Phil. Trans. R. Soc. Lond. A **319**, 291–335 (1986)

Printed in Great Britain

SURVEY OF TETRAHEDRAL STRUCTURES

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(*Communicated by J. M. Thomas, F.R.S. – Received* 26 *February* 1985)

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Vol. 319. A 1548 [Published 28 August 1986

Structures built from tetrahedral AX_4 groups that share some or all of their X atoms may be classified according to the numbers of tetrahedra to which the X atoms belong. If v_x is the number of X atoms of each AX_4 group in a structure of composition $A_m X_n$ which are common to x such groups (that is, x is the coordination number of X) then $\Sigma v_x = 4$ and $\Sigma(v_x/x) = n/m$. The solutions of these equations for any composition $A_m X_n$ may be examined systematically. The present survey is restricted to structures which can be constructed from regular tetrahedral AX_4 groups, all of which share their X atoms in the same way and have no X–X separations shorter than the edge of a tetrahedron. A study is made of the types of possible structure, finite, one-, two- or three-dimensional, and the emphasis is on the topology rather than the geometry of the structures.

1. Introduction

The two most important coordination polyhedra in crystal chemistry are the tetrahedron and octahedron. Structures of composition AX_n and A_2X_n built from regular octahedral AX_6 groups have recently been surveyed (Wells 1984*c*); here we attempt a survey, on similar lines, of structures built from regular tetrahedral AX_4 groups. There is an indefinitely large number of ways of joining together tetrahedra to form structures which may be finite or extend indefinitely in one, two or three dimensions. We shall consider structures in which only vertices or edges are shared, for face-sharing results in very short A–A distances and is not observed in actual crystal structures, and we shall limit the survey to the compositions listed in table 1. Also we shall introduce the following restrictions: (i) the arrangement of shared vertices or edges of each tetrahedron is the same (or its mirror image if the arrangement is chiral); (ii) it must be possible to build the structure from *regular* tetrahedra; (iii) all distances between X atoms of different tetrahedra must be at least equal to the length of the edge of a tetrahedron (this is what is meant later by 'acceptable X–X distance').

Each X atom of each AX_4 coordination group is bonded to some number, x, of A atoms; this number, the coordination number of X, may be different for different X atoms. If v_x is the number of X atoms of each AX_4 group which belong to x such groups, then $\Sigma v_x = 4$ and $\Sigma(v_x/x) = n/m$ in a compound $A_m X_n$. Solutions involving values of $x > 8$ are omitted from table 1 because no more than eight regular tetrahedra can meet at a point while maintaining acceptable X–X distances. $x = 5$ and $x = 7$ are excluded because there are no solutions of the equations involving these values of x for the formulae listed in table 1. The primary classification of table 1 is only the first step in deriving and describing tetrahedral structures, and two general points should be mentioned here before proceeding to the systematic derivation of structures.

The first is that not only are there several solutions for most compositions $A_m X_n$ but also a particular solution of the equations may usually be realized in more than one way, by the sharing of vertices only, edges only or by some combination of edges and vertices. For example, the solution $v_2 = 4$ for AX_2 is the result of sharing (*a*) each vertex with one other tetrahedron, (*b*) two vertices and one edge or (*c*) two edges which have no common vertex. The description of many structures is simplified by describing them in terms of the number, p, of tetrahedra to which each is joined by sharing X atoms, either singly as shared vertices or in pairs as shared edges. In the above types of AX_2 structure the values of p are 4, 3 and 2 respectively. The underlying systems of p-connected points on which a structure is based range from a pair of points ($p = 1$) through rings or chains ($p = 2$) to systems in which each point is connected to

TABLE 1. TETRAHEDRAL STRUCTURES CLASSIFIED ACCORDING TO THE NUMBERS (v_x) OF x-CONNECTED VERTICES

formula	class	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, $S_2O_7^{2-}$, $P_2O_7^{4-}$, $Si_2O_7^{6-}$
AX_3		2	2	—	—	—	—	Al_2Cl_6, S_3O_9, $Se_4O_{12}.(SO_3)_n$
A_2X_5	I	1	3	—	—	—	—	P_4O_{10}, $(Cu_4Si_{10})Na_2$, $(Be_2O_5)Li_2$
	II	2	—	—	2	—	—	—
		2	—	1	—	1	—	—
AX_2	I	—	4	—	—	—	—	SiO_2, HgI_2, ZnI_2, $(GaP)S_4$
	II	1	—	3	—	—	—	AlOCl, GaOCl
	III	1	1	—	2	—	—	—
		1	1	1	—	1	—	—
A_2X_3	I	—	1	3	—	—	—	Si_2N_2O, Ga_2S_3
	II	—	2	—	2	—	—	$(Cu_2Cl_3)Cs$
	III	1	—	—	—	3	—	—
		1	—	—	1	—	2	—
		—	2	1	—	1	—	—
A_3X_4	I	—	—	4	—	—	—	Si_3N_4, Be_2SiO_4, Cu_2HgI_4
		—	2	—	—	2	—	—
		—	1	1	2	—	—	—
AX	I	—	—	—	4	—	—	ZnO, ZnS, BeO, OPd, SPt, OPb, LiOH
	II	—	1	—	—	3	—	—
		—	—	2	—	2	—	—
		—	—	1	2	1	—	—
A_4X_3	I	—	—	—	1	3	—	—
	II	—	—	—	2	—	2	$(Cu_4S_3)K$
A_3X_2		—	—	—	—	4	—	Be_3N_2, P_3Mg_2, O_3Mn_2
A_2X		—	—	—	—	—	4	Li_2O, Li_2S

three or more others, when structures of all four major types (polyhedral or extending indefinitely in one, two or three dimensions) become possible. (A particular type of structure may not be possible in all cases, for purely geometrical reasons, for example, polyhedral AX_2 structures of class I built from tetrahedral AX_4 groups.) It is perhaps worth noting here that one of the less familiar types of infinite one-dimensional structure, the tubular chain, is intermediate from the topological standpoint between polyhedra and two-dimensional nets. A polyhedron may be represented as a net of connected points (tessellation) on a closed surface (for example, a sphere) whereas a two-dimensional net is a tessellation on an infinite surface (for example, a plane surface). The tubular chain corresponds to a tessellation inscribed on a cylindrical surface, and results from wrapping a strip of two-dimensional net around this surface which extends indefinitely in one dimension. Tetrahedral structures based on tubular chains will be noted for the compositions A_2X_5 and AX_2.

The second point is that this classification is based on the coordination number of X and, whereas the bond angles at an A atom are defined by condition (ii) as six of 109½°, there is *apparently* no reference to the interbond angles at X which are obviously an important feature of any actual crystal structure. However, certain limitations on these bond angles are implicit in the restrictions (ii) and (iii) *taken together*. If we insist that the distance between X atoms of different tetrahedra must be at least equal to the length of a tetrahedron edge, then if two tetrahedra share a vertex the angle A–X–A may range from 180° to 102°, but if an edge is shared one A–X–A angle at each X atom must lie within the very small range 66°–70½°. Considerable distortions from such a structure are to be expected in actual crystal structures because of the small value of this angle in the 'idealized' structure built from regular tetrahedra.

This is illustrated later by the structure of SPt, in which S forms tetrahedral and Pt coplanar bonds. A related point is that some tetrahedral structures in which X is four-coordinated can be constructed *only* if the bond arrangement is essentially coplanar as opposed to tetrahedral (as in SPt) or pyramidal (as in the OPb layer). A similar problem is encountered in three-dimensional nets. For example, the cubic diamond net is derived topologically, that is as a system of four-connected points in which all shortest circuits contain six points, without reference to geometrical factors (bond lengths or interbond angles). However, such a net (6^6) cannot be constructed with coplanar bonds from each point and, conversely the four-connected net $6^4 8^2$ which represents the structure of NbO cannot be constructed with tetrahedral bonds at each point.

The present study, like the survey of octahedral structures, is a logical sequel to the study of two- and three-dimensional nets for the gross topology of many structures may be described in terms of the number of tetrahedra to which each is joined, whether the junction be a single vertex or a shared edge. The relation of structures to nets is clearly seen for A_2X_5 structures of class I in which each tetrahedron shares one vertex with each of three other tetrahedra or for AX_2 structures of class I(*b*) in which each tetrahedron shares one edge and two vertices. In structures of both types each tetrahedron is connected to three others, and therefore the resulting structures must be based on three-connected systems; these could be finite or extend indefinitely in one, two or three-dimensions.

We shall refer to a number of three-dimensional nets by symbols which are analogous to the Schläffli symbols for polyhedra and two-dimensional nets. These symbols indicate the smallest polygonal circuits of which the net is composed, a circuit being defined as the shortest path starting from a point along one link and returning to the starting point along another link. In a p-connected net there are $\frac{1}{2}p(p-1)$ ways of selecting two of the links that meet at a point. It is therefore necessary to specify three circuits for a three-connected net, six for a four-connected net, and so on. A three-dimensional three-connected net in which all the shortest circuits are n-gons has a symbol n^3 and the known nets of this type (*uniform* nets), namely, 7^3, 8^3, 9^3, 10^3 and 12^3 represent the continuation of the series that begins with the tetrahedron, 3^3, hexahedron, 4^3, pentagonal dodecahedron, 5^3, and planar net, 6^3. In two dimensions there is the unique 6^3 net but, except for 12^3, there are several uniform three-dimensional three-connected nets with the same numerical symbol; these are distinguished as n^3-a n^3-b and so on. Corresponding to the Archimedean solid, 4.6^2, (truncated octahedron) and the two-dimensional net, 4.8^2, there is a double layer, 4.10^2, and three-dimensional nets, 4.12^2, 4.14^2 and 4.16^2. An introduction to nets is available (Wells 1984*a*) and also more detailed treatments (Wells 1977, 1979).

We now consider how the formulae listed in table 1 may be realized as structures built from regular tetrahedra. Detailed descriptions will not be given of structures which are adequately described elsewhere.

2. TETRAHEDRAL A_2X_7 STRUCTURES

The only possible structure is a pair of tetrahedra sharing one vertex, as in Cl_2O_7, oxy-ions formed by S, P, Si, etc., and ions such as $Al_2Cl_7^-$.

3. TETRAHEDRAL AX_3 (A_2X_6) STRUCTURES

The single solution ($v_1 = 2, v_2 = 2$) can be realized in two ways: by the sharing of two separate vertices or of one edge. The first leads to the familiar cyclic and linear molecules S_3O_9, Se_4O_{12} and $(SO_3)_n$, and the meta-ions of, for example, phosphorus and sulphur. The sharing of one edge gives the dimer A_2X_6 of halides such as $AlCl_3$ and $FeCl_3$ in the vapour state and of $AlBr_3$, $GaCl_3$ and InI_3 in the crystalline state.

This dimer is the first member of the family of structures listed at the left of table 2 and illustrated in figure 1. This figure also illustrates a family of A_2X_3 structures if figure 1*a* represents the projection of a double chain of edge-sharing tetrahedra normal to the plane of the projection The pair of v_2 vertices shown as a double circle then represents a column of v_4 vertices, the X atoms forming four coplanar bonds. We refer later to the other structures of table 2.

4. TETRAHEDRAL A_2X_5 STRUCTURES

Structures may be built in both classes I and II of table 1.

(*a*) *Structures of class* I: $v_1 = 1, v_2 = 3$

The three v_2 vertices may be shared either (*a*) as separate vertices or (*b*) as an edge and one vertex.

Class I(*a*)

Each tetrahedron is joined to three others, and the relevant three-connected systems include polyhedral, one-, two- and three-dimensional structures.

Polyhedral structures are based on three-connected polyhedra, of which the most symmetrical are 3^3 (tetrahedron), 4^3 (cube) and 5^3 (pentagonal dodecahedron), prisms and certain of the Archimedean solids. The three polyhedral complexes based on the regular solids and built of tetrahedra AX_4 are illustrated in figure 2, plate 1; they have the compositions A_4X_{10} ('super-tetrahedron'), A_8X_{20}, and $A_{20}X_{50}$. We refer later to the first two for they can be joined through all their v_1 vertices to form more extensive AX_2 structures.

One-dimensional structures. The chain (figure 3) has various configurations with the unshared vertices on one side or the other of the mean plane of the chain. This chain represents the arrangement of the Si and four-coordinated Al atoms in sillimanite, $Al(AlSiO_5)$, in which one half of the Al atoms are four-coordinated and the remainder are in positions of octahedral coordination. The family of prismatic structures, of which the A_8X_{20} complex of figure 2 is the second member, may be formed from portions of the chain of figure 3 joined end-to-end with atoms such as A and A′ or B and B′ coinciding and all unshared vertices lying to one side of the chain.

Tubular chains are formed by wrapping strips of two-dimensional nets around a cylinder as shown in figure 4 for the 6^3 and 4.8^2 nets. The strips are joined along lines such as A and B or A and C and so on. The simplest tubular chains formed from the 6^3 net were illustrated some years ago (Wells 1954), but at that time no examples were known of actual crystal structures containing tubular ions. Subsequently tubular chain ions built of SiO_4 tetrahedra, based on 6^3 and 4.8^2 and also on the more complex net $(6.8^2)\,(4.6.8)_2$ of figure 5*d* have been found in minerals and in the synthetic $Na_2Cu_4Si_{10}$ (Kamamura & Kawahara 1977). Numerous

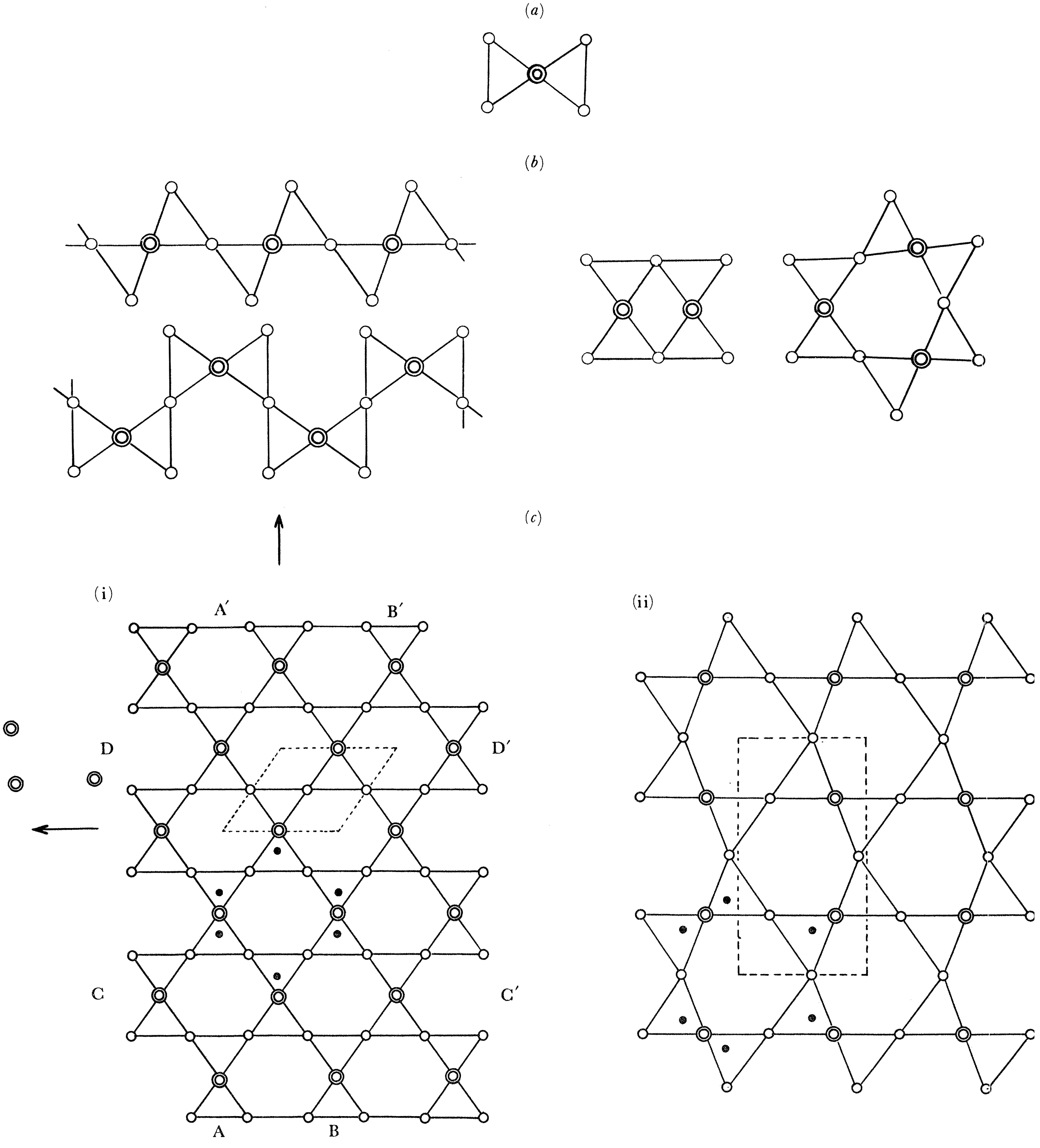
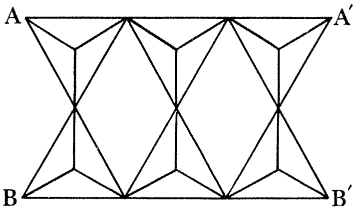


FIGURE 1. The family of related structures of table 2. (*a*) Pair of tetrahedra sharing an edge (A_2X_6), (*b*) *trans* and *cis* A_2X_5 chains and four- and six-membered rings, (*c*) two configurations of AX_2 layer based on the 6^3 net. ◎, tetrahedron edge perpendicular to the plane of the paper; ○, X atoms; ●, A atoms of only one ring.

Table 2. Two families of related tetrahedral structures

figure 1	vertices v_1	v_2	formula	type of structure	vertices v_1	v_2	v_4	formula	type of structure
(*a*)	2	2	A_2X_6	finite (dimer)	2	—	2	A_2X_5	chain (class II)
(*b*)	1	3	A_2X_5	ring or chain (class I)	1	1	2	AX_2	layer or tubular chain (class III)
(*c*)	—	4	AX_2	layer or tubular chain (class I(*b*))	—	2	2	A_2X_3	three-dimensional structure (class II)

3



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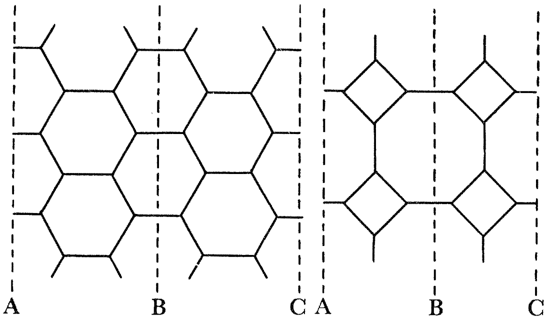


Figure 3. The double A_2X_5 chain of class I.

Figure 4. Formation of tubular chains from strips AB, AC, and so on of plane nets.

