	12	Cuboctahedron	3^24^2	12
Truncated cube	3.8^2	24	Rhombicuboctahedron	3.4^3	24
Truncated octahedron	4.6^2	24	Icosidodecahedron	3^25^2	30
Truncated cuboctahedron	$4.6.8$	48	Rhombicosidodecahedron	3.4^25	60
Truncated dodecahedron	3.10^2	60	5-connected		
Truncated icosahedron	5.6^2	60	Snub cube	3^44	24
Truncated icosidodecahedron	$4.6.10$	120	Snub dodecahedron	3^45	60

symbol n^p of a polyhedron or net shows the numbers of points (n) in the shortest circuit (ring) and the superscript is the number of such circuits meeting at each point. For a 3-connected Archimedean solid, which has faces of more than one kind, the sum of the superscripts is 3, *e.g.* 4.6^2 for the truncated octahedron, and similarly for 2D or 3D nets containing circuits of more than one kind, as in the planar net 4.8^2 or the 'Archimedean' 3D nets 6.8^2 and 6.10^2 (Wells, 1979, p. 10). For a 4-connected polyhedron or 2D net the sum of the superscripts is 4 (*e.g.* the square planar net, 4^4), and for a 3D 4-connected net it is 6 (*e.g.* diamond, 6^6).

In addition to the simplest p-connected systems noted above we shall refer later to certain more complex 1D and 2D structures. Just as portions of the simple chain of 2-connected points may be joined end-to-end to form rings so portions of the (3-connected) ladder form prisms and portions of the 4-connected ribbon form antiprisms:



Strips cut from 2D nets may be wrapped around a cylinder and joined together to form infinite 1D structures (cylindrical or tubular chains), as shown in Fig. 1 for the simplest 4-connected planar net. In turn, portions of such tubular chains could be joined end to end to form torus-like structures of triangular, square, *etc.* cross section. In the sequence

layer ($p \geq 3$)	→	tubular chain	→	torus
2D		1D		finite

the connectedness (p) of each point remains the same. Another possibility is the linking of two p-connected layers by an additional link from each point *on the same side of the layer* to form a double layer in which each point becomes $(p + 1)$-connected. An example is the double-layer anion in $Ca(Al_2Si_2O_8)$. We see that the *topologically* possible structures for a 4-connected subunit such as a tetrahedral AX_4 group sharing each X atom with one other such group include not only the well-known simple layer of red HgI_2 and the 3D frameworks of silica and aluminosilicate structures but also finite structures (polyhedral or torus-like), tubular chains, and double layers.

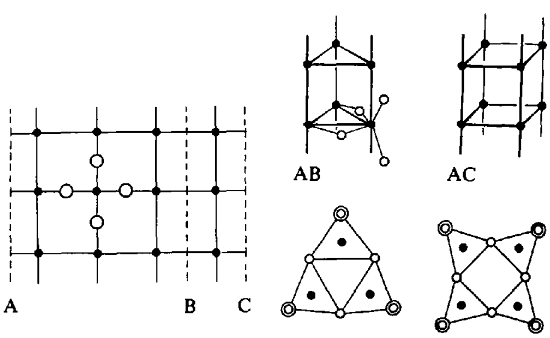


Fig. 1. Formation of tubular chains from strips AB, AC, and so on of the planar 4^4 net.

We now consider in turn the three solutions of Table 1 for structures of composition AX_2, namely,

class I: $v_2 = 4$

class II: $v_1 = 1, v_3 = 3$

class III: $v_1 = 1, v_2 = 1, v_4 = 2.$

Structures of class I: $v_2 = 4$

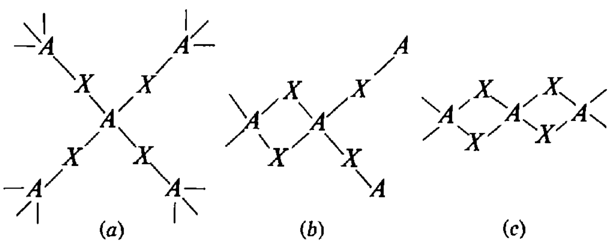
The 2-coordination of each X atom can be realized by

(a) the sharing of each vertex with a different tetrahedron,

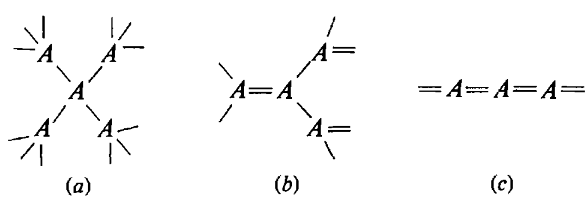
(b) the sharing of one edge and two vertices, or

(c) the sharing of two edges which have no common vertex.

Since all X atoms in structures of this class are 2-connected and since 2-connected points may be eliminated from a topological diagram the bond diagrams



may be simplified to



The gross topology of a structure (whether a finite, 1D, 2D, or 3D system) may be described in terms of the number of tetrahedra to which each is connected. This is the number of A atoms to which each is connected, disregarding the difference between double and single links, that is, between edge and vertex sharing. The required structures are accordingly based on 4-, 3-, or 2-connected nets of A atoms in (a), (b), and (c) respectively. We need not consider (c) further since it leads only to the linear chain of $BeCl_2$ or SiS_2 or to improbably large (unknown) rings formed from portions of such a chain.