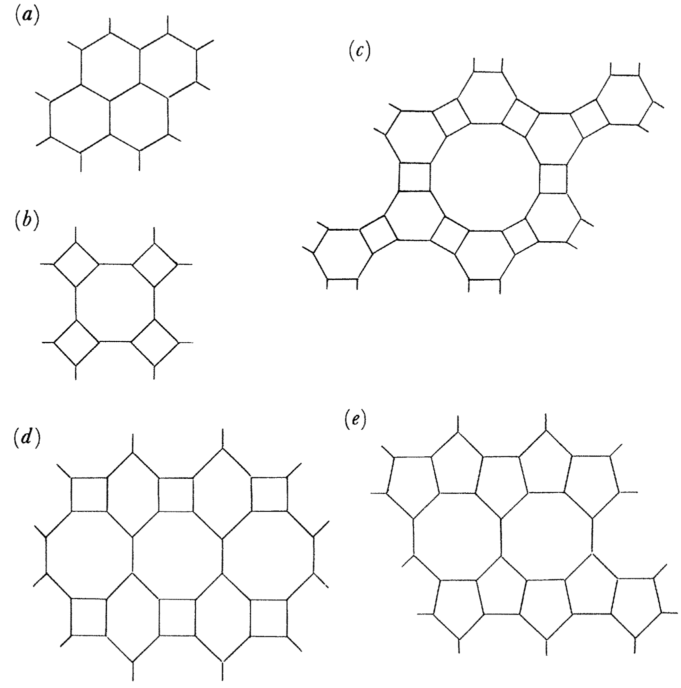


Figure 5. Three-connected plane nets on which certain layer structures are based: (*a*) the regular net, 6^3, (*b*, *c*) the semi-regular nets 4.8^2 and $4.6.12$ respectively, (*d*) $(6.8^2)(4.6.8)_2$, (*e*) $(5.8^2)(5^28)_2$.

tubular chains are illustrated in Hefter & Kenney (1982) which describes the synthesis of the mineral litidionite, $NaKCu_4Si_{10}$, the structure of which contains the same type of chain, based on 4.8^2, as $Na_2Cu_4Si_{10}$.

Tubular chains built from tetrahedral AX_4 groups may be based on two-dimensional, three- or four-connected nets, as will be noted later for AX_2 structures of classes I(*a*, *b*), II(*a*, *b*) and III.

Two-dimensional structures are layers based on three-connected nets, of which the simplest is the hexagonal 6^3 net. Silicates are known with structures based on all the nets of figure 5. The 6^3 layer built from tetrahedra is illustrated in figure 6.

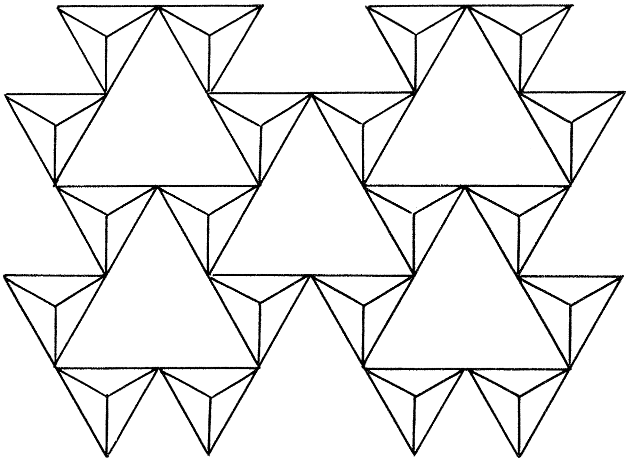


FIGURE 6. The tetrahedral A_2X_5 layer based on 6^3.

A tetrahedral A_2X_5 structure based on the double layer 4.10^2 (figure 6.15, page 85 in Wells (1977)) can be built, but it has not been ascertained that it has acceptable X–X distances if constructed from regular tetrahedra.

Three-dimensional structures are based on the numerous three-dimensional three-connected nets. Examples of three types of structure are provided by P_2O_5, namely, the 'super-tetrahedral' P_4O_{10} molecule, the layer based on 6^3, and the three-dimensional structure based on 10^3-b. Also based on 10^3-b are the anion frameworks of $La_2Be_2O_5$ and $(Zn_2Cl_5)(H_5O_2)$, whereas that of $CsBe_2F_5$ is based on 10^3-a.

Class I(*b*)

Here each tetrahedron is joined to two others by sharing one edge and one vertex, and therefore only two-connected systems (rings or chains) are possible (figure 1 (*b*)). No examples of this type of A_2X_5 structure appear to be known.

(*b*) *Structures of class* II: $v_1 = 2, v_4 = 2$

If the pair of tetrahedra of figure 1*a* represents the projection of a chain normal to the plane of the paper the composition is A_2X_5 (table 2), and each X forms four coplanar bonds. In another configuration of the chain alternate pairs of edge-sharing tetrahedra are rotated through 90° so that X forms four tetrahedral bonds (figure 7). No examples are known of either of these structures.

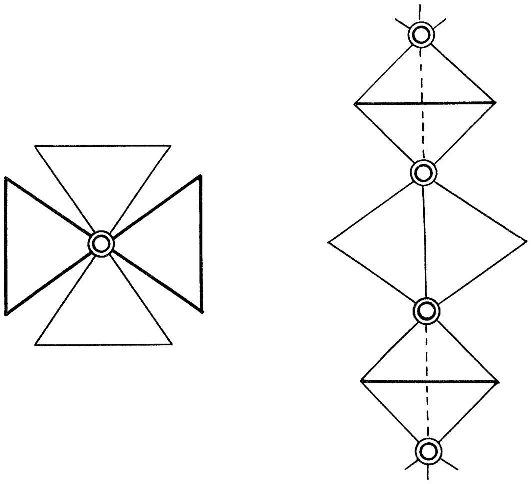


FIGURE 7. Plan and elevation of A_2X_5 chain of class II.

5. TETRAHEDRAL AX_2 STRUCTURES

These have been reviewed in an earlier article (Wells 1983). We take the opportunity to include here a number of structures that were omitted from this account, notably those of class III. Structures have been found in the three classes I–III of table 1.

(*a*) *Structures of class* I: $v_2 = 4$

The two-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. The required structures are based on four-, three- or two-connected nets in (*a*), (*b*) and (*c*) respectively.

Class I(*a*)

Structures of all four major types (finite, one-, two- and three-dimensional) are *topologically* possible because there are four-connected polyhedra, chains, layers and three-dimensional structures. However, polyhedral complexes in which the A atoms would be situated at the vertices of four-connected polyhedra cannot be built from tetrahedral AX_4 groups. (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.) Structures of three types are therefore possible in class I(*a*).

One-dimensional structures. Tubular chains may be formed from strips of planar four-connected nets of various widths, as shown in figure 8 for the 4^4 net. The end-on view of these chains show that they consist of vertex-sharing rings stacked one above the other.

Two-dimensional structures. Of the layer structures based on planar four-connected nets the simplest, based on 4^4, represents the structure of (red) HgI_2 (figure 9*a*) and of the corrugated ZnO_2 layer, the anion in $Sr(ZnO_2)$ (figure 9*b*). Double layers are formed from pairs of the A_2X_5 layers of figure 5 related by a mirror plane, and the simplest of these, based on 6^3, represents the structure of the anion in $Ca(Al_2Si_2O_8)$. The double layer formed from 4.8^2 can obviously be built from the cubical units A_8X_{20} (figure 2*b*).

Three-dimensional structures. Vertex-sharing AX_2 structures are based on the numerous

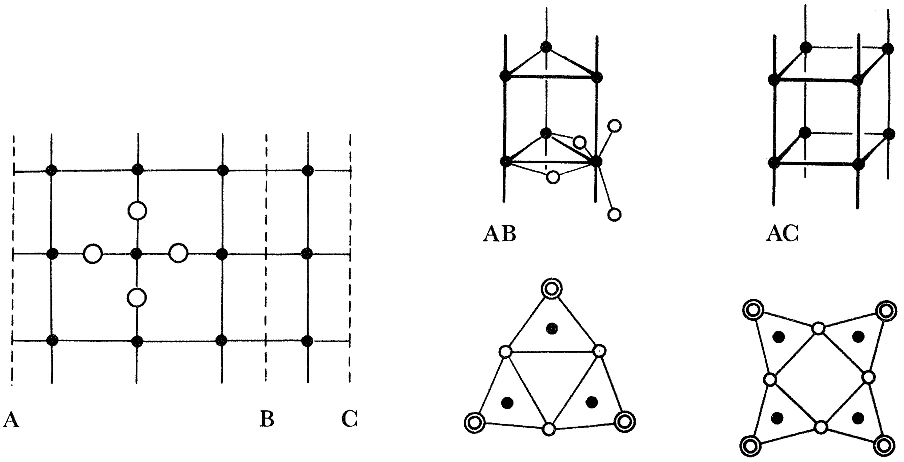


FIGURE 8. Formation of tubular chains from strips AB, AC, and so on of the plane net 4^4.

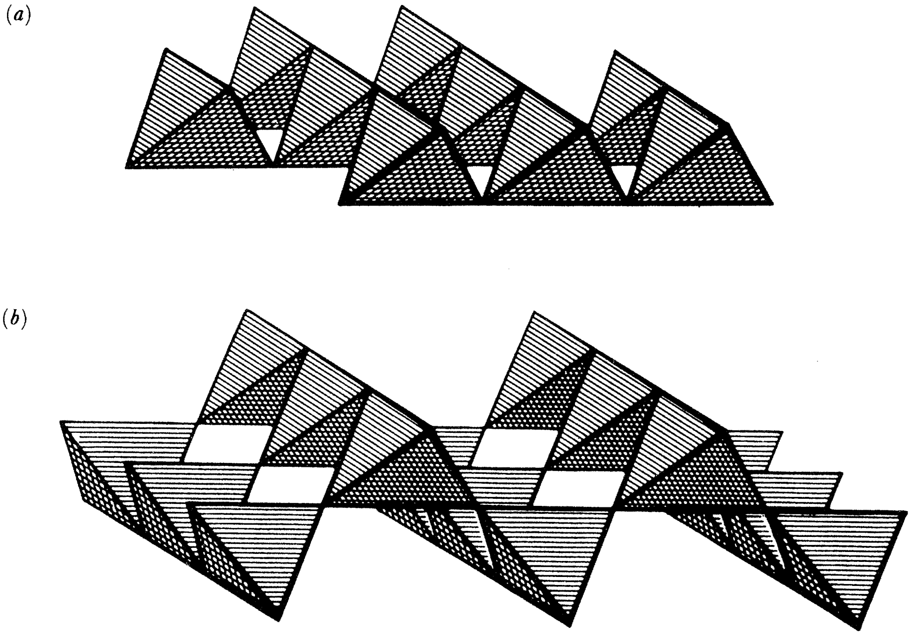


FIGURE 9. Tetrahedral AX_2 layers based on 4^4: (a) HgI_2, (b) $(ZnO_2)Sr$.

three-dimensional four-connected nets, and range from cristobalite-like structures based on the simplest of these nets (the cubic diamond net 6^6) to the complex frameworks of aluminosilicates such as felspars and zeolites. The net formed from cubes at the nodes of the BC lattice is related to the tubular chain and double layer in the following way. All may be built from cubical A_8X_{20} sub-units. The eight v_1 vertices of this group are the two groups of four belonging to opposite faces of the cube to form the tubular chain AC of figure 8, the four groups of two to form the double layer based on 4.8^2, and the eight joined to eight different A_8X_{20} groups to form the BC structure. The symbols of the underlying nets are 4^56, 4^46^2, and 4^38^3.

Structures of all the above types are also possible if the simple AX_4 groups are replaced by 'super-tetrahedral' groups A_4X_{10} (figure 2*a*). This group represents the structure of the P_4O_{10} molecule and of ions such as $Si_4S_{10}^{4-}$. Such groups may be joined by sharing each of the outermost vertices with one other similar group to form AX_2 structures of class I(*a*). Examples are the layer structures of orange HgI_2 and the three-dimensional structures of $ZnBr_2$ (White *et al.* 1984) and ZnI_2 (Fourcroy *et al.* 1978). In the simplest three-dimensional structure built from super-tetrahedra the A_4X_{10} groups are situated at the nodes of the cubic diamond net, but as yet there is no example of a compound with this structure.

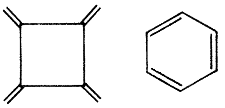
The structures of ZnP_2 and $ZnAs_2$ are excluded from the present survey because although they contain vertex-sharing tetrahedral AX_2 frameworks an essential feature of the structures is the presence of covalent X–X bonds between X atoms of different tetrahedra; these are much shorter than the tetrahedron edge. The distances in black monoclinic ZnP_2 are: P–P, 2.2A, and P–P (edge of tetrahedral ZnP_4 coordination group), 4A (Fleet & Mowles 1984.)

Class I(*b*)

Structures in which each tetrahedron is joined to three others by sharing one edge and two vertices are of all four major types.

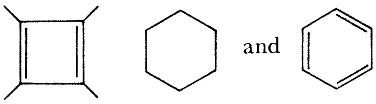
Polyhedral structures. The most symmetrical polyhedral structures are based on certain of the three-connected regular and semi-regular (Archimedean) solids or on prisms. These based on the tetrahedron or cube are not acceptable because they have very short X–X distances. The most symmetrical form of the pentagonal dodecahedral complex is illustrated in figure 10*a*. 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 three-connected Archimedean solids (table 3). 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 **1**. In the less symmetrical cubic isomer **2** there are hexagonal faces of two kinds, 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 (figure 10, plates 2 and 3). This isomerism is reminiscent of that of the octahedral Keggin complexes $A_{12}X_{40}$.

1



*m*3*m* isomer,

2



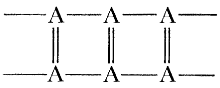
$\bar{4}3m$ isomer,

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

TABLE 3. POLYHEDRAL AX_2 STRUCTURES OF CLASS I(*b*) : $v_2 = 4$

three-connected polyhedron defined by A atoms	formula	four-connected polyhedron defined by inner (or outer) shell of X atoms	figure 10
5^3	$A_{20}X_{40}$	3^35	(*a*)
3.8^2	$A_{24}X_{48}$	3^24^2	(*b*)
4.6^2			(*c*)
$4.6.8$	$A_{48}X_{96}$	3.4^3	(*d*)
3.10^2	$A_{60}X_{120}$	3^25^2	(*e*)
5.6^2			(*f*)
$4.6.10$	$A_{120}X_{240}$	3.4^25	(*g*)

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 observed that in the isomers of type **2** 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.



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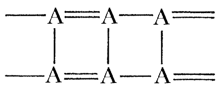

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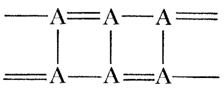

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One-dimensional prismatic structures. We consider first the simplest chain, which is based on the (three-connected) ladder, and then prismatic structures formed from portions of this chain. There is an indefinitely large number of isomers of this chain; the simplest are shown in **3**, **4** and **5**. Two projections of the chain **4** are illustrated in figure 11. In figure 11*a* the shared edges are perpendicular to the plane of the paper; in figure 11*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

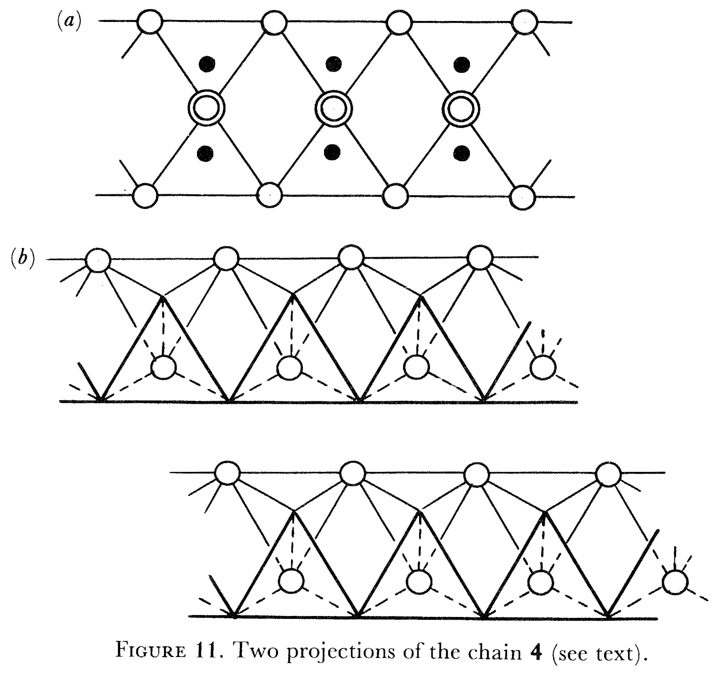


FIGURE 11. Two projections of the chain **4** (see text).

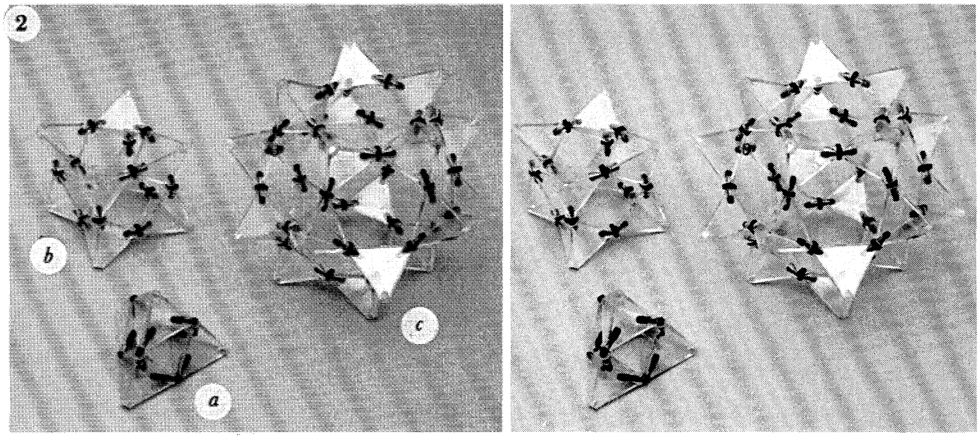


FIGURE 2. The polyhedral $(A_2X_5)_n$ complexes A_4X_{10}, A_8X_{20}, and $A_{20}X_{50}$. In models illustrated by stereo-pairs rubber connectors represent X atoms.

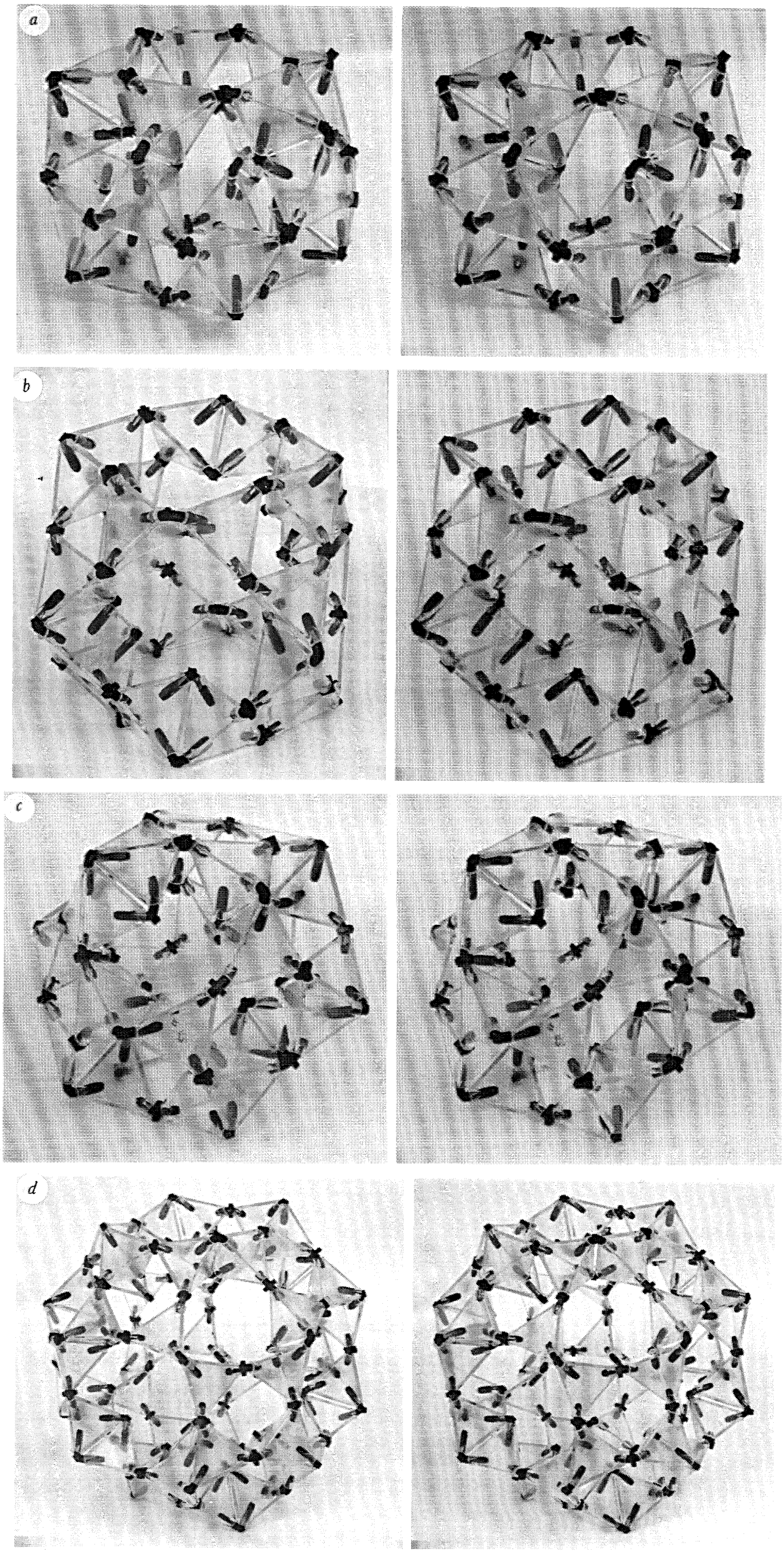


FIGURE 10*a–d*. For description see opposite.

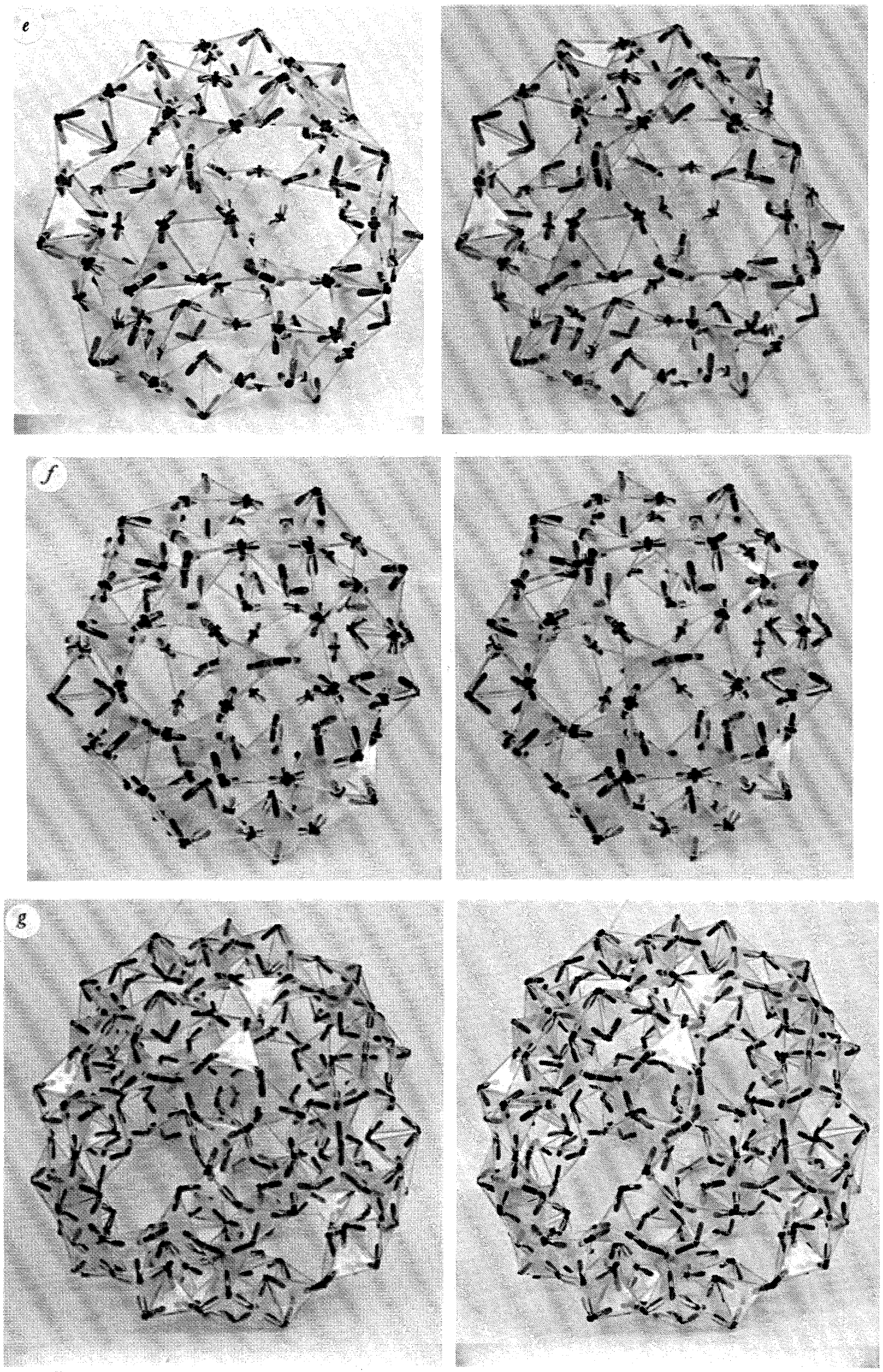


FIGURE 10. The polyhedral structures $(AX_2)_n$ of table 3 based on (*a*) pentagonal dodecahedron, (*b*) truncated cube, (*c*) truncated octahedron, (*d*) truncated cuboctahedron, (*e*) truncated dodecahedron, (*f*) truncated icosahedron, (*g*) truncated icosidodecahedron.

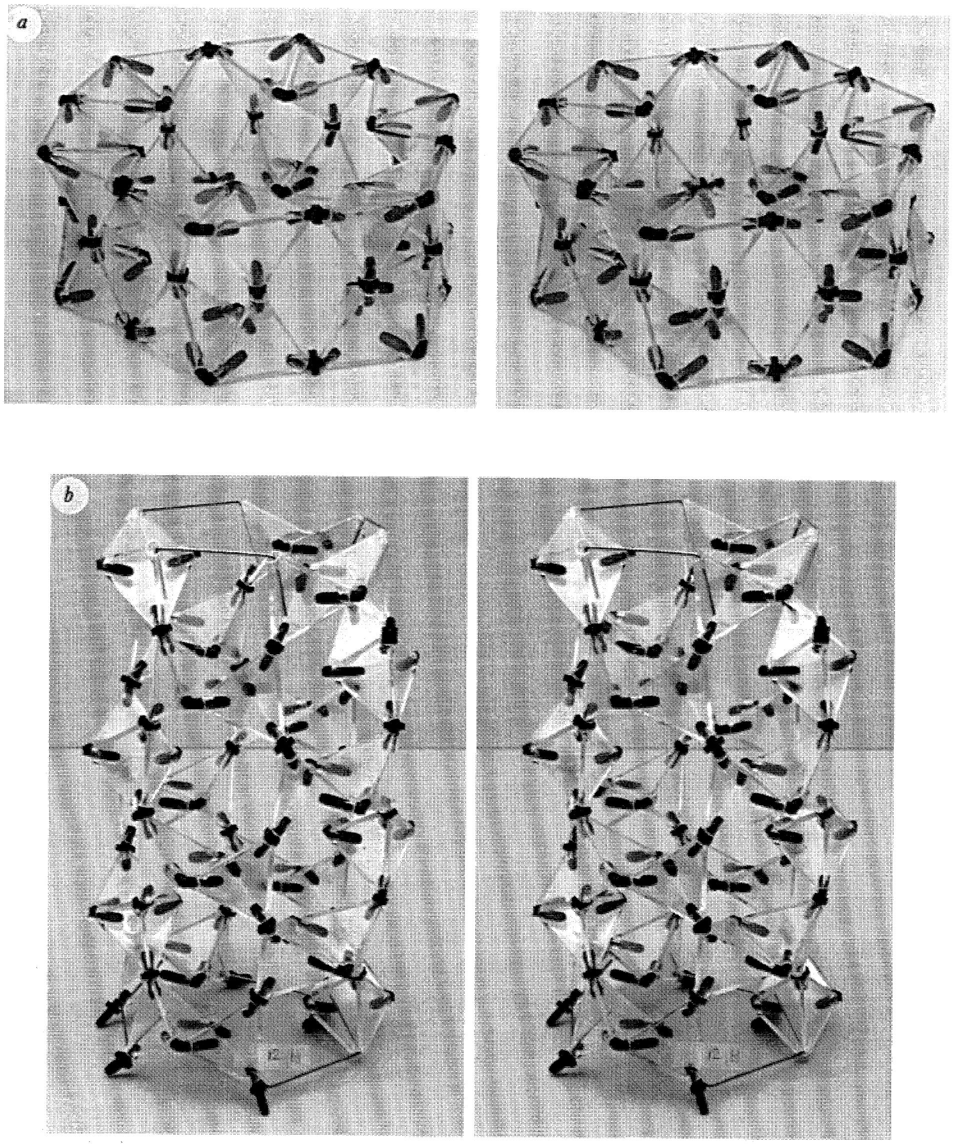


FIGURE 12*a*, *b*. For description see opposite.

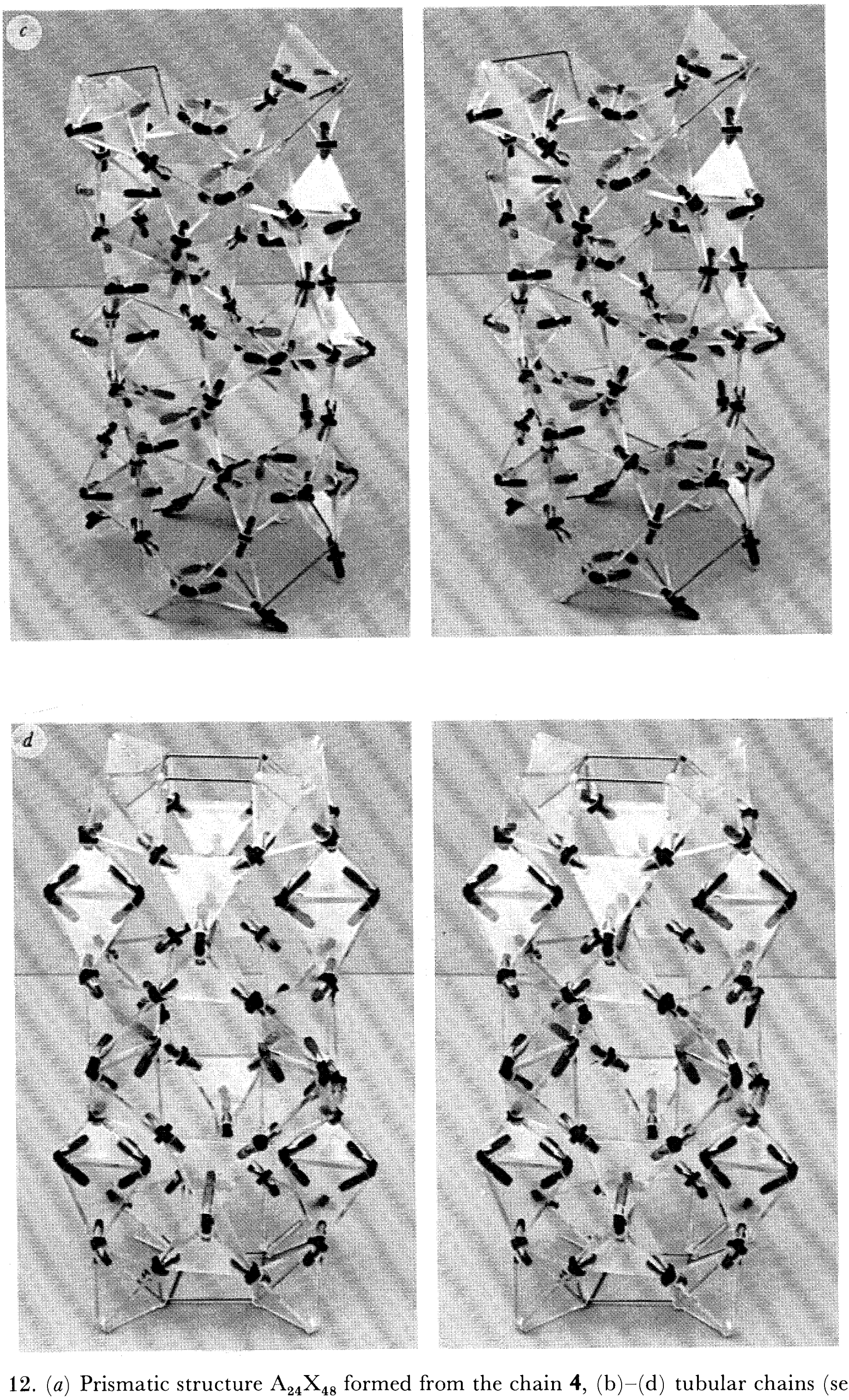


FIGURE 12. (*a*) Prismatic structure $A_{24}X_{48}$ formed from the chain **4**, (b)–(d) tubular chains (see text).

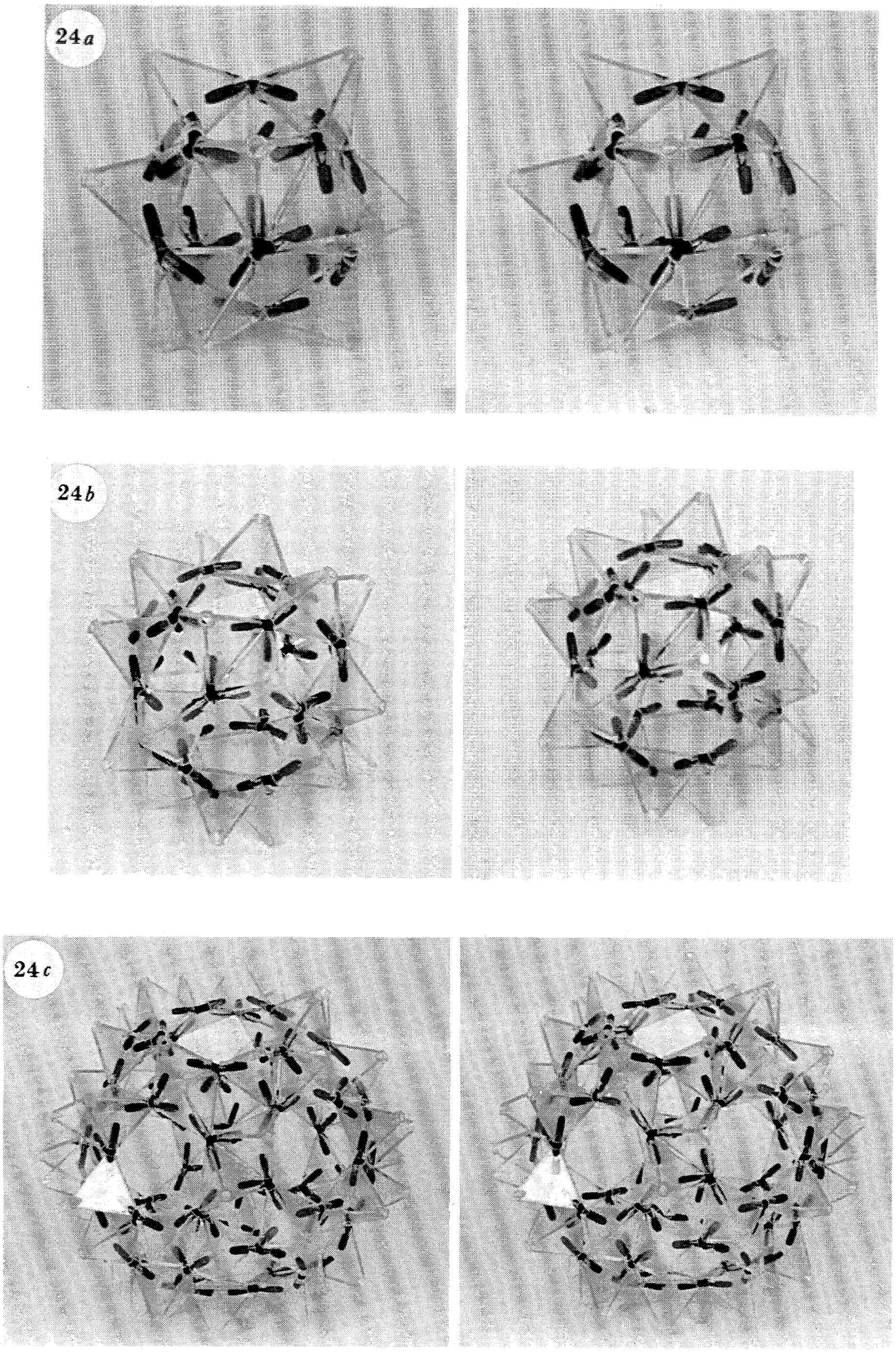


FIGURE 24*a–c*. For description see opposite.

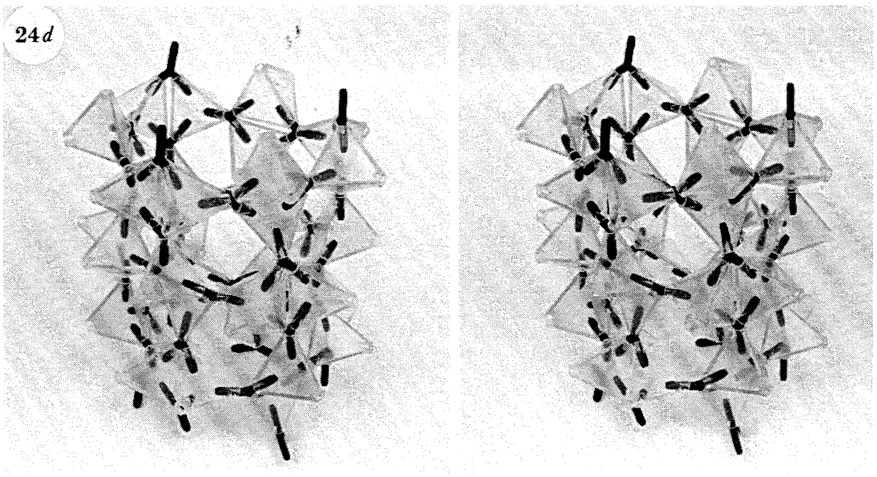


FIGURE 24. (*a*)–(*c*) Polyhedral AX_2 complexes of class II(*b*): (*a*) icosahedron $A_{12}X_{24}$, (*b*) snub cube $A_{24}X_{48}$, (*c*) snub dodecahedron $A_{60}X_{120}$, (*d*) tubular AX_2 chain of class II(*b*) (see text).

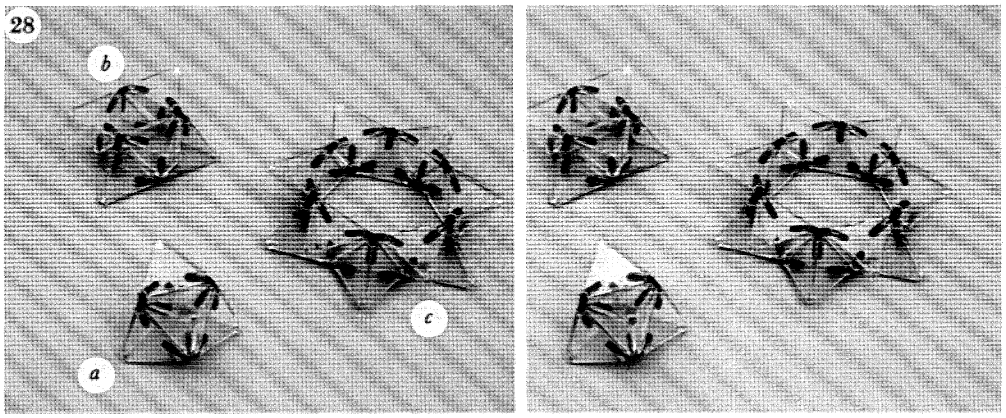


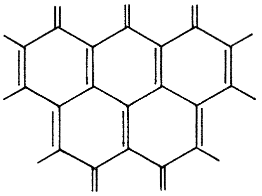
FIGURE 28. Three finite $(AX_2)_n$ complexes: (*a*) A_4X_8 of class II(*d*), (*b*) and (*c*) A_6X_{12} and $A_{12}X_{24}$ of class II(*c*).