Structures of class I(*a*)

We have noted in the *Introduction* that structures of all four main types (finite, 1D, 2D, and 3D) are *topologically* possible if AX_4 groups share each X atom with one other similar group. However, polyhedral complexes, in which the A atoms would be situated at the vertices of 4-connected polyhedra, cannot be built from *tetrahedral* AX_4 groups, nor can the torus-like complexes noted above. [The Pt_6Cl_{12} molecule is an example of a polymeric $(AX_2)_n$ complex based on the octahedron, but it is built from planar AX_4 groups.]. Three types of structure are therefore possible in class I(*a*).

1*D structures:* Tubular chains may be formed from strips of planar 4-connected nets of various widths, as shown in Fig. 1 for the 4^4 net. The end-on views of these chains show that they consist of vertex-sharing rings stacked above one another.

2*D structures:* The layer structure of red HgI_2 is based on the simplest planar 4-connected net (4^4), and the double-layer anion in $Ca(Al_2Si_2O_8)$ results from joining together two layers based on the simplest planar 3-connected net (6^3).

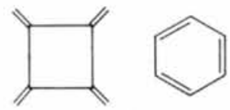
3*D structures:* The vertex-sharing 3D AX_2 structures are based on the numerous 3D 4-connected nets, and range from cristobalite-like structures based on the simplest of these nets (the diamond net, 6^6) to the complex frameworks of aluminosilicates such as felspars and zeolites.

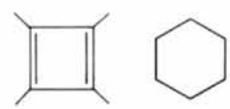
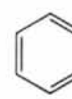
Structures of all the above types are also possible if the simple AX_4 groups are replaced by 'super-tetrahedral' groups A_4X_{10} formed from four AX_4 tetrahedra joined as in the P_4O_{10} molecule or the $Si_4S_{10}^{4-}$ ion. Such groups may be joined by sharing each of the outermost vertices with one other similar group to form structures of class I(*a*), when the composition becomes A_4X_8 (AX_2). Examples are the layer structure of orange HgI_2 and the 3D structure of ZnI_2.

Structures of class I(*b*)

Structures in which each tetrahedron is joined to three others by sharing one edge and two vertices ($>A=$) are of all four major types, that is, the A atoms are situated at the vertices of 3-connected polyhedra or at the nodes of 3-connected 1D, 2D, or 3D nets.

Polyhedral structures: The most symmetrical polyhedral structures are based on certain of the 3-connected regular and semi-regular (Archimedean) solids or on prisms. Those based on the tetrahedron or cube are not acceptable because they have very short interior X–X distances; the most symmetrical form of the pentagonal dodecahedral complex is illustrated in Fig. 2. We may also rule out the $A_{12}X_{24}$ structure based on the truncated tetrahedron because of short interior X–X distances, but structures can be built which are based on the other six 3-connected Archimedean solids (Table 2). There is not a unique structure corresponding to each of these polyhedra. Isomerism is possible in this family of structures because an edge of the polyhedron outlined by the A atoms may represent either a shared vertex (–) or a shared edge (=), subject to the condition that the bond arrangement at each vertex is $>A=$. For example, in the most symmetrical isomer of the truncated octahedral complex all four edges of each square face correspond to vertex sharing and all hexagonal faces are of the same kind, with alternate vertex and edge sharing, as shown in (*a*). In the less-symmetrical cubic isomer (*b*) there are hexagonal faces of two kinds,

(*a*)  $m3m$ isomer

(*b*)  and  $\bar{4}3m$ isomer,

and other less-symmetrical isomers include five with trigonal symmetry and possibly others of lower symmetry. There are at least two isomers of each of the other five structures of Table 3 based on Archimedean solids and of the pentagonal dodecahedral complex, but only the most symmetrical isomers are illustrated (Figs.

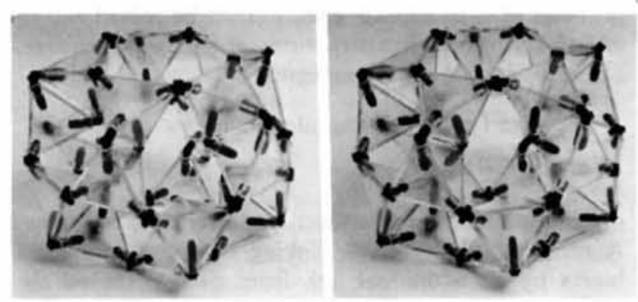


Fig. 2. The $A_{20}X_{40}$ structure based on the pentagonal dodecahedron.

Table 3. *Polyhedral structures of class* I(*b*): $v_2 = 4$

3-connected polyhedron defined by A atoms	Formula	4-connected polyhedron defined by inner (or outer) shell of X atoms	Fig.
5^3	$A_{20}X_{40}$	3^35	2
3.8^2	$A_{24}X_{48}$	3^24^2	3
4.6^2			4
$4.6.8$	$A_{48}X_{96}$	3.4^3	5
3.10^2	$A_{60}X_{120}$	3^25^2	6
5.6^2			7
$4.6.10$	$A_{120}X_{240}$	3.4^25	8

3–8). This isomerism is reminiscent of that of the octahedral Keggin complexes $A_{12}X_{40}$.

Since these polyhedral complexes, certainly the larger ones, are unlikely to form unless atoms of some kind occupy the central void, we include in Table 3 the shape of the polyhedral group formed by the inner X atoms of each complex. The X atoms of each complex fall into three groups. One half lie on links of the polyhedral shell, these being the shared vertices, and the remainder, in equal numbers, lie at the ends of shared edges, within or outside this shell. The isomerism of these complexes has not been studied in detail, but it has been noted that in the isomers of type (*b*) of 4.6^2, 4.6.8, and 4.6.10 the polyhedra defined by the inner X atoms are respectively 3.6^2, 3.8^2, and 3.10^2.

1D and prismatic structures: There is an indefinitely large number of isomers of the chain formed from tetrahedra each sharing two vertices and one edge; the

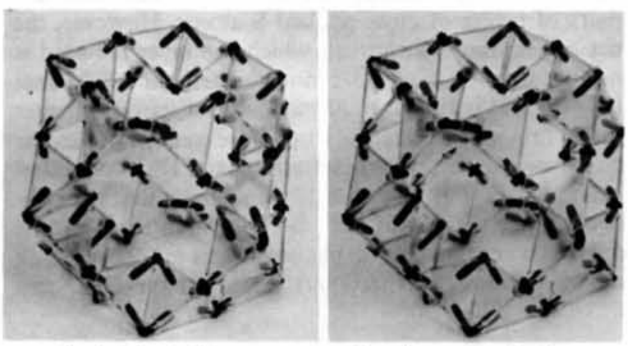


Fig. 3. The $A_{24}X_{48}$ structure based on the truncated cube.

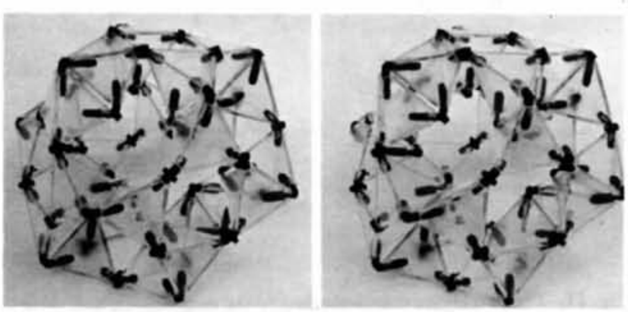


Fig. 4. The $A_{24}X_{48}$ structure based on the truncated octahedron.

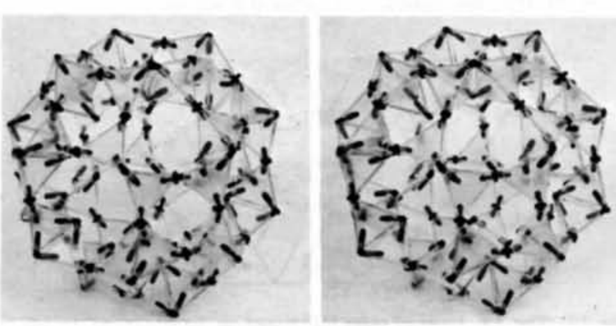


Fig. 5. The $A_{48}X_{96}$ structure based on the truncated cuboctahedron.

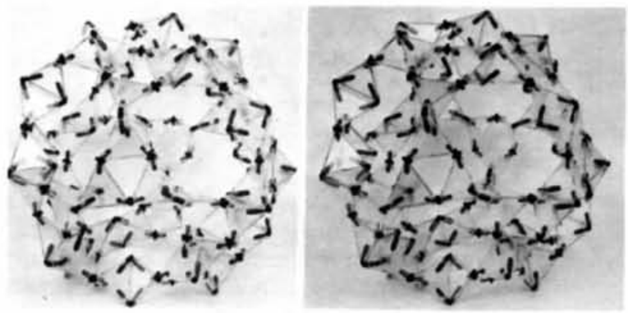


Fig. 6. The $A_{60}X_{120}$ structure based on the truncated dodecahedron.

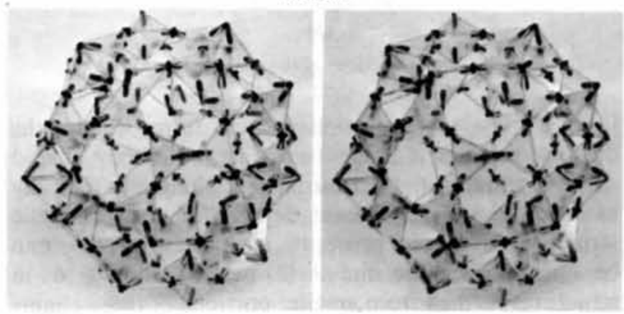


Fig. 7. The $A_{60}X_{120}$ structure based on the truncated icosahedron.