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 figure 11*b* represent the X atoms of one close-packed layer.

Prismatic structures can be formed from portions of chains joined end to end. Those formed from the chain **3** are not likely to form because the distance between X atoms belonging to different shared edges is equal to the tetrahedron 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 **4** and **5** if $n \geqslant 6$; in structures formed from smaller portions of these chains there would be short interior X–X distances. Figure 12*a*, plate 4 shows the $A_{24}X_{48}$ structure formed from the chain **4**.

The tubular chains formed from strips of two-dimensional nets wrapped around a cylinder are conveniently described after the layer structures.

Two-dimensional structures. Layers are based on three-connected nets of A atoms, and we consider first the simplest three-connected two-dimensional 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 shown below.



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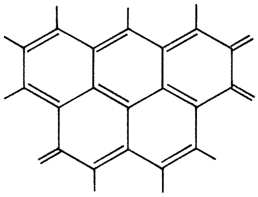

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The corresponding layers built from tetrahedra are shown in figure 1*c*, where the shared edges are perpendicular to the plane of the layer. Figures 13, 14 and 15 show the tetrahedral layers based on the nets 4.8^2, 3.12^2 and $4.6.12$.

An indefinitely large number of tubular chains may be built from strips of three-connected layers. If horizontal strips of the layer of figure 1*c* (i) are joined along the lines AB... and A′B′...

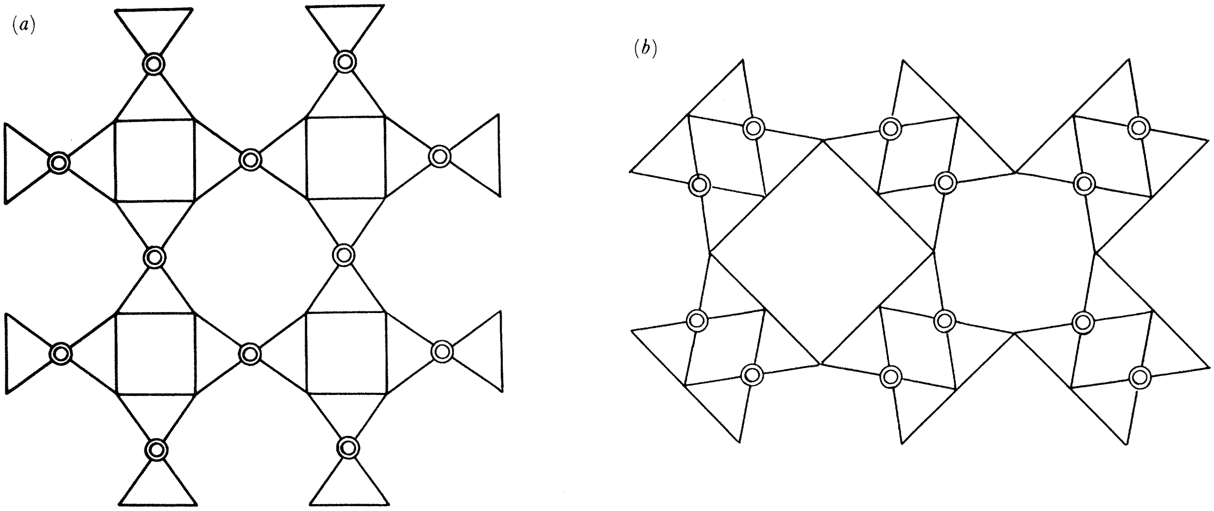

FIGURE 13. Two isomers of the tetrahedral layer based on 4.8^2.

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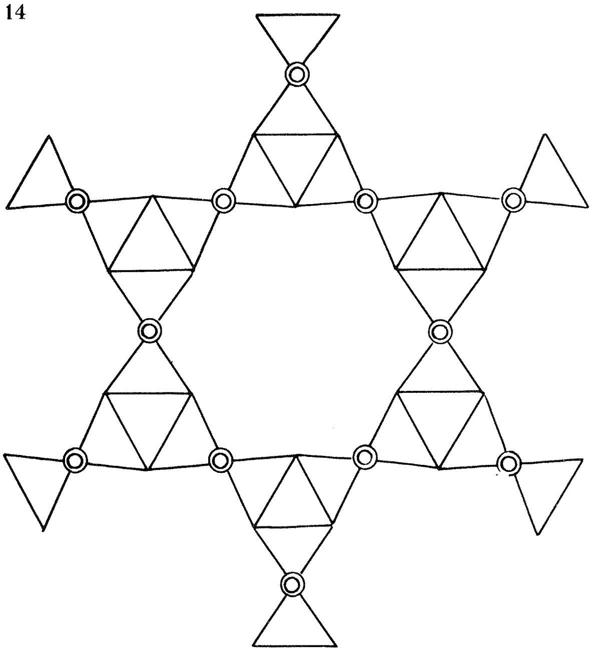

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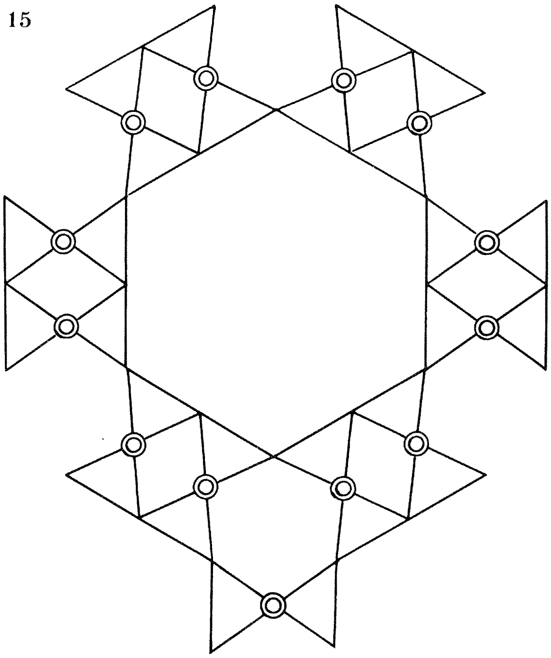

FIGURE 14. Tetrahedral AX_2 layer based on 3.12^2.
FIGURE 15. Tetrahedral AX_2 layer based on 4.6.12.

a tubular chain is formed (figure 12*b*) in the direction of the left-hand arrow. This chain, $(A_{12}X_{24})_n$, has trigonal symmetry and horizontal and vertical planes of symmetry. If the joins are made at AB′... and so on instead of AA′... the result is a helical chain (figure 12*c*). Joining vertical strips at points such as CC′, DD′, and so on produces chains extending in the direction of the upper arrow. The simplest of these chains which has acceptable X–X distances in the interior of the chain is the $(A_{16}X_{32})_n$ chain of figure 12*d*.

There is a second configuration of the layer of figure 1*c*(i) in which the shared tetrahedron edges are inclined to the plane of the layer which is of special interest as having the most compact arrangement possible of X atoms. This is illustrated in figure 16; the right-hand portion 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 in $GaPS_4$ (Buck & Carpenter 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 close-packed S atoms. However, the net of Ga and P atoms on which the layer is based is not the simplest planar three-connected net but the 4.8^2 net (figure 17). It is therefore of interest to discover whether there are similar layers with close-packed X atoms based on the other two semi-regular two-dimensional three-connected nets, namely 3.12^2 and 4.6.12. It appears that the only two AX_2 structures of this family in which the X atoms form two complete close-packed layers are those based on 6^3 and

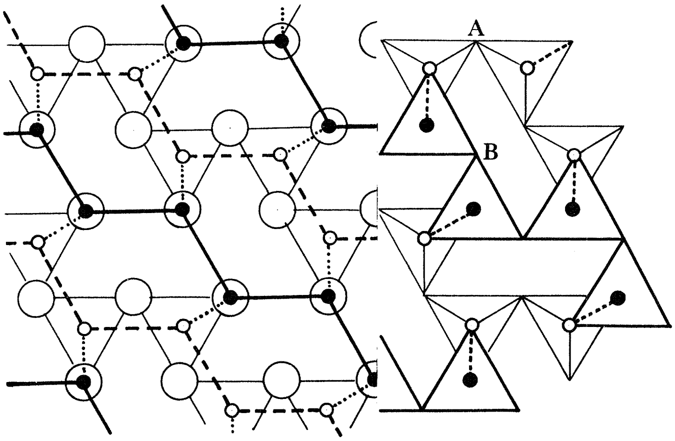

FIGURE 16. Second configuration of AX_2 layer of class I(*b*) based on 6^3 (with shared edges inclined to plane of paper). At the left the heavy full lines and the broken lines connect A atoms and outline the basic net on which the layer is based.

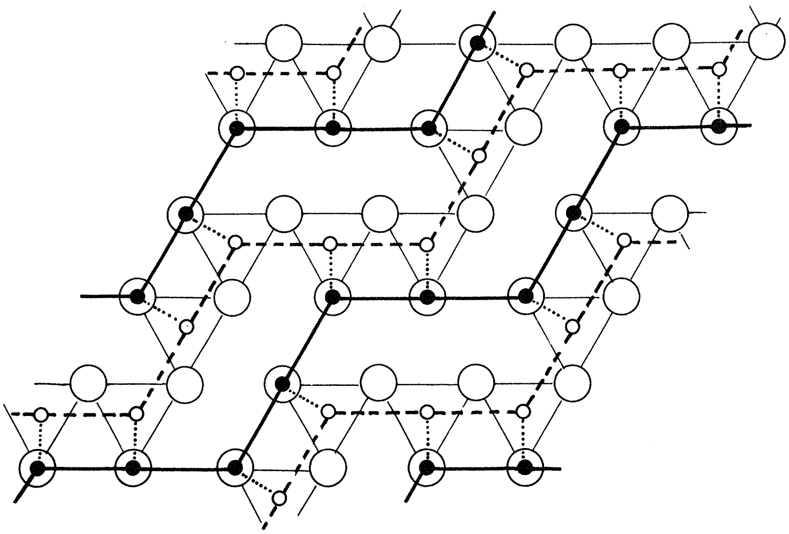

FIGURE 17. Second configuration of AX_2 layer of class I(*b*) based on 4.8^2.

4.8^2; in the layers based on 3.12^2 and $4.6.12$ (figures 18 and 19) the X atoms occupy respectively $\frac{2}{3}$ and $\frac{3}{4}$ of the close-packed positions.

Three-dimensional structures. It was noted in the earlier account that tetrahedral AX_2 structures based on three-dimensional three-connected nets are numerous, but they were not examined systematically. The construction of models has subsequently shown that structures can indeed be built which are based on each of the nets 8^3-a, 8^3-b, 9^3-a, 10^3-b and 10^3-c; the last two have been described (Wells 1984*b*). The structure based on the tetragonal configuration of 10^3-b and built from regular tetrahedra with collinear A–X–A bonds projects on (100) as in figure 20*a*, which shows one ring of ten tetrahedra. There are unacceptably short X–X distances of 0.73 times the length of a tetrahedron edge between the chains (dotted lines), and these are also seen in figure 20*b*, which shows two chains projected on (001). This difficulty is overcome by 'shearing' the structure (figure 20*c*) when the X atoms in the bases of the tetrahedra form a close-packed layer, and the remaining X atoms occupy one third of the positions of closest

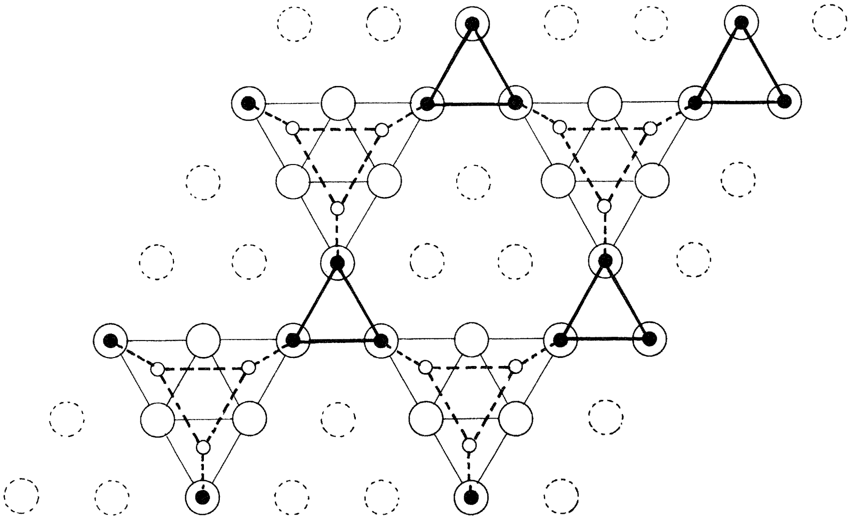

FIGURE 18. Second configuration of AX_2 layer of class I(*b*) based on 3.12^2.

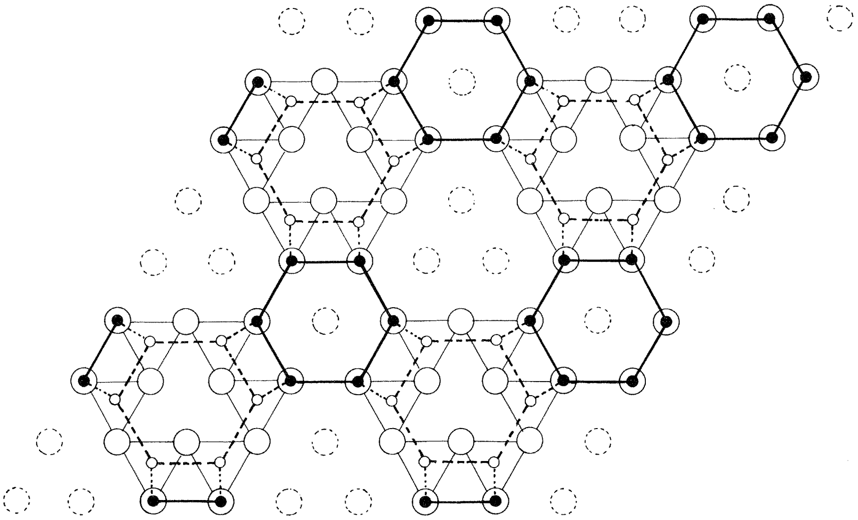

FIGURE 19. Second configuration of AX_2 layer of class I(*b*) based on 4.6.12.

packing on each side of the CP layer. These 'layers', strictly sets of parallel chains, may be stacked in various ways and joined by sharing the X atoms which are not shared in the chains. Stacking of the layers vertically above one another gives a set of discrete layers based on 6^3 perpendicular to the projection of figure 20*c*. Alternatively, successive layers may be rotated relative to one another through 60° (or 120°), the chains lying in the directions (i), (ii), or (iii), to form a family of three-dimensional structures. There are two different structures which repeat after two layers (along *c*) because the sequences (i) (ii) and (i) (iii) result in *c* or *hc* packing of the X atoms, respectively†. There is a similar pair of structures, with three-layer repeats, based on 10^3-c, and a series of polytypic structures in all of which the X atoms occupy two thirds

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† In a concise nomenclature for close-packed (CP) structures a layer is denoted by *h* if the two neighbouring layers are of the same kind, i.e. both A, both B, or both C, or by *c* if they are of different kinds. Hexagonal closest packing (HCP) is then denoted simply by *h* (i.e. *hhh*...) and cubic closest packing (CCP) by *c*. The symbols for more complex layer sequences include both *h* and *c* (for example, *chch* for ABAC...).

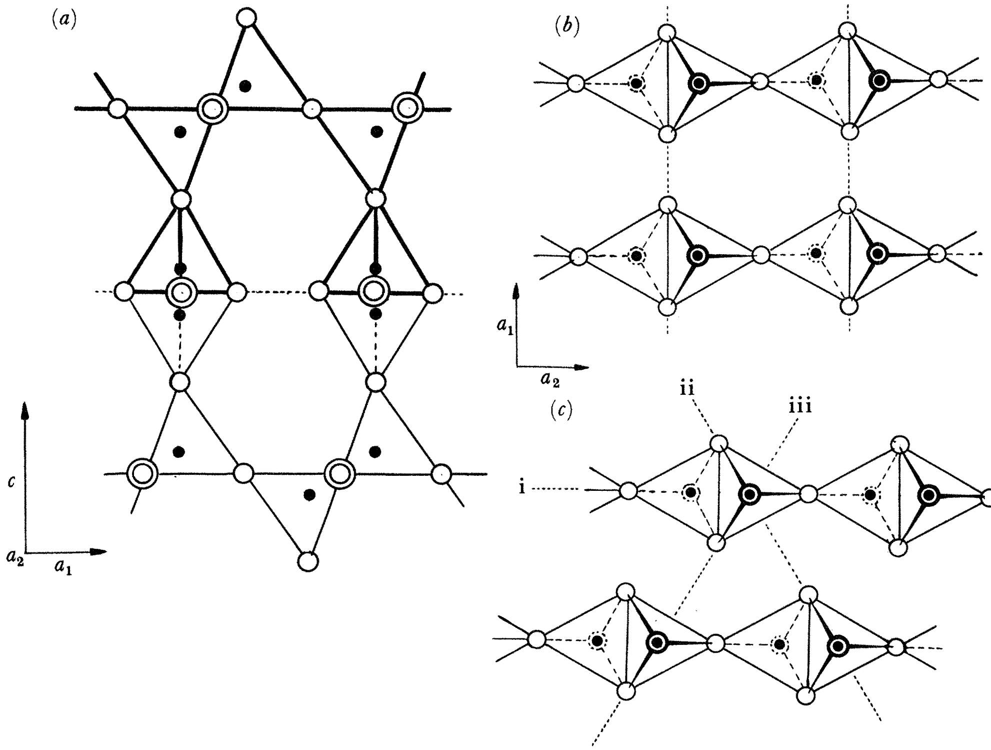

FIGURE 20. (a) Projection on (100) of tetrahedral structure based on 10^3-b showing one ring of ten tetrahedra; (b, c) projections of two chains on (001) in the orthogonal and sheared forms, respectively, of the structure.

of the positions of more complex types of closest packing. Since the positions of the X atoms in any one chain are those of cubic closest packing alternate layers must be *c* layers, from which it follows that the CP symbol must contain an *odd* number of consecutive *c* layers (for example, *c*, *ch*, *ccch*, but not *cch* or *cccch* and so on).

Class I(*c*)

The sharing of two edges that have no vertex in common leads only to the linear chain ($BeCl_2$, SiS_2) or to improbably large (unknown) rings formed from portions of such a chain.

(*b*) *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, (*b*) one edge of each tetrahedron shared, (*c*) two edges of each tetrahedron shared or (*d*) three edges of each tetrahedron shared.

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

Class II(*a*)

The smallest permissible circuit is a ring of six atoms (alternately A and X) because a ring of 2A+2X implies edge-sharing. This condition excludes all three-connected polyhedra and all two-dimensional three-connected nets other than 6^3.

One- and two-dimensional structures. The net 6^3 represents the topology of the layer of figure 21, 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 one-dimensional structures. There are two special configurations of these chains. In one (E type) there are continuous lines of tetrahedron edges parallel to the axis of the chain. This type of chain is possible only if the number of tetrahedra in the shortest circuit around the tunnel is even; otherwise the continuous line of tetrahedron edges runs helically around the surface of the cylinder. The two simplest E type chains are therefore E_4 and E_6, shown in projection in figure 22. In the second configuration of a chain (F type, figure 23) one face of each tetrahedron is normal to the chain axis, and in these chains the number of tetrahedra in the shortest circuit around the tunnel may be even or odd. More extensive structures are formed from these chains by joining them together so that the outer (v_1) vertices become either v_2, when the composition becomes A_2X_3, or v_3 when the composition becomes A_3X_4. The structures derived from chains of these two types are summarized in table 4.