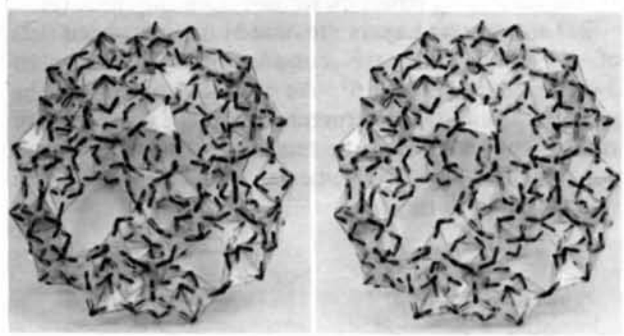


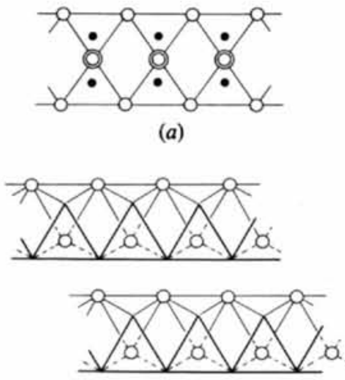
Fig. 8. The $A_{120}X_{240}$ structure based on the truncated icosidodecahedron.

simplest are shown at (*d*), (*e*), and (*f*). Two projections of the chain (*d*) are illustrated in Fig. 9. In Fig. 9(*a*) the

$$\begin{array}{ccc} \begin{array}{c} -A-A-A- \\ \Vert \quad \Vert \quad \Vert \\ -A-A-A- \end{array} & \begin{array}{c} -A=A-A= \\ | \quad | \quad | \\ -A=A-A= \end{array} & \begin{array}{c} -A=A-A= \\ | \quad | \quad | \\ =A-A=A- \end{array} \\ (d) & (e) & (f) \end{array}$$

shared edges are perpendicular to the plane of the paper; in Fig. 9(*b*) one face of each tetrahedron is parallel to that plane. The latter projection shows that the X atoms of this chain are in the positions of closest packing. Such chains could therefore be packed side by side to form a pair of layers of close-packed X atoms, between which A atoms occupy one half of the tetrahedral interstices. The circles in Fig. 9(*b*) represent the X atoms of one close-packed layer.

We now consider prismatic structures formed from portions of chains joined end to end. Those formed



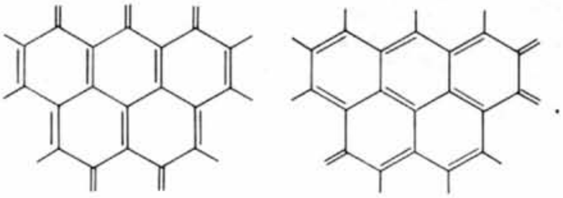
(a)

(b)

Fig. 9. Two projections of the chain (d) (see text).

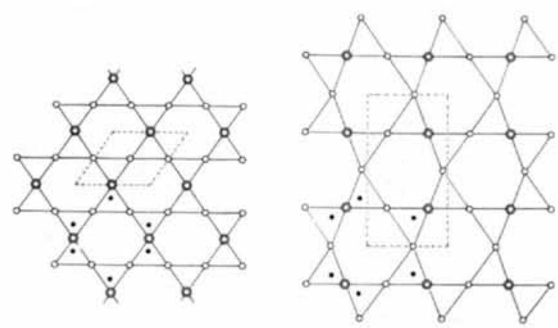
from the chain (d) are not likely to form because the distance between X atoms belonging to different shared edges is equal to the tetrahedral edge length in the fully extended chain, and would be smaller in a prismatic structure. However, prismatic structures $(A_4X_8)_n$ can be formed from the chains (e) and (f) if $n \geq 6$; in structures formed from smaller portions of these chains there would be short interior X–X distances. Fig. 10 shows the $A_{24}X_{48}$ structure formed from the chain (e).

2D structures: Layers are based on 3-connected nets of A atoms, and we consider first the simplest 3-connected 2D net, 6^3. As in the isomers of the polyhedral and chain structures different sequences of vertex and edge-sharing tetrahedra in a ring are possible. The two arrangements in which the sequence is the same in all rings are:



(i) (ii)

The corresponding layers built from tetrahedra are shown in Fig. 11, where the shared edges are perpendicular to the plane of the layer. Various configurations of these layers are possible, one of special interest being the most compact form of the layer of Fig. 11(i). This is illustrated in Fig. 12, the right-hand portion of which shows two rings of six tetrahedra and the left-hand portion indicates the basic topology of the layer. The X atoms form two parallel close-packed layers but only those of the lower layer are shown (larger open circles), and the A atoms at the two levels are indicated as small open and filled circles. This type of layer may be described as the tetrahedral analogue of the octahedral AX_2 layer (of CdI_2, $CdCl_2$, and polytypes), that is, a layer in which one half of the tetrahedral interstices are occupied by A atoms between a pair of layers of close-packed X atoms. No example is known of an AX_2 compound with a structure of this kind, but it was noticed that in $GaPS_4$ (Buck & Carpentier, 1973) tetrahedral groups (alternately GaS_4 and PS_4) each share an edge and two vertices to form such a layer. The Ga and P atoms together occupy one half of the tetrahedral interstices between alternate pairs of layers of close-packed S atoms. However, the net of Ga and P atoms on which the layer is based is not the simplest planar 3-connected net, but the 4.8^2 net (Fig. 13). It is therefore of interest to discover whether there are similar layers with close-packed X atoms based on the other two semi-regular 2D 3-connected nets, namely 3.12^2 and 4.6.12. It appears that the only two AX_2 structures of this class in which the X atoms form two complete close-packed layers are those based on 6^3 and 4.8^2; in the layers based on the 3.12^2 and



(i) (ii)

Fig. 11. The two layers corresponding to the diagrams (i) and (ii) in the text. The A atoms of only one ring are shown, as small black circles. The small open circles represent X atoms.

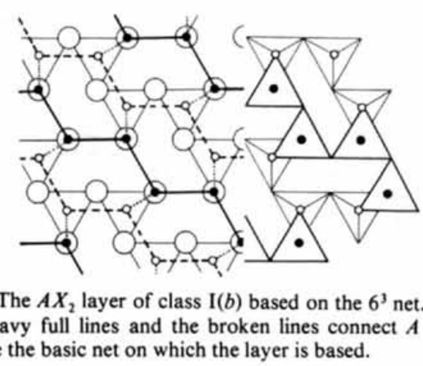


Fig. 12. The AX_2 layer of class I(b) based on the 6^3 net. At the left the heavy full lines and the broken lines connect A atoms and outline the basic net on which the layer is based.

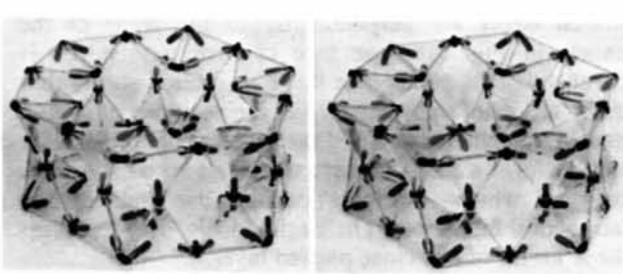


Fig. 10. Prismatic structure $A_{24}X_{48}$ formed from the chain (e) (see text).

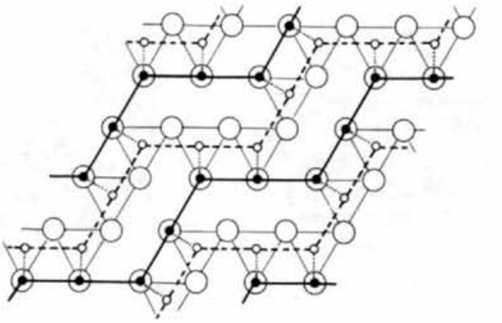


Fig. 13. The AX_2 layer of class I(b) based on the 4.8^2 net of A atoms.

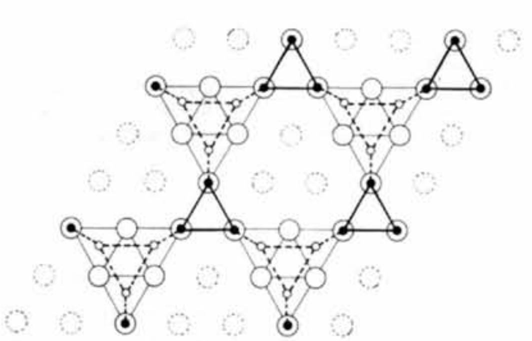


Fig. 14. The AX_2 layer of class I(b) based on the 3.12^2 net.

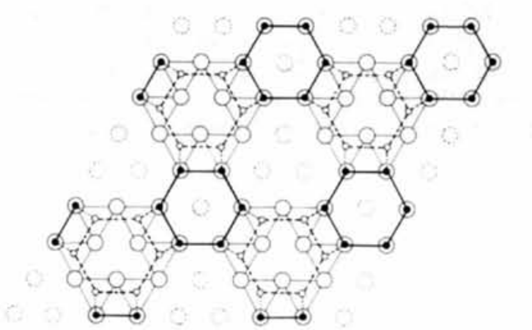


Fig. 15. The AX_2 layer of class I(b) based on the 4.6.12 net.

4.6.12 nets (Figs. 14 and 15) the X atoms occupy respectively $\frac{2}{3}$ and $\frac{3}{4}$ of the close-packed positions.

3D structures: No systematic study has been made of structures based on 3D 3-connected nets. They are presumably numerous, the most symmetrical being based on the n^3 nets ('uniform' nets of Wells, 1977) or the 'Archimedean' nets (Wells, 1979).

Structures of class II: $v_1 = 1, v_3 = 3$

The sharing of each of three vertices of every tetrahedron with two other tetrahedra can be realized in the following ways:

(a) vertices only shared (Fig. 16a),
(b) one edge of each tetrahedron shared (Fig. 16b),
(c) two edges of each tetrahedron shared (Fig. 16c), or
(d) three edges of each tetrahedron shared; for the single example see Fig. 24(a).