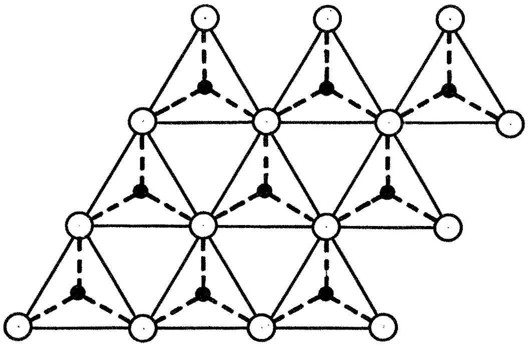

FIGURE 21. AX_2 layer of class II(*a*).

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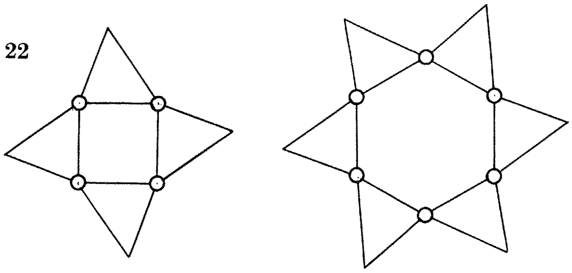

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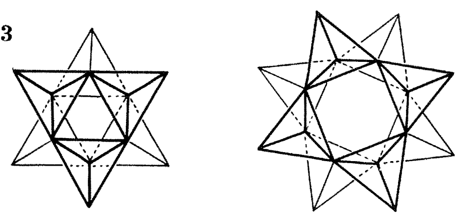

FIGURE 22. The two simplest E type tubular chains (E_4 and E_6) viewed along their length. One edge of each tetrahedron is perpendicular to the paper.

FIGURE 23. Tubular AX_2 chains F_3 and F_4 viewed along their length. One face of each tetrahedron is normal to the chain axis.

Three-dimensional structures. These structures would be based on three-connected nets in which A and X atoms alternate and all circuits have even numbers of links, this number being greater than six. The simplest three-connected three-dimensional nets of this kind are uniform nets 8^3,

TABLE 4. THREE-DIMENSIONAL STRUCTURES FORMED FROM THE TUBULAR AX_2 CHAINS OF CLASS II(a)

	v_1	v_2	v_3	E_4	E_6 (figure numbers)	F_3	F_4
A_2X_3	—	1	3	33	34	35	36
A_3X_4	—	—	4	—	54	51	—

10^3, and 12^3. It has not been ascertained whether any of these structures can be constructed with regular tetrahedra and without any unacceptably short distances between X atoms of different tetrahedra.

Class II(b)

Structures of all four major types are possible, polyhedral, one-, two- and three-dimensional.

Polyhedral structures. The polyhedra defined by the A and the shared X atoms taken together must be three-connected and must have four-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 figure 24a–c, plates 6 and 7 and table 5. The models illustrated in these 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 figure 25). The most symmetrical are therefore the icosahedron (3^5), snub cube ($3^4 4$), and snub dodecahedron ($3^4 5$). In the icosahedral structure (figure 24a) tetrahedra are placed on 12 of the 20 faces of a regular icosahedron, in the second (figure 24b) on 24 of the 32 triangular faces of a snub cube, and in the third (figure 24c) on 60 of the 80 faces of a snub dodecahedron.

TABLE 5. POLYHEDRAL AX_2 STRUCTURES OF CLASS II(b): $v_1 = 1, v_3 = 3$

polyhedron defined by the A and the shared X atoms (three-connected)	formula	polyhedron defined by the shared X atoms (five-connected)	figure 24
4.6^2	$A_{12}X_{24}$	$3^4 3$	(a)
$4.6.8$	$A_{24}X_{48}$	$3^4 4$	(b)
$4.6.10$	$A_{60}X_{120}$	$3^4 5$	(c)

One- and two-dimensional structures. Because all two-dimensional 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 figures 25 and 26. In the layer of figure 25 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 figure 25 there are four vertical strings of tetrahedra. In the 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 figure 24d. 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.

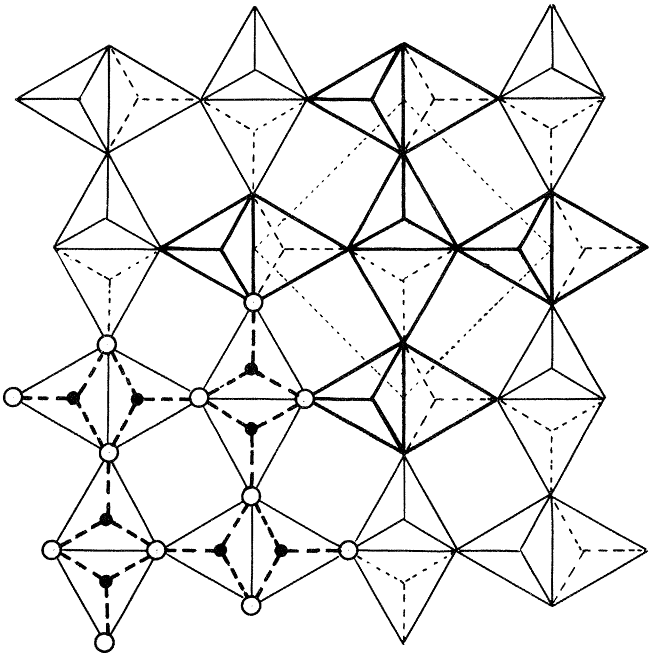

FIGURE 25. AX_2 layer of class II(*b*) based on 4.8^2, a portion of which is shown at the bottom left. The heavier broken lines connect A atoms (●) and three-connected X atoms (○) which form the underlying net.

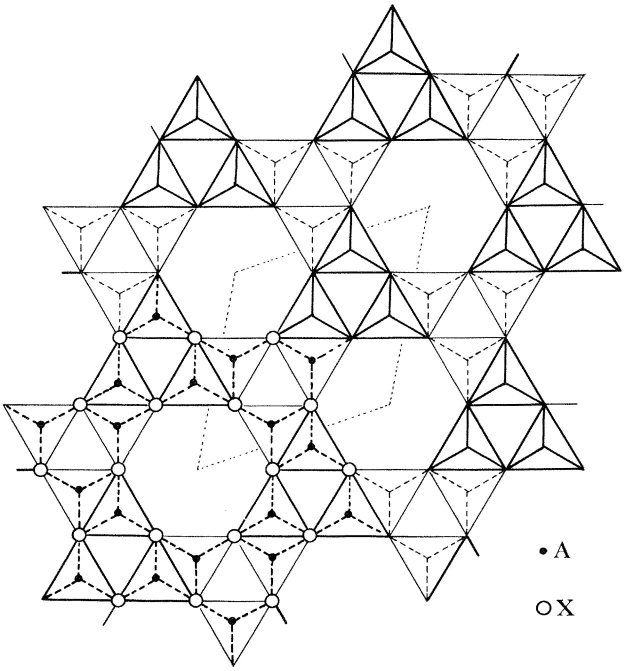

FIGURE 26. AX_2 layer of class II(*b*) based on 4.6.12, a portion of which is shown at the bottom left (----).

Tubular chains may also be formed from the 4.6.12 net, but their detailed geometry has not been studied.

Three-dimensional structures. These must be based on three-connected nets in which A and X atoms alternate, and the nets must contain four-gon circuits (of two A and two X atoms). The known nets of this type are twelve of the 'Archimedean' nets (Wells 1979, p. 10, 1983), namely 4.6.8, 4.8.10 (two), 4.12^2 (five), 4.14^2 (three), and 4.16^2. The geometry of tetrahedral AX_2 structures based on these nets remains to be studied.

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 figure 27 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 figure 27*a* 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*), but the higher members belong to class II(*c*). The structures with $n = 3$ and 6 are illustrated in figure 28*b*, *c*, plate 7 and in projection in figure 29; they have the compositions A_6X_{12} and $A_{12}X_{24}$ 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 figure 27 which has unshared X atoms alternately on opposite sides of the plane of the shared X atoms because of short X–X distances.

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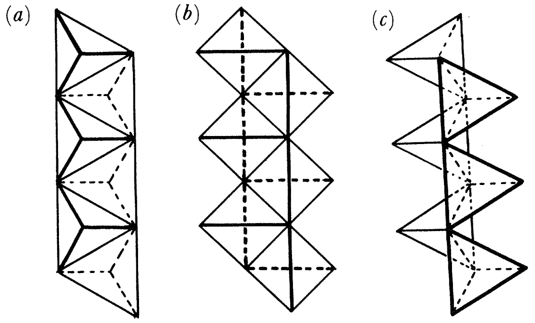

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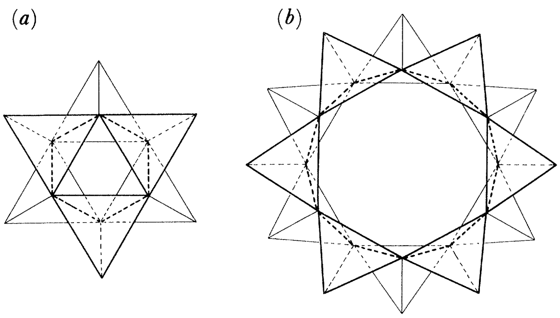

FIGURE 27. Three views of the AX_2 chain of class II(*c*).

FIGURE 29. Projections of the prismatic complexes A_6X_{12} and $A_{12}X_{24}$ of figure 28(*b*, *c*).

Class II(*d*)

The only structure found in this class is the A_4X_8 complex of figure 28*a*. It consists of a group of four tetrahedra enclosing a central tetrahedral cavity. The four A atoms and the four shared X atoms are situated at alternate vertices of a distorted cube.

(*c*) *Structures of class* III: $v_1 = 1, v_2 = 1, v_4 = 2$

No structures of this class were described in the earlier account. Each tetrahedron has to share one X with one other tetrahedron ($v_2 = 1$) and two with three other tetrahedra ($v_4 = 2$). This could presumably be achieved in the following ways: (*a*) vertices only shared, or (*b*) one edge shared, either the edge between two four-connected X atoms (b_1) or the edge between the two-connected X atom and one of the four-connected X atoms (b_2). The only structures found so far in this class are the tubular chains and layers of type b_1 noted in table 2. They project as in figure 1 (*b*) if figure 1 (*a*) represents a double chain of tetrahedra normal to the plane of the paper. The tubular chains have compositions $(A_2X_4)_n$, $n \geqslant 2$. With the tubular chains of classes I(*a*) and (*b*) and II(*a*) and (*b*) they form the fifth group of tubular AX_2 chains.

6. TETRAHEDRAL A_2X_3 STRUCTURES

Compounds of composition A_2X_3 are relatively few in number. They include oxides (sulphides, selenides and tellurides) of elements of Groups III and V of the Periodic Table and of some transition metals, including 4f and 5f metals. The small number of compounds containing an element in two valence states (for example, Tl_2Cl_3 and Sn_2S_3) are not of interest here, for apart from the fact that the known examples are not tetrahedral structures they contain non-equivalent A atoms. The coordination numbers of A atoms in compounds A_2X_3 range from 3 to 7, but examples of A_2X_3 structures built from tetrahedral AX_4 groups appear to be limited to a very small number of sesquisulphides (for example Ga_2S_3), a group of compounds which includes some with statistical defect sphalerite or wurtzite structures. Table 1 shows that in any tetrahedral A_2X_3 structure there must be at least two kinds of coordination of the X atoms, in contrast to octahedral A_2X_3 structures which include the corundum (α-Al_2O_3) structure of 6:4 coordination.

(*a*) *Structures of class* I: $v_2 = 1, v_3 = 3$

Many of these may conveniently be derived from AX_2 structures of class II ($v_1 = 1, v_3 = 3$) by joining v_1 vertices in pairs, and the subgroups may be labelled (*a*)–(*d*) to correspond to those of the AX_2 structures: (*a*) only vertices shared, (*b*) one edge shared, (*c*) two edges shared, or (*d*) three edges shared.

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

Class I(*a*)

The relevant AX_2 structures (class II) are the net of figure 21 and tubular chains formed by wrapping strips of the net around a cylinder, the E and F type chains of figures 22 and 23. If all the v_1 vertices of the layer of figure 21 lie on the same side of the layer a pair of layers related by a mirror plane form a double layer (not illustrated), but if equal numbers of the v_1 vertices lie above (U) or below (D) the plane of the layer three-dimensional structures may be formed. In the simplest structure of this family there are alternate rows of U and D tetrahedra. If adjacent layers are related by mirror planes there is formed a structure (figure 30) in which

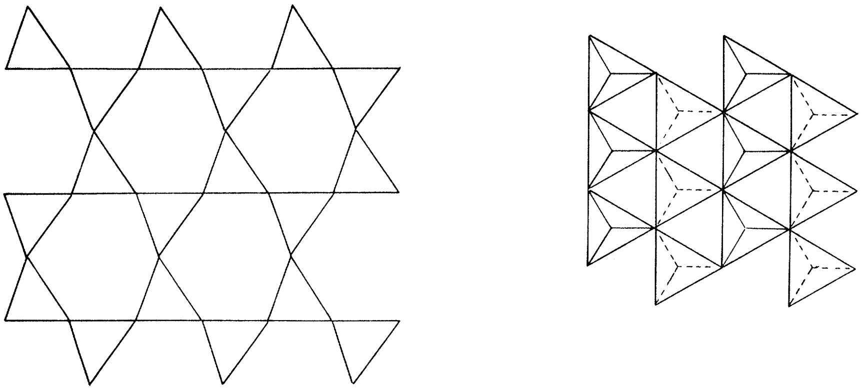

FIGURE 30. Elevation and projection of A_2X_3 structure of class I(*a*) formed from layers of the type shown at the right.

the X atoms occupy three-quarters of the positions of hexagonal closest packing, with alternate layers fully and one half occupied. The analogous 'defective cubic closest packed' structure is not possible because the X atoms of one UD layer are in the positions of hexagonal closest packing. The next simplest structure arises by rotating alternate layers through 180°, when the X atoms occupy three-quarters of the positions of *hc* packing. Polytypes are therefore possible. If there are pairs of rows of U and D tetrahedra in the single layer of figure 21 the simplest structure is that of figure 31, with X atoms in three-quarters of the positions of hexagonal closest packing.

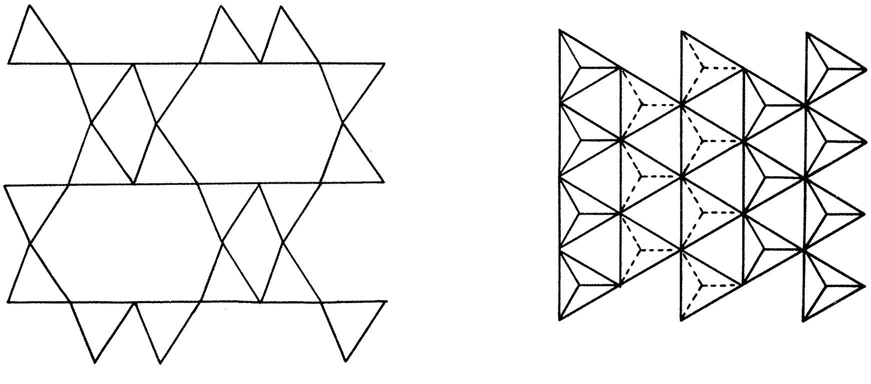

FIGURE 31. Elevation and projection of A_2X_3 structure of class I(*a*) formed from layers of the type shown at the right.

The oxynitride Si_2N_2O is an example of a structure of the type of figure 30. It consists of puckered hexagonal nets of directly bonded Si and N atoms, the nets being bonded through O atoms which complete the tetrahedral SiN_3O coordination groups of the Si atoms. The coordination numbers of Si, N, and O are therefore 4, 3, and 2 respectively (figure 32). The structure of hemimorphite, $Zn_4(OH)_2Si_2O_7 . H_2O$ (figure 32*b*) is of the same general type, as may be seen by writing the formulae

$$\begin{array}{lllll} Si_4 & Si_2 & N_6 & O_3 & \\ Zn_4 & Si_2 & O_6 & O, & (OH)_2. \end{array}$$

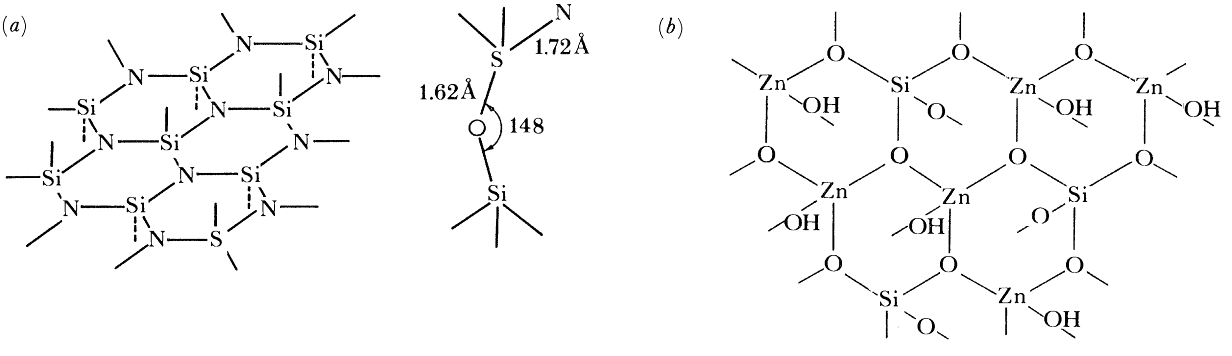

FIGURE 32. (a) The structure of Si_2N_2O (diagrammatic), (b) the structure of hemimorphite.

(The H_2O molecules in hemimorphite do not form part of the three-dimensional framework but are accommodated in the tunnels.)

The tubular chains seen in projection in figures 22 and 23 may be joined through their outer (v_1) vertices to form three-dimensional framework structures which are shown in projection in figures 33 (E_4) and 34 (E_6), 35 (F_3) and 36 (F_4). In the structures built from F_3 and F_4 chains the central axes of the chains intersect the plane of projection at the nodes of the 6^3 and 4^4 planar nets. These two structures may also be derived by stacking layers based on the semi-regular nets 3.12^2 and 4.8^2. In the F_3 structure (figure 35) the X atoms occupy three-quarters of the positions of hexagonal closest packing.

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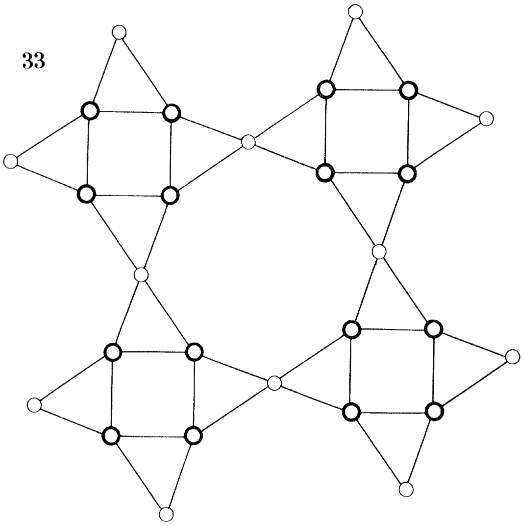

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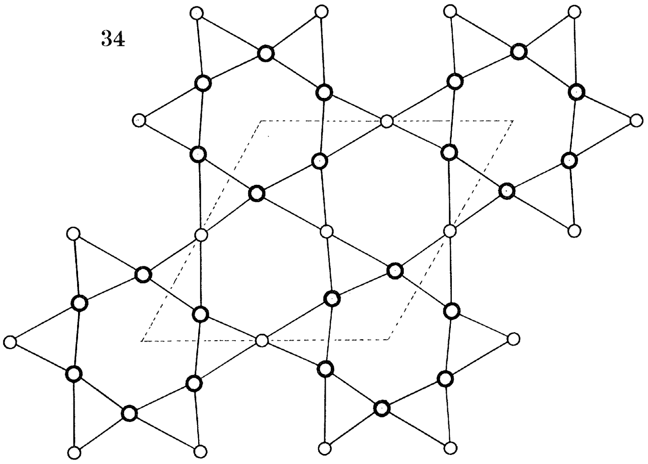

FIGURE 33. Projection of A_2X_3 structure of class I(a) built from E_4 chains.
FIGURE 34. Projection of A_2X_3 structure of class I(a) built from E_6 chains.