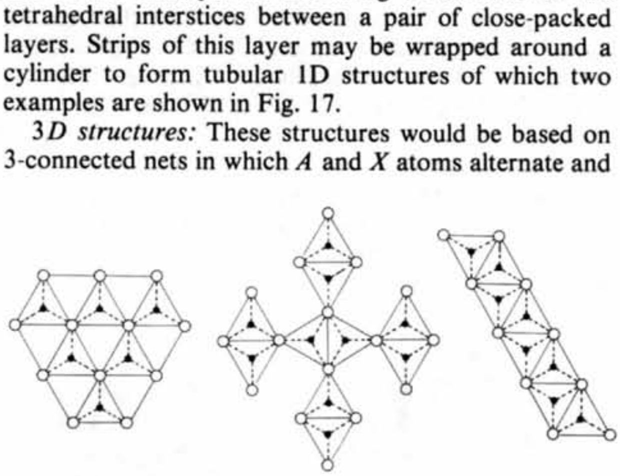
In all structures of this class each A atom is connected to three shared X atoms and each X to three A, and therefore the possible structures are based on 3-connected nets in which A and X atoms alternate. Accordingly all polygonal circuits in the nets must have even numbers of links (edges).

Structures of class II(a)

Here the smallest circuit is a ring of six atoms (alternately A and X) since a ring of $2A + 2X$ atoms implies edge sharing. This condition excludes all 3-connected polyhedra and all 2D 3-connected nets other than 6^3.

1D and 2D structures: The net 6^3 represents the topology of the layer of Fig. 16(a), from which the unshared X atoms are omitted. Since the unshared vertex of each tetrahedron may lie either above or below the plane of the paper an indefinitely large number of configurations of this layer is possible, one of which represents the structure of AlOCl (and GaOCl). The configuration with all unshared vertices on the same side of the plane of the shared X atoms is our fourth example of the filling of one-half of the tetrahedral interstices between a pair of close-packed layers. Strips of this layer may be wrapped around a cylinder to form tubular 1D structures of which two examples are shown in Fig. 17.

3D structures: These structures would be based on 3-connected nets in which A and X atoms alternate and



(a) (b) (c)

Fig. 16. The sharing of vertices and/or edges in the three families (a)–(c) of class II. The broken lines indicate the nets formed by the 3-connected A atoms (black circles) and 3-connected X atoms (open circles); the unshared X atoms are omitted.

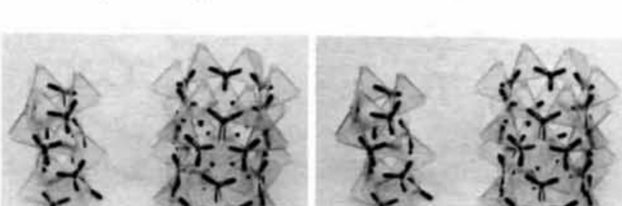


Fig. 17. Two tubular chains of class II(a).

all circuits have even numbers of links, this number being greater than six. The simplest 3-connected 3D nets of this kind are uniform nets 8^3, 10^3, and 12^3. It has not been ascertained whether any of these structures are geometrically possible, that is whether they can be constructed with reasonably regular tetrahedra and without any unacceptably short distances between X atoms of different tetrahedra.

Structures of class II(b)

Structures of all four major types are possible, polyhedral, 1D, 2D, and 3D.

Polyhedral structures: The polyhedra defined by the A and the shared X atoms taken together must be 3-connected and must have 4-gon faces. The structures derived from the cube and from prisms do not belong to class II(b), as noted later, but the relevant Archimedean solids 4.6^2, 4.6.8, and 4.6.10 produce the structures of Figs. 18, 19, and 20 and Table 4. The models illustrated in these figures and other stereo-pairs do not show the A atoms, for the connectors represent shared X atoms. For this reason the polyhedra of this group are perhaps more easily visualized in terms of the polyhedral shells outlined by the shared X atoms. These polyhedral shells must have pairs of edge-sharing triangular faces and five edges meeting at each vertex (see Fig. 16b). The most symmetrical are therefore the icosahedron (3^5), snub cube ($3^4.4$), and snub dodecahedron ($3^4.5$). In the icosahedral structure (Fig. 18) tetrahedra are placed on 12 of the 20 faces of a regular icosahedron, in the second (Fig. 19) on 24 of the 32 triangular faces of a snub cube, and in the third (Fig. 20) on 60 of the 80 faces of a snub dodecahedron.

1D and 2D structures: Because all 2D nets of this family must contain 4-gons the most symmetrical ones are the semi-regular nets 4.8^2 and 4.6.12. The AX_2 layers based on these nets are illustrated in Figs. 21 and 22. In the layer of Fig. 21 we have shown the unshared X atoms of each edge-sharing pair of tetrahedra lying on opposite sides of the plane of the layer, because if they lie on the same side there are very short X–X distances between these atoms (0·58 of the tetrahedron edge length). Tubular chains may be built from strips of this net. In the portion of the net shown in Fig. 21 there are four vertical strings of tetrahedra. In the

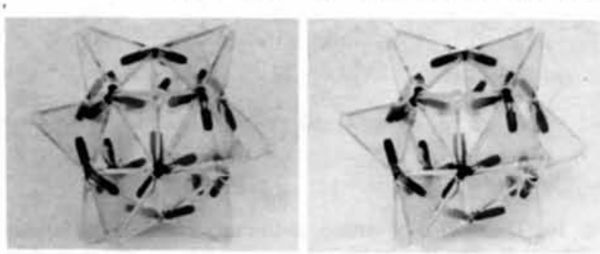


Fig. 18. The icosahedral complex $A_{12}X_{24}$ of class II(b).