The structures we have described are derivable from AX_2 structures by converting v_1 into v_2 vertices, and include certain structures in which the X atoms occupy three quarters of the positions of closest packings, *h*, *hc*, or more complex types of closest packing. In these structures complete closest packed layers alternate with half-filled layers, the latter being the v_2 vertices of the tetrahedra. There is another family of A_2X_3 structures in which the X atoms occupy all the positions of closest packing and the A atoms one third of the total number of tetrahedral

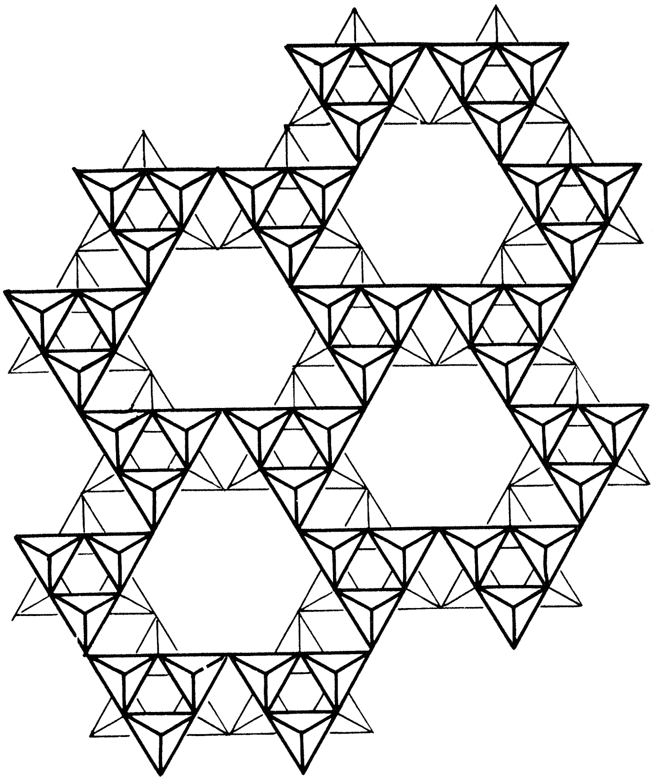

FIGURE 35. Projection of A_2X_3 structure of class I(a) built from F_3 chains.

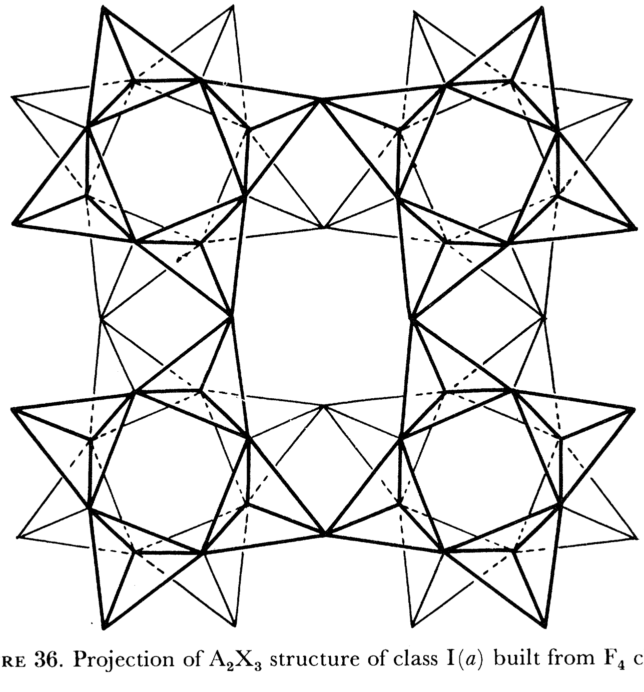

FIGURE 36. Projection of A_2X_3 structure of class I(a) built from F_4 chains.

interstices, that is, two thirds of the positions occupied in a tetrahedral AX structure. The two simplest tetrahedral AX structures are the wurtzite (HCP) and sphalerite (CCP) structures. These A_2X_3 structures may be dissected into (or built from) A_2X_5 layers of the kind shown in figure 6 in which every third tetrahedron has been removed from each row. The layers, in which each tetrahedron has $v_1 = 1$ and $v_2 = 3$, are to be joined so as to leave one v_2 vertex, the other three becoming v_3 vertices. The simplest (HCP and CCP) structures are shown in projection in figure 37*a*, *b*; they are defective wurtzite and sphalerite structures respectively. The ordered form of Ga_2S_3 (Collin *et al.* 1976) is of the former kind, with ordered vacancies in the wurtzite structure. Polytypes are possible, in which there are more complex types of closest packing, and also disordered structures with statistical distribution of A atoms in two thirds of the A positions of one of the AX structures. Structures of this kind have been suggested for two other polymorphs of Ga_2S_3.

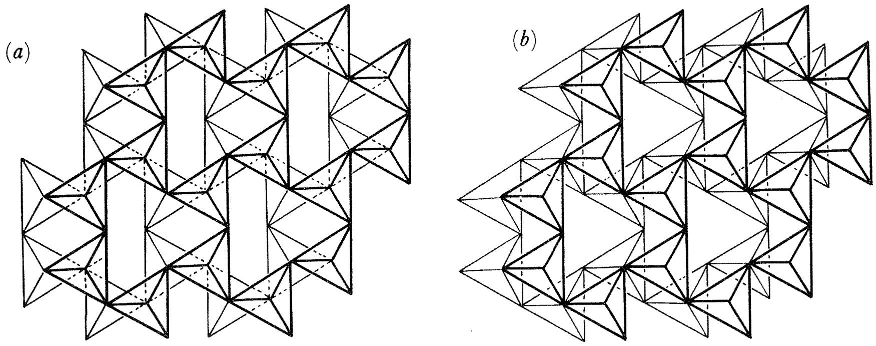

FIGURE 37. (*a*) Hexagonal close-packed A_2X_3 structure (defective wurtzite); (*b*) cubic close-packed A_2X_3 structure (defective sphalerite).

Class I(*b*)

As in class I(*a*) A_2X_3 structures are derived from AX_2 layers and tubular chains, in this case the structures of class II(*b*). All the three-connected two-dimensional nets (of alternate A and X atoms) on which these structures are based must contain 4-gons, and therefore 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 those of figures 25 and 26. The unshared X atoms of each edge-sharing pair of tetrahedra are shown 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). Since there is an indefinitely large number of ways of selecting equal numbers of U and D vertices a family of three-dimensional A_2X_3 structures may be built from the layers of figures 25 and 26. The layers are stacked with adjacent ones related by a mirror plane so that the pattern of D vertices of one layer corresponds to that of the U vertices of the layer below. The simplest structure formed from the 4.8^2 net projects as shown at the upper right of figure 25. The unit cell of this elegant structure contains two layers, each of four tetrahedra, that is $4(A_2X_3)$. This very simple structure built of edge-sharing pairs of tetrahedra may be described as the A_2X_3 analogue of the BeO structure; compare figure 25 with figure 55*a*.

Although certain tubular chains can be formed from strips of the two-dimensional AX_2 chains they do not lead to three-dimensional A_2X_3 structures. This would require that all v_1 vertices of the AX_2 tubular chain lay beyond the outer surface of the chain so that the chains could be connected together. It appears that in such structures there are inevitably some short X–X distances, and for this reason these chains have not been considered further.

Class I(*c*)

The sharing of two edges by each tetrahedron in the AX_2 structures of class II(*c*) leads to the chain of figure 27 or cyclic structures formed from portions of the chain joined end-to-end. The prismatic complexes A_6X_{12} and $A_{12}X_{24}$ were illustrated in figure 28*b*, *c* and figure 29. The A_2X_3 structures formed from these $(AX_2)_n$ sub-units include the layer of which two configurations are shown in figure 38 (compare with figure 27*c*) and the double layers of figures 39 and 40 formed from prismatic A_6X_{12} units and based on the 6^3 and 4^4 plane nets. Figure 41 shows the elevation of a corrugated configuration of the 4^4 layer. The six external v_1 vertices of the A_6X_{12} complex lie at the vertices of a non-regular octahedron. These units may therefore form a 'sheared' ReO_3-like structure, A_6X_{12} replacing a single octahedron of that structure. The composition is A_2X_3 as each unit is joined to six others through v_2 vertices. This structure, built with collinear X bonds at the v_2 vertices, is shown in projection in figure 42.

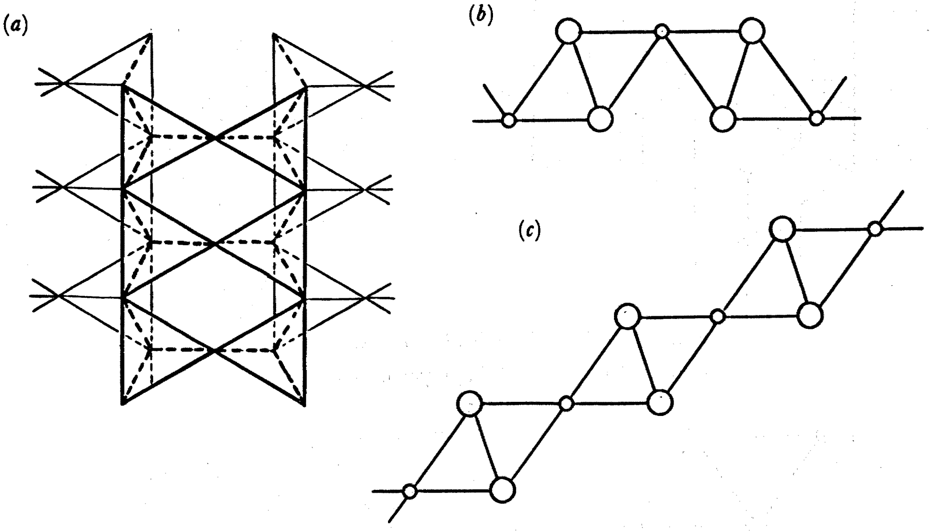

FIGURE 38. A_2X_3 layers of class I(*c*) formed from the chain of figure 27.

Class I(*d*)

The single AX_2 structure of class II(*d*) is the finite A_4X_8 complex of figure 28*a* formed from four tetrahedra enclosing a tetrahedral cavity. The four outer (v_1) vertices form a tetrahedral group, and it might be expected that such finite units could form A_2X_3 structures analogous to those formed by simple tetrahedra, A_4X_8 replacing AX_4; compare with the replacement of AX_4 tetrahedra by 'super-tetrahedra' A_4X_{10} to form AX_2 structures. Such structures would include the HgI_2 layer, based on 4^4, tubular chains formed from strips of this layer wrapped around a cylinder and structures based on three-dimensional four-connected nets of which the simplest is the cubic diamond net 6^6. However, it appears that the only structures in which there are acceptable X–X distances are three-dimensional structures based on the cubic and hexagonal diamond nets, the nets, 3.6^5, 3.7^5, 4.6^5, and possibly others which have been illustrated as stereoscopic pairs in Wells (1977, 1979).

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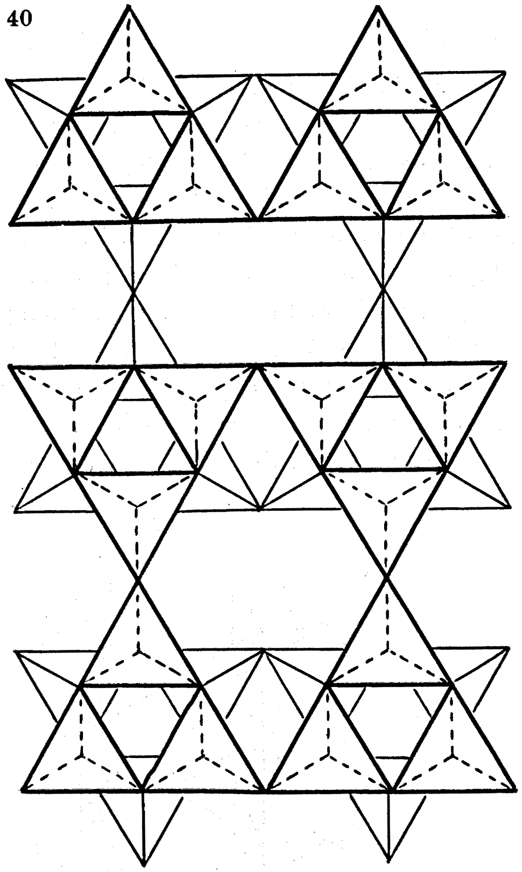

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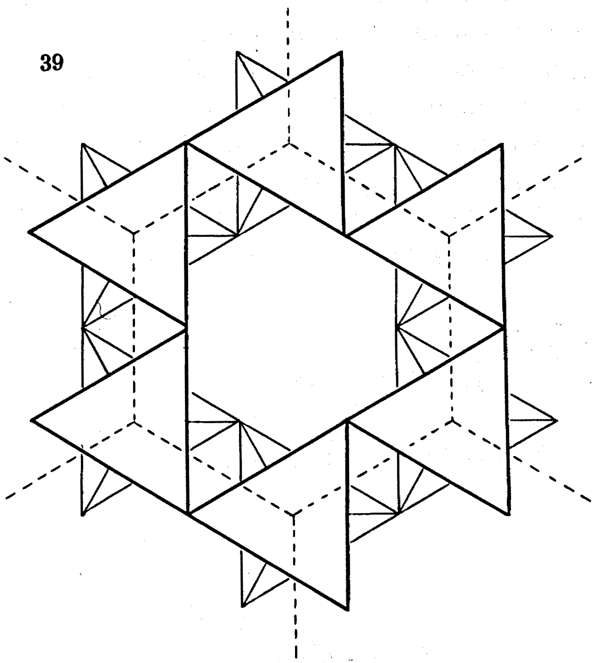

FIGURE 39. Double A_2X_3 layer based on 6^3.
FIGURE 40. Double A_2X_3 layer based on 4^4 (plan).

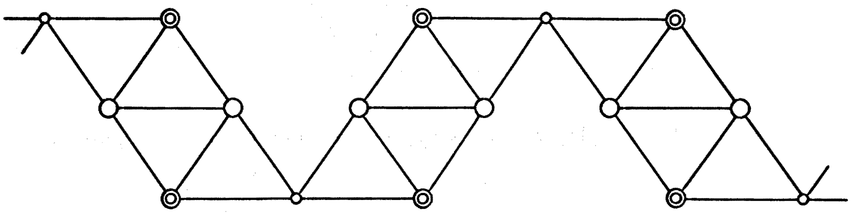

FIGURE 41. Elevation of layer of figure 40.

(*b*) *Structures of class* II: $v_2 = 2, v_4 = 2$

In the first structure of this class (table 6) only vertices are shared; in the others one or more edges are shared. The double layer of figure 43 is formed from two simple vertex-sharing AX_2 layers (figure 9*a*) related by the translation AB. Only two tetrahedra of the upper layer are illustrated, sufficient to show that the bond arrangement at an X atom is tetrahedral. If two AX_2 layers of figure 9*a* are related by a mirror plane parallel to the plane of the layer there is formed a double layer (figure 44) in which each tetrahedron shares one edge (and two vertices). In this and in all the remaining structures of table 6 there is square planar coordination of the X atoms.

Figure 1*a* represents a pair of tetrahedra sharing one edge which is normal to the plane of the paper and represented by a double circle; the composition is $(AX_3)_2$ ($v_1 = 2, v_2 = 2$). This

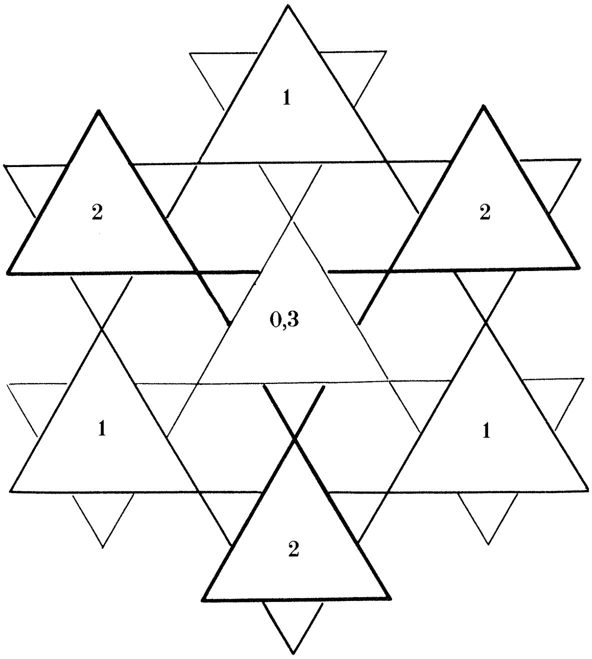

FIGURE 42. Three-dimensional A_2X_3 structure formed from prismatic A_6X_{12} units.

TABLE 6. A_2X_3 STRUCTURES OF CLASS II

tetrahedra sharing	type of structure		figure
vertices only	double layer		43
one edge and two vertices	double layer		44
	three-dimensional structures projecting as	6^3	1*c*
		3.12^2	13
		4.8^2	14
		$4.6.12$	15
two edges	single layer		45
three edges	double chain		see figure 61

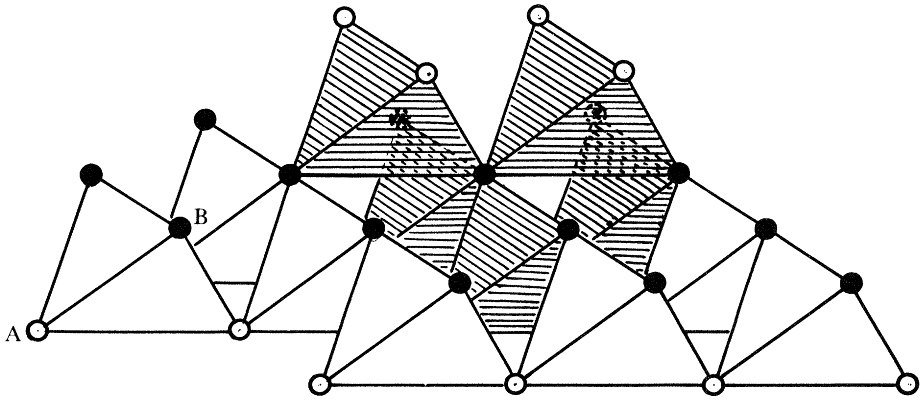

FIGURE 43. Double vertex-sharing A_2X_3 layer of class II. ○, v_2; ●, v_4 vertices.

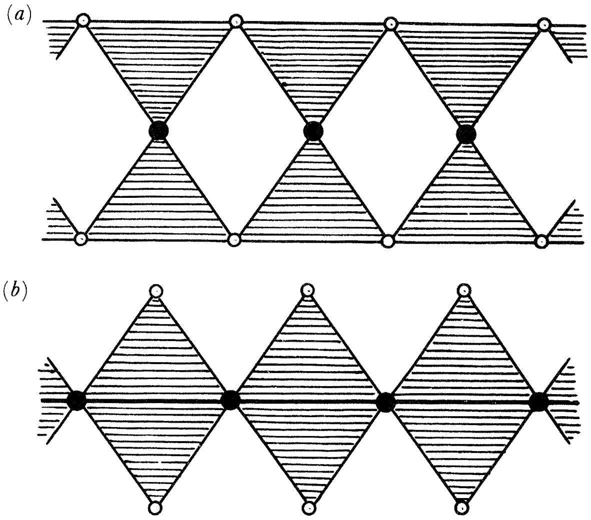

FIGURE 44. Two elevations of the double A_2X_3 layer formed from two HgI_2 layers related by a mirror plane. ○, v_2; ●, v_4 vertices. In (a) the v_4 vertices and in (b) the v_2 vertices lie on lines normal to the paper.

diagram is also the *projection* of an infinite chain of tetrahedra normal to the plane of the paper, where the double circle represents a continuous row of shared edges, that is, a string of v_4 vertices. This infinite chain has the composition A_2X_5 ($v_1 = 2, v_4 = 2$). If these chains are joined so as to convert the v_1 into v_2 vertices the composition becomes A_2X_3, as in the double layer of figure 44. Alternatively, they may be joined to form three-dimensional structures that project as figure 1 (c) or as figures 13–15.

A single layer in which each tetrahedron shares two edges is formed from edge-sharing ($BeCl_2$) chains joined as in figure 45. Three edges are shared by each tetrahedron in a double

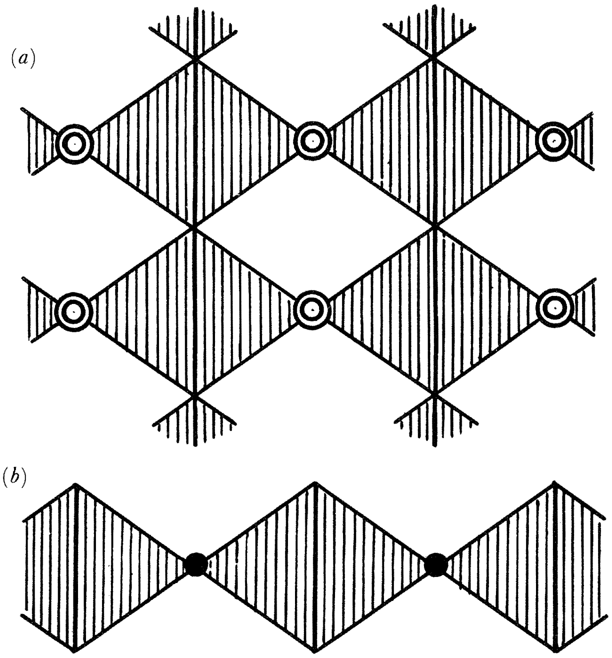

FIGURE 45. Single A_2X_3 layer of class II. In the plan (a) ◎ represents a shared edge normal to the paper (i.e. two v_2 vertices) and in the elevation (b) ● represents a continuous line of shared edges normal to the paper (i.e. a row of v_4 vertices).

chain which represents the structure of the anion in $CsCu_2Cl_3$, $CsAg_2I_3$, and $C_6H_5N_2(Cu_2Br_3)$. This chain is simply a strip, two tetrahedra in width, of the OPb layer of figure 61.

(*c*) *Structures of class* III: $v_1 = 1, v_6 = 3$

The only example we have found of a structure in this class is the layer of figure 46. One half of the unshared (v_1) vertices must lie on each side of the plane defined by the v_6 vertices to avoid unacceptably short X–X distances. The arrangement of six tetrahedra around each X atom is the symmetrical one illustrated in figure 47*a*.

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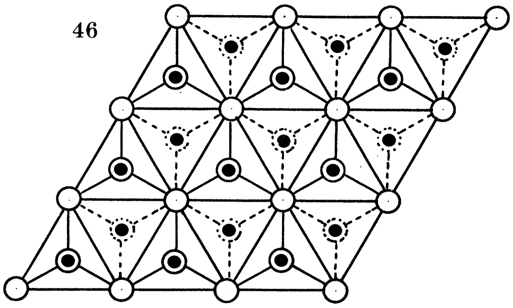

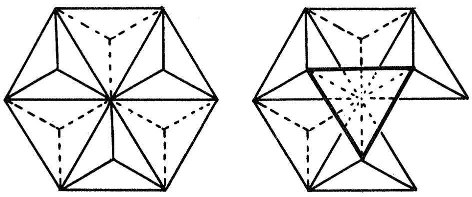
47*a* 47*b*

FIGURE 46. A_2X_3 layer of class III.

FIGURE 47. Types of six-coordination of X atoms (see text).

7. TETRAHEDRAL A_3X_4 STRUCTURES

Compounds A_3X_4 are necessarily few in number for purely 'chemical' reasons. They include the nitrides of Si and Ge; larger A atoms prefer a higher coordination number, as in the 8.6 coordinated structure of Th_3P_4. Oxides such as Fe_3O_4 contain metal atoms in two valence states and two different types of coordination by oxygen, as in the spinel structure. Ternary compounds A_2BX_4 include some in which one-third of the A positions in an A_3X_4 structure are occupied by atoms of a second element. They fall into two groups (table 7). The oxides and fluorides are structurally different from the compounds of the second group which includes sulphides, selenides, tellurides and iodides. The compounds of group (*a*) all have structures

TABLE 7. STRUCTURES OF TERNARY COMPOUNDS A_2BX_4

(*a*)

phenacite structure

Li_2SeO_4	Li_2CrO_4	Li_2MoO_4	Li_2WO_4	Li_2BeF_4
Be_2SiO_4	Be_2GeO_4	Zn_2SiO_4	Zn_2GeO_4	Li_2ZnF_4
Al_2CdO_4				

(*b*)

defective sphalerite structure			defective wurtzite structure	
regular		random	regular	random
Al_2CdS_4	β-Cu_2HgI_4	α-Ag_2HgI_4	β-Ga_2CdS_4	β-Al_2ZnS_4
α-Ga_2CdS_4†	β-Ag_2HgI_4	α-Cu_2HgI_4	—	—
In_2CdSe_4	—	Ga_2HgTe_4	—	—

† Ga_2CdS_4 has two forms. The stable form is tetragonal ($I\bar{4}$) *with* $Z = 14$ (sphalerite superstructure) and a quenched (β) form has a wurtzite superstructure with $Z = 28$ and space group $Pna2_1$ (Pardo *et al.* 1984).

of the phenacite type, which is described shortly, whereas those of group (*b*) have defective sphalerite or wurtzite structures in which there is either regular or random arrangement of the vacancies in the parent structure. Compounds of the second group are numerous, for they include not only compounds of metals which are normally tetrahedrally coordinated in their sulphides etc. but also 3d elements which in the +2 state do not usually exhibit tetrahedral coordination. Examples include Ga_2MS_4 in which M is Mn, Fe, or Co (Pardo 1977). An important difference between the phenacite-like structures of the compounds of group (*a*) and the structures of compounds of group (*b*) is that in the former the coordination of the X atoms is trigonal coplanar (or approximately so), whereas in the defect sphalerite and wurtzite structures the coordination of X is pyramidal, ideally three of the four tetrahedral positions. This is presumably the reason why the more ionic compounds adopt the phenacite structure and the sulphides, etc., the structures with pyramidal coordination of X.

Structures of class I: $v_3 = 4$

All the tetrahedral A_3X_4 structures we have found belong to this class. These structures will be illustrated here as assemblies of tetrahedra, but we should mention an alternative way of describing these structures. The connected systems of A and X atoms in these A_3X_4 structures are three- and four-connected nets in which A and X atoms alternate. The sum of the numbers of three- and four-connected points in the repeat unit (unit cell) of such a net must be a multiple of seven. We call this number Z' to distinguish it from Z, which is conventionally used for the number of formula-masses in the unit cell of a crystal structure. For example, if the unit cell of an A_3X_4 structure contains only 3A and 4X atoms $Z = 1$ and $Z' = 7$. The only nets previously described in this $Z' = 7m$ family (Wells 1979) were one with $Z' = 7$ and two with $Z' = 14$, and one of the last two is not of interest here because the A_3X_4 structure, $(Pt_3O_4)Na_x$, based on the net has square coplanar coordination of the A atoms. The present study has led to the recognition of three more nets with $Z' = 14$ (Wells 1986).

The structures we shall describe first can be built from layers of the two kinds shown in figure 48*a* or *b*, which have the composition A_3X_7. In these layers the X atoms at the bases of the tetrahedra form a complete close-packed layer, and the remaining (upper) vertices are in three-quarters of the positions of a second close-packed layer; contrast the AX_2 layers of figures 16 and 17, in which the X atoms form two complete close-packed layers. Two of the layers of figure 48*a* or *b* may be joined to form a double layer if the unshared vertices of the tetrahedra of the lower layer are directed upwards and those of the upper layer downwards (figure 49*a*, *b*). In these double layers each tetrahedron shares two edges, and the composition is A_3X_4. (The double layer of figure 49*a* may obviously be built from the prismatic A_6X_{12} units of figure 28*b* or figure 29*a*.) There are two kinds of three-coordination of the X atoms in these double layers, and this is also true of the three-dimensional structures formed from the layers of figure 48. In these three-dimensional structures, in which only vertices are shared, the X atoms form a complete close-packed assembly in which the A atoms occupy three quarters of the tetrahedral positions occupied in the parent AX structure. The two simplest structures are therefore defective sphalerite (CCP) and wurtzite (HCP) structures; polytypes are possible as in the case of the AX structures. Since each of the layers of figure 48 forms a structure with cubic or hexagonal close-packed X atoms there are four three-dimensional structures to be described.

If the layers of figure 48*a* are stacked so that successive layers are related by the translation indicated by the arrow there is formed a structure in which there is cubic closest packing of

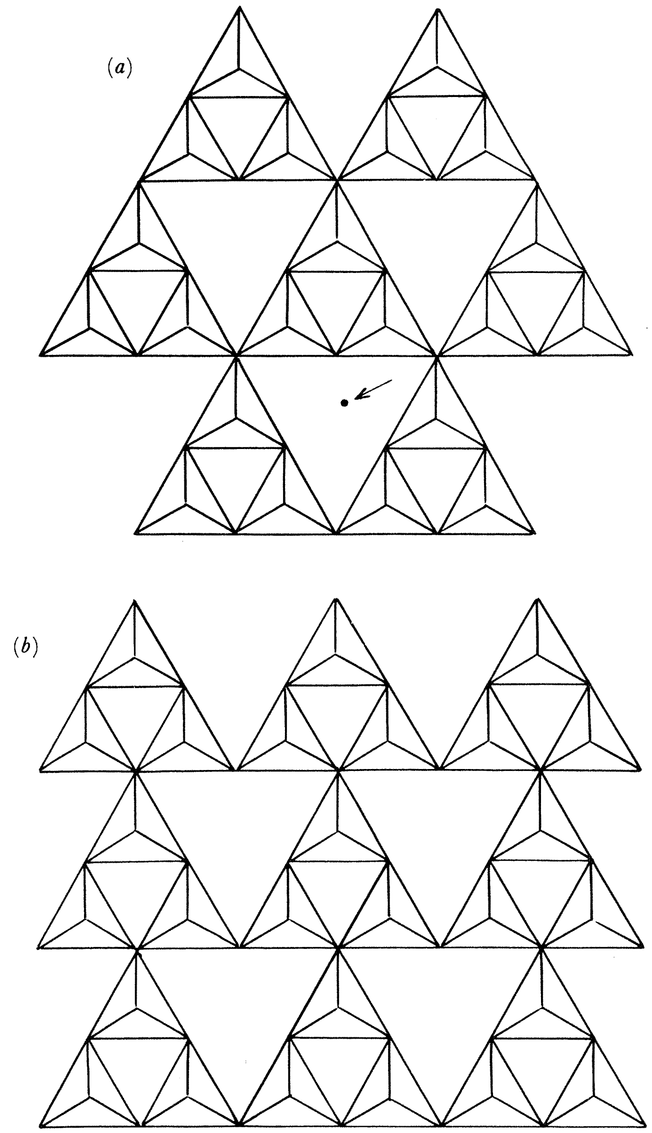

Figure 48. Two layers of composition A_3X_7 (see text).

the X atoms. This structure is referable to a unit cell containing one A_3X_4 unit which is shown in figure 50. It is based on the simplest known three-dimensional (3,4)-connected net of the 7*m* family, having $Z' = 7$, and the positions of the A and X atoms in the unit cell are 3(*d*), $\frac{1}{2}00$, and 4(*e*), *xxx* with $x = \frac{1}{4}$, in the space group $P\bar{4}3m$ (no. 215). The structure of In_2CdSe_4 is based on this net, that is, it is a superstructure of the (unknown) cubic A_3X_4 structure of figure 50. It retains the simple ($Z' = 7$) cell but owing to the non-equivalence of the A atoms the space group is $P\bar{4}2m$ compared with $P\bar{4}3m$ for the cubic structure. If the A_3X_7 layers of figure 48*a* are stacked with successive layers related by a rotation through 60° the result is a structure in which there is hexagonal closest packing of the X atoms. This structure is referable to the hexagonal cell shown in projection in figure 51. The unit cell contains two A_3X_4 and therefore the net on which it is based has $Z' = 14$. Evidently this structure could be built from

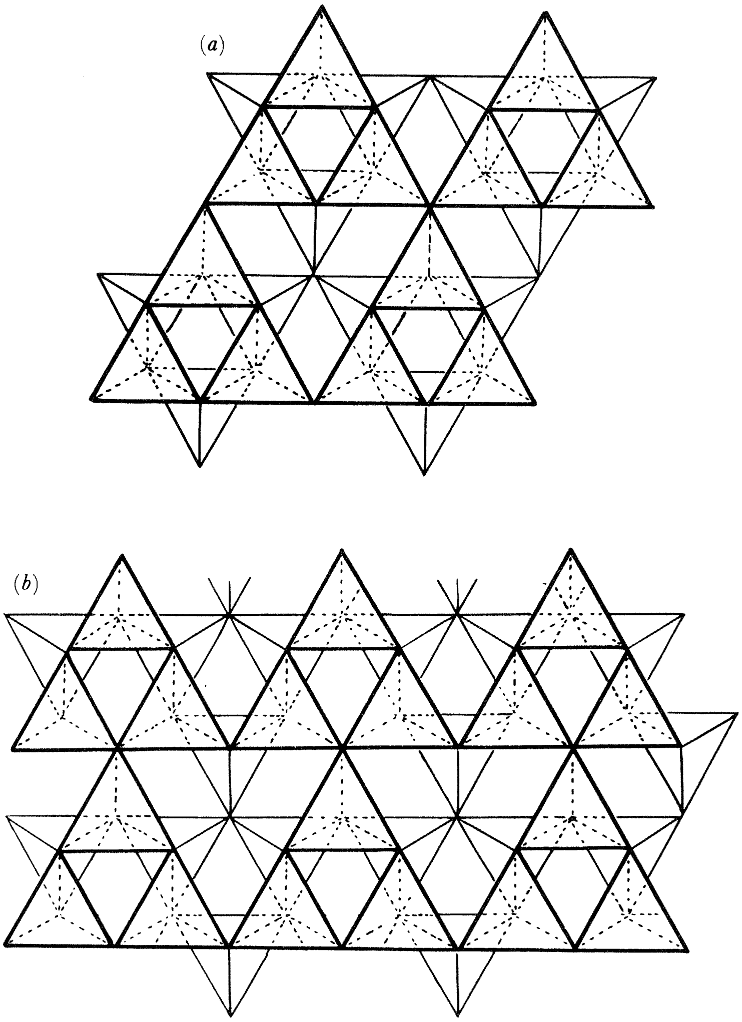

Figure 49. Double A_3X_4 layers formed from the layers of figure 48.

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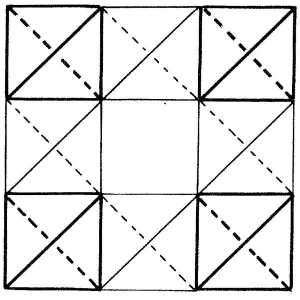

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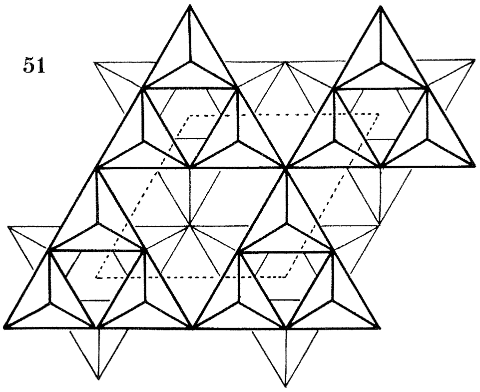

Figure 50. The cubic tetrahedral A_3X_4 structure based on the (three, four)-connected net with $Z' = 7$. Heavy and light lines outline tetrahedra at heights 0 and $\frac{1}{2}$.

Figure 51. Unit cell of hexagonal A_3X_4 structure formed from the layer of figure 48(*a*).

the F_3 chains of figure 23 joined together at threefold junctions; these chains form the A_2X_3 structure of figure 35 if joined through v_2 vertices.

Corresponding to the cubic and hexagonal structures formed from the layer of figure 48(*a*) there are CCP and HCP structures formed from the layer of 48(*b*). The first, like the cubic structure described above, is a defective sphalerite structure. It represents the structure of the ordered (β) form of Cu_2HgI_4 and other compounds listed in table 7. The relation of this tetragonal structure to the cubic structure may be more easily seen from the projections of these tetrahedral structures along a cubic axis and tetragonal *c* axis respectively (figure 52*a*, *b*). To simplify the diagrams a HgI_4 layer is represented by the diagonal lines which are the continuous lines of tetrahedron edges on the upper and lower surfaces of the layer (compare figure 9*a*). Layers of the HgI_2 type at the heights indicated in figure 52 are joined through tetrahedra in one half of the available positions. The arrangement of metal atoms of figure 52*b* implies a tetragonal cell with doubled *c* axis. There is a second tetragonal A_2BX_4 structure (β-Ag_2HgI_4) in which the same positions are occupied by B and X atoms but the distribution of the A atoms in two sets of equivalent positions leads to lower symmetry; space group $I\bar{4}$ (no. 82) instead of $I\bar{4}2m$ (no. 121).

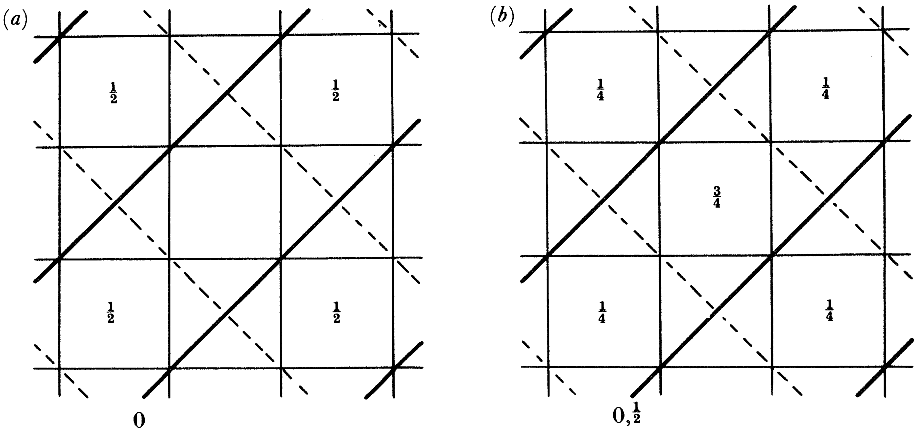

FIGURE 52. Projections of cubic and tetragonal A_3X_4 structures (see text).

The fourth structure of this group is the HCP structure formed from the layer of figure 48*b* if alternate layers are rotated through 180°. (In the CCP structure all layers are similarly oriented and related by a simple translation.) This HCP structure is repeated after two layers, as shown in the projection of figure 53. It is referable to an orthogonal unit cell containing 2 A_3X_4 and is therefore the third member of this family of structures based on three-dimensional nets with $Z' = 14$. It may be helpful to summarize the structures formed from the layers of figure 48*a*, *b* in table 8. As layers of each type may be joined to give either cubic or hexagonal closest packing of the X atoms an indefinitely large number of more complex polytypes may be built.

The tetrahedral structure shown projected along a sixfold axis in figure 54 is based on a fourth net with $Z' = 14$; a prominent feature is the hexagonal tunnel of the E_6 type. This net represents the structure of β-Si_3N_4 (Goodman & O'Keeffe 1980) which has the most symmetrical configuration of the net (space group $P6_3/m$). The structure of α-Si_3N_4 has a less regular arrangement of the SiN_4 groups along the *c* axis which requires a doubled *c*

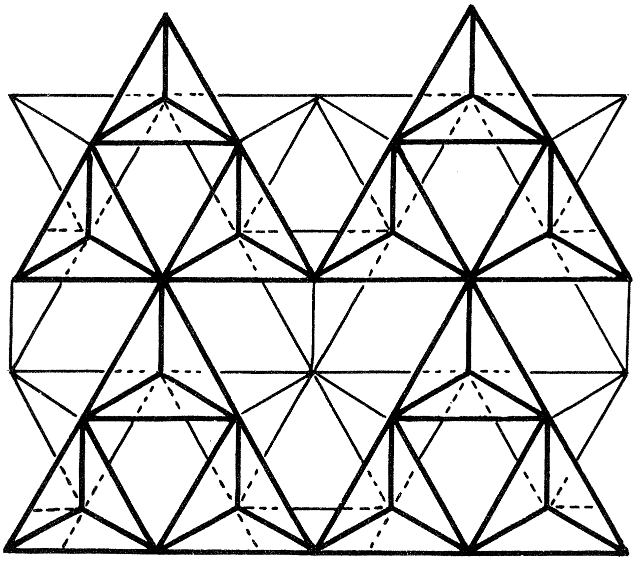

FIGURE 53. A_3X_4 structure formed from the layer of figure 48(*b*).

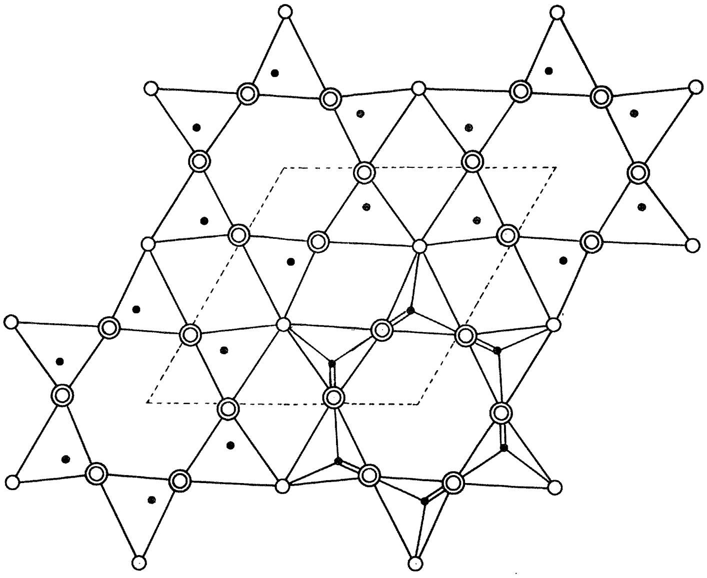

FIGURE 54. The structure of β-Si_3N_4 shown as a system of tetrahedral SiN_4 groups. ●, Si atoms; ○, N atoms; ◎, columns of tetrahedron edges normal to the plane of the paper.

TABLE 8. DERIVATION OF A_3X_4 STRUCTURES FROM A_3X_7 LAYERS

single (A_3X_7) layer	double (A_3X_4) layer	three-dimensional structure	*Z'*
figure 48*a*	figure 49*a*	figures 50, 52*a* CCP	7
		figure 51 HCP	14
figure 48*b*	figure 49*b*	figure 52*b* CCP	14
		figure 53 HCP	14

parameter, 4 Si_3N_4 in the unit cell, and space group $P31c$ (Marchand *et al.* 1967). In this structure the hexagonal tunnels are interrupted to form two large closed interstices in each unit cell at intervals of $\frac{1}{2}c$. Other structures of the same topological type include those of the polymorphs of Ge_3N_4 and numerous ternary complex oxides and halides A_2BX_4 with the phenacite structure (table 7). The non-equivalence of the two kinds of tetrahedrally coordinated atom and minor adjustments in the atomic positions lead to lower symmetry, as in the case of the mineral phenacite, Be_2SiO_4, which has rhombohedral symmetry ($R\overline{3}$) and 18 A_2BX_4 in the unit cell.

8. TETRAHEDRAL AX STRUCTURES

(*a*) *Structures of class* I: $v_4 = 4$

In this class both the A and X atoms are four-connected; the structures may therefore be derived from four-connected nets in which A and X atoms alternate. Such nets are possible structures for elements forming four bonds, and corresponding to the two simplest uniform (6^6) three-dimensional four-connected nets of cubic and hexagonal diamond, there are the sphalerite (zinc blende) and wurtzite structures of ZnS and other chalcogenides. They are built from AX_4 tetrahedra (ZnS_4 or SZn_4) which share only vertices, each vertex being common to four tetrahedra. In other structures of this class AX_4 tetrahedra share edges, and we may conveniently list them in order of increasing numbers of shared edges (table 9).

TABLE 9. TETRAHEDRAL EDGE-SHARING AX STRUCTURES OF CLASS I

number of edges shared	figure	coordination of X	examples	
1	55	tetrahedral	BeO	$(AlLi)O_2$
2	56	coplanar	SPt	OPd
3	58	skew tetrahedral	—	
4	60	pyramidal	OPb	LiOH

One edge shared. In the structure of β-BeO (and isostructural γ-$AlLiO_2$) pairs of edge-sharing tetrahedra are joined to form a three-dimensional structure in which each O atom is also in tetrahedral coordination and these atoms are arranged in approximately hexagonal closest packing. The arrangement of the O atoms (figure 55) is essentially the same as in the rutile (TiO_2) structure; pairs of edge-sharing tetrahedra occupy the spaces between the octahedra in the rutile structure.

Two edges shared. Chains in which each tetrahedron shares two (*trans*) edges, as in $BeCl_2$ or SiS_2, are joined as in figure 56. In the projection (*a*) these chains are perpendicular to, and in the elevation (*b*) parallel to, the plane of the paper. In this structure X has four coplanar A neighbours. In the 'ideal' structure with (cubic) closest packing of the X atoms and regular tetrahedral coordination of A the interbond angles at X would be $70\frac{1}{2}°$ and $109\frac{1}{2}°$ (two of each). These are so far removed from the preferred values for dsp^2 hybridization (four of 90°) that the structures of actual compounds are considerably different from the ideal structure. A number of compounds have structures of this basic topological type, and of these the most symmetrical is the tetragonal structure of SPt and OPd. (A less symmetrical structure is adopted by SPd and an appreciably less symmetrical variant by OCu and OAg.) In SPt the angles at S are two of $97\frac{1}{2}°$ and four of 115°, whereas those at Pt are two of $82\frac{1}{2}°$ and two of $97\frac{1}{2}°$.

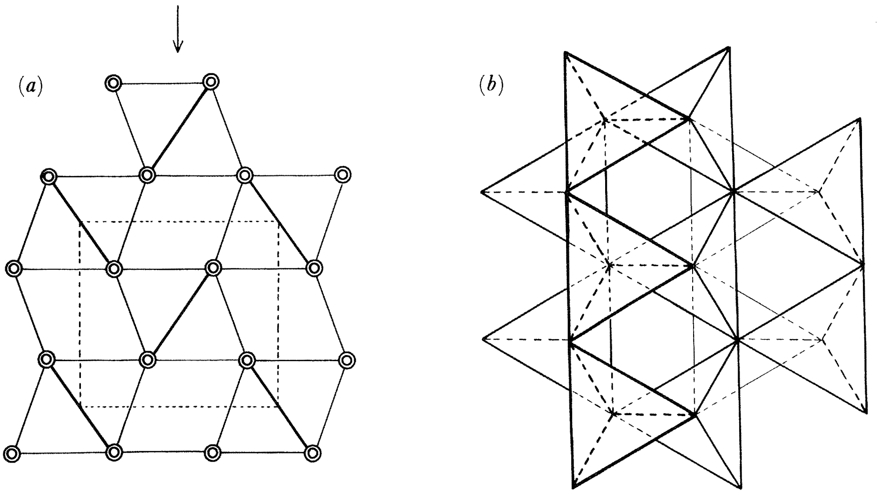

Figure 55. Idealized BeO structure: (*a*) elevation, with HCP layers normal to the plane of the paper and shared edges drawn with heavy lines; (*b*) view in direction of the arrow in (*a*) showing the four-coordination of X.

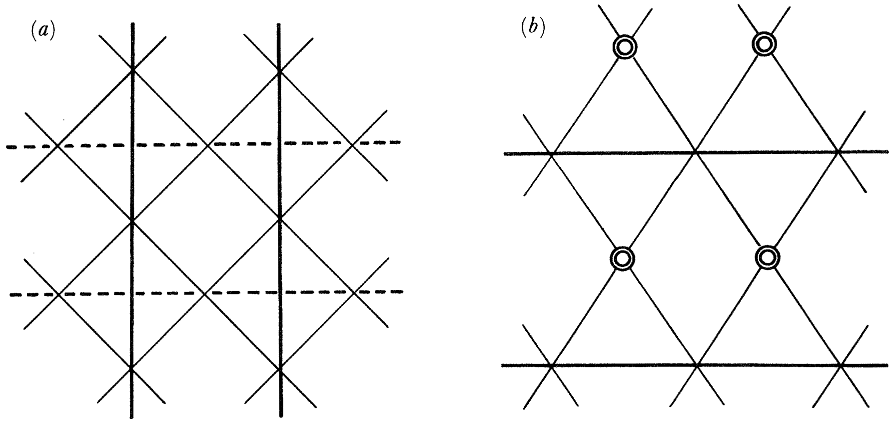

Figure 56. Plan and elevation of the structure of SPt. Heavy lines (full and broken) represent shared edges, and in (*b*) ◎ represent continuous lines of shared edges normal to the paper.

Three edges shared. Structures in which each tetrahedron shares three edges include a layer structure and two three-dimensional structures. The AX layer (figure 57) is formed by filling all the tetrahedral interstices between a pair of closest packed X atoms.

We have described two special configurations of the AX_2 layers of class I(*b*) based on 6^3 and other three-connected planar nets, in which the edges shared between each pair of tetrahedra are (*a*) perpendicular to the plane of the layer (figure 1*c*) or (*b*) inclined to that plane (figure 16). In the layers of type (*b*) based on 6^3 and 4.8^2 the X atoms form two complete CP layers, between which the A atoms occupy one half of the tetrahedral interstices, while in those based on 3.12^2 and $4.6.12$ the X atoms occupy respectively $\frac{2}{3}$ and $\frac{3}{4}$ of the CP positions. The layers of type (*a*) may be superposed to form three-dimensional structures of composition A_2X_3 which have already been described. The layers of type (*b*) on the other hand may be stacked to form three-dimensional AX structures of class I. We consider first the 6^3 layer of figure 16, the right-hand portion of which shows two rings of six tetrahedra. If successive layers are related by the translation AB in figure 16 there is cubic closest packing of the X atoms. Figure 58 shows

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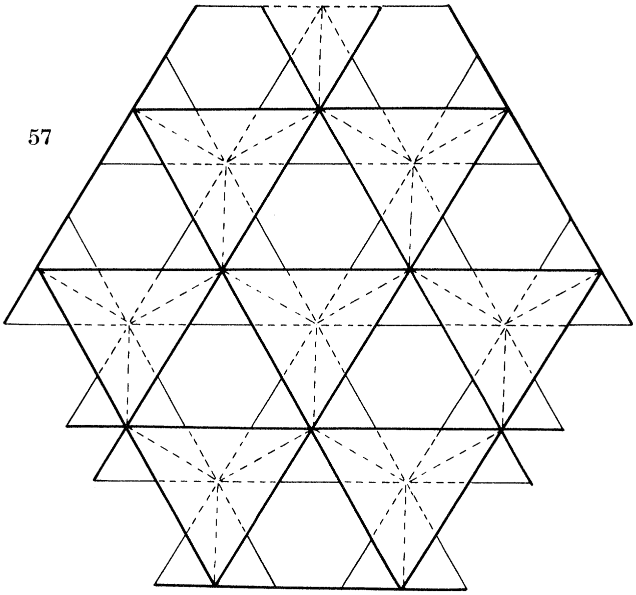

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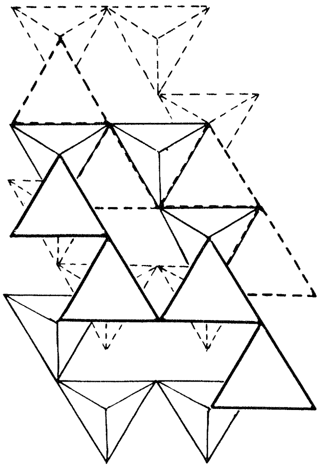

FIGURE 57. AX layer in which all tetrahedral holes are filled between two CP X layers.
FIGURE 58. The three-dimensional AX structure formed from the layer of figure 16.

two layers (full and broken lines) that should be compared with figure 16. In this three-dimensional structure each tetrahedron shares three edges, and the coordination of all X atoms is the skew tetrahedral arrangement of figure 59*a*. The layers based on 4.8^2 (figure 17) may also be stacked to form a CCP structure in which each tetrahedron shares three edges (figure 60); in this structure there are two types of four-coordination of the X atoms (figure 59*a*, *b*). In the layers based on 3.12^2 and $4.6.12$ (figures 18 and 19) there are not complete CP layers of X atoms. No edge-sharing three-dimensional structures are possible, but structures may be built in which tetrahedra share faces and X atoms occupy $\frac{2}{3}$ or $\frac{3}{4}$ of the positions of hexagonal closest packing.

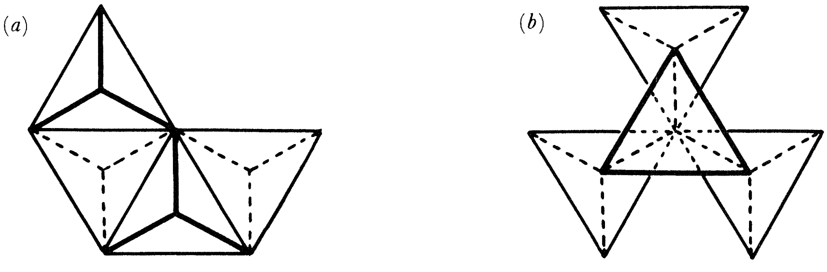

FIGURE 59. Types of four-coordination in AX structures derived from the layers of figures 16 and 17.

Four edges shared. Four edges of each tetrahedron are shared in the layer of figure 61, which is simply a slice of the antifluorite structure cut perpendicularly to a fourfold axis; compare with the layer of figure 57 which is a slice of the same structure cut perpendicularly to a threefold axis. This layer is the idealized structure of a layer of the OPb or LiOH structures, in which the O or Li atoms respectively are in tetrahedral coordination. The neighbours of an X atom (Pb or OH) are four A atoms at the corners of the base of a tetragonal pyramid with X at the apex.

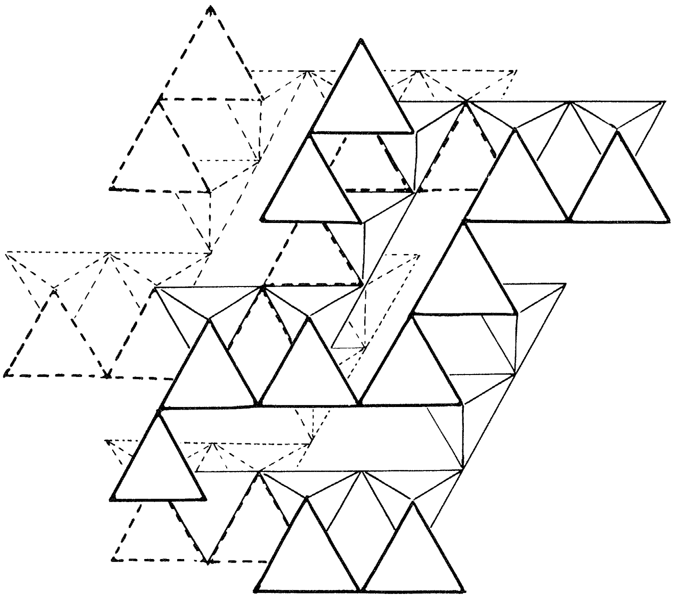

FIGURE 60. The three-dimensional AX structure formed from the layer of figure 17.

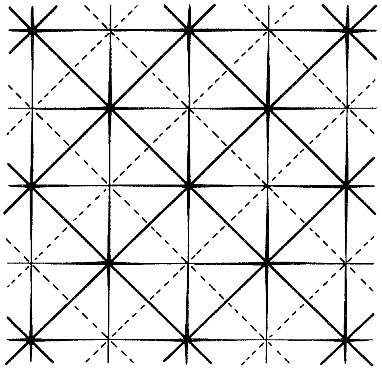

FIGURE 61. One layer of the structure of OPb or LiOH.

(*b*) *Structures of class* II: $v_2 = 1, v_6 = 3$

The double layer of figure 62 is formed from the AX_2 chains of figure 27 ($v_1 = 1, v_3 = 3$) by sharing the edges drawn with heavy full lines in figure 27 *b* with those shown as broken lines. It is necessary to rotate alternate chains through 180° in the plane of the paper; otherwise the

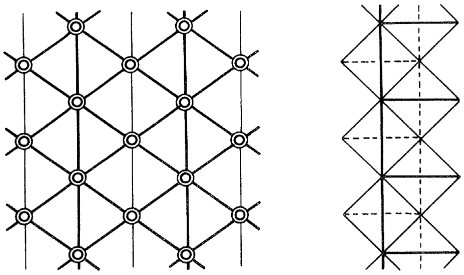

FIGURE 62. Double AX layer of class II: plan and elevation.

AX layer of figure 57 is formed. In the double layer of figure 62 each tetrahedron shares four edges. The arrangement of the six tetrahedra meeting at an X atom is that of figure 47*b*.

The A_2X_3 layer (figure 46) of class III ($v_1 = 1, v_6 = 3$) can be joined in obvious ways to form three-dimensional structures, pairs of v_1 vertices being converted into v_2 vertices. The type of six-coordination of X (figure 47*a*) is, of course, the same as in the layer of figure 46. The X atoms in these structures are arranged in closest packing. As the layers may be joined so that the X layers are in the positions of *h* or *c* packing there is an indefinite number of polytypes. However, there is the same limitation on types of closest packing as in the AX_2 structures based on 10^3-b or 10^3-c (see figure 20) for alternate layers of X atoms must be *c*. The CP symbol must therefore contain an odd number of consecutive *c* layers, as in *c* or *ch*.

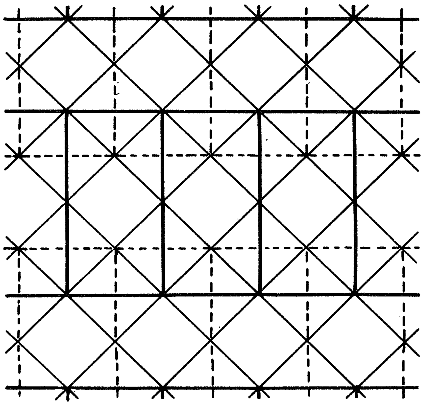

FIGURE 63. The three-dimensional A_4X_3 structure of class I.

9. TETRAHEDRAL A_4X_3 STRUCTURES

One structure has been found in each of the classes I and II.

(*a*) *Structures of class* I: $v_4 = 1, v_6 = 3$

The three-dimensional structure of figure 63 is formed from the AX layer of figure 62 by joining the v_2 vertices in pairs to become v_4 vertices. The AX layer is perpendicular to the paper in the end-on view of figure 62*b* and also in figure 63 where it is rotated through 90°.

(*b*) *Structures of class* II: $v_4 = 2, v_8 = 2$

A double layer of composition A_4X_3 is formed from two AX layers of figure 61 related by a mirror plane parallel to the plane of the layer. Alternatively, it is a slice two tetrahedra thick of the antifluorite structure. In this double layer, which