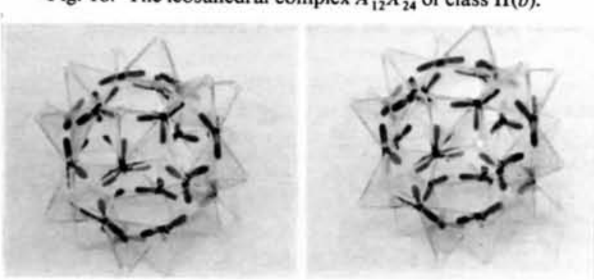


Fig. 19. The snub cube complex $A_{24}X_{48}$ of class II(b).

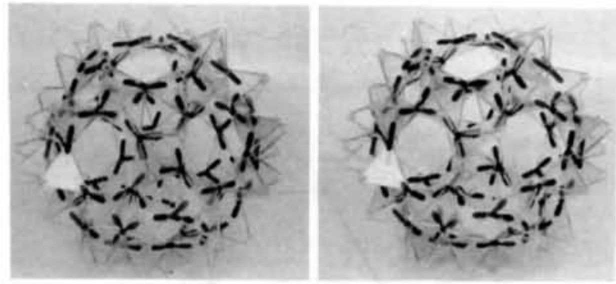


Fig. 20. The snub dodecahedral complex $A_{60}X_{120}$ of class II(b).

Table 4. *Polyhedral structures of class* II(b): $v_1 = 1$, $v_3 = 3$

Polyhedron defined by the A and the shared X atoms (3-connected)	Formula	Polyhedron defined by the shared X atoms (5-connected)	Fig.
4.6^2	$A_{12}X_{24}$	$3^4.3$	18
4.6.8	$A_{24}X_{48}$	$3^4.4$	19
4.6.10	$A_{60}X_{120}$	$3^4.5$	20

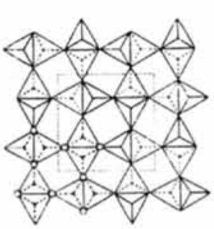


Fig. 21. AX_2 layer of class II(b) based on the 4.8^2 net, a portion of which is shown at the bottom left. Full lines and light broken lines represent tetrahedron edges. The heavier broken lines (bottom left) connect A atoms (small black circles) and 3-connected X atoms (open circles) which form the underlying net.

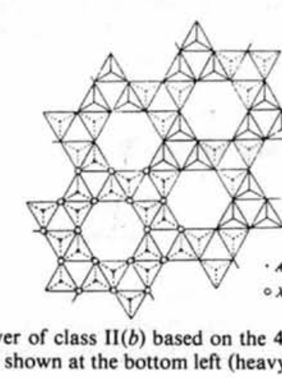


Fig. 22. AX_2 layer of class II(b) based on the 4.6.12 net, a portion of which is shown at the bottom left (heavy broken lines).

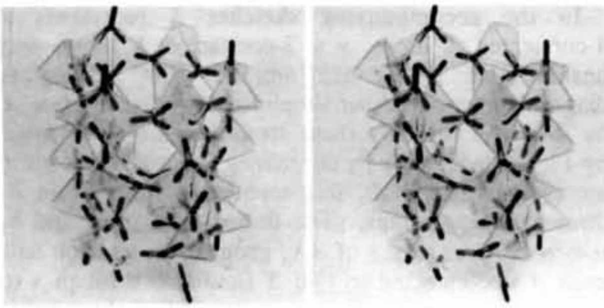


Fig. 23. Tubular chain of class II(b).

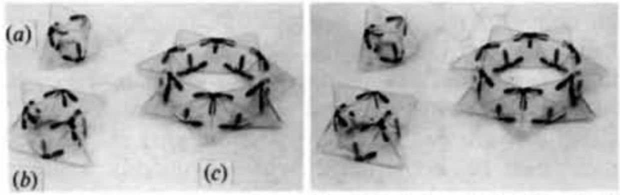
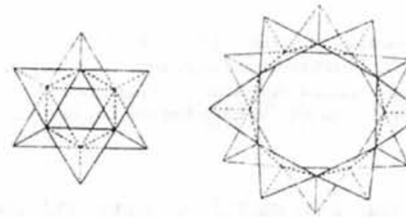


Fig. 24. Three finite complexes: (a) A_4X_8 of class II(d); (b) and (c) A_6X_{12} and $A_{12}X_{24}$ of class II(c).



(a) (b)

Fig. 25. Projections of the cyclic complexes A_6X_{12} and $A_{12}X_{24}$ of Fig. 24(b) and (c).

tubular chain formed from a strip of this width such short X–X distances cannot be avoided, but they do not occur in chains built from wider strips if, for example, the unshared X atoms of both tetrahedra of alternate edge-sharing pairs lie on the outer surface of the chain, as in Fig. 23. This chain is built from a strip of the layer six 'strings' in width, and the innermost (unshared) X atoms lie at the vertices of a column of face-sharing octahedra. Tubular chains may also be formed from the 4.6.12 net, but their detailed geometry has not been studied.

3D *structures:* These must be based on 3-connected nets in which A and X atoms alternate, and the nets must contain 4-gon circuits (of two A and two X atoms). The known nets of this type are six of the 'Archimedean' nets (Wells, 1979, p. 10), namely, 4.6.8, 4.8.10 (two), 4.12^2 (two), and 4.14^2. The geometry of tetrahedral AX_2 structures based on these nets remains to be studied.

Structures of class II(c)

Only cyclic and chain structures are possible, and it is convenient to deal with the latter first, since the cyclic structures are built from portions of the chain structure. If the chain of Fig. 16(c) is broken at any point there are two ways of choosing a second edge which has a vertex in common with the edge already shared. There is therefore an indefinitely large number of configurations of this chain. In the fully extended configuration of Fig. 16(c) all the shared X atoms lie in the plane of the paper; the fourth vertex of each tetrahedron could therefore lie to one side or the other of this plane. If any pair of unshared X atoms of adjacent tetrahedra lie on the same side of this plane there are unacceptably short X–X distances. However, portions of the chain with all unshared X atoms lying on the same side and consisting of even numbers of tetrahedra may be joined end-to-end to form cyclic structures $(AX_2)_{2n}$. In these structures the A and shared X atoms define prisms. The first member of this family, $n = 2$, belongs to class II(d), for each tetrahedron shares three edges (Fig. 24a). It consists of a group of four tetrahedra enclosing a central tetrahedral hole, and the four A and the four shared X atoms are situated at alternate vertices of a distorted cube. Higher members of the family belong to class II(c). The structures with $n = 3$ and 6, with compositions A_6X_{12} and $A_{12}X_{24}$ respectively, are illustrated in Figs. 24(b) and (c) and also in Fig. 25, where the heavier broken lines indicate the shared tetrahedron edges. The topological representations of these complexes, the 3-connected systems of A and shared X atoms, are the hexagonal and dodecagonal prisms respectively. Since the distance between *un*shared X atoms of adjacent tetrahedra approaches the value for the linear chain as n increases there is an upper limit to the value of n (around 18–20). No cyclic structures can be formed from the configuration of the chain of Fig. 16(c) which has unshared X atoms alternately on opposite sides of the plane of the shared X atoms because of short X–X distances.

Structures of class III: $v_1 = 1, v_2 = 1, v_4 = 2$

In structures of this class each AX_4 tetrahedron shares one X with one other tetrahedron ($v_2 = 1$) and two with three other tetrahedra ($v_4 = 2$). This can be achieved in the following ways:

(a) vertices only shared, or

(b) one edge shared, which can be either the edge between two 4-connected X atoms (b_1) or the edge

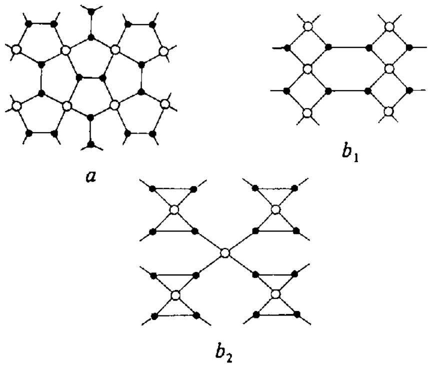
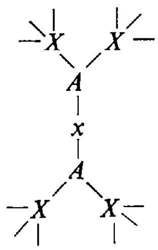
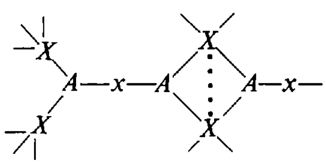


Fig. 26. Examples of planar (3,4)-connected nets containing pairs of adjacent 3-connected points in which $c_3 = 2c_4$ (see text). The small black circles represent A atoms and the open circles 4-connected X atoms; the unshared and 2-connected X atoms are omitted.

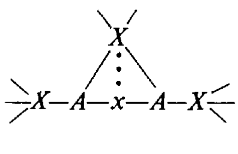
between the 2-connected X atom and one of the 4-connected X atoms (b_2).



(a)



(b_1)



(b_2)

In the accompanying sketches X represents a 4-connected X atom, x a 2-connected X atom, and unshared X atoms are omitted. The topological diagrams may be further simplified by replacing A–x–A by A–A. Accordingly these structures are represented by (3,4)-connected nets containing pairs of adjacent A atoms and also in b_1 four-membered rings or in b_2 three-membered rings. (The dotted lines in b_1 and b_2 indicate shared edges of AX_4 groups.) In all such nets each A is connected to two X (and also through x to one A) and each X to four A, and therefore the number (c_3) of 3-connected points (A atoms) is equal to twice the number (c_4) of 4-connected points (X atoms). [On replacing the 1- and 2-connected X atoms, which are omitted from the (3,4)-connected nets, the ratio A:X becomes 1:2.]

No examples appear to be known of structures of this class, which have not been studied in detail. It seems unlikely that finite or 1D structures are possible for tetrahedral coordination of A, but 2D and/or 3D structures may well be possible. Fig. 26 shows a planar net of each type with the following numbers of points in their repeat units: (a) $c_3 = 8$, $c_4 = 4$, (b_1) $c_3 = 2$, $c_4 = 1$, and (b_2) $c_3 = 4$, $c_4 = 2$, on which structures of this class might be based. Very few 3D (3,4)-connected nets having $c_3 = 2c_4$ are known (Wells, 1977, p. 92; 1979, pp. 55, 58), and we have not ascertained whether any tetrahedral AX_2 structures can be constructed.

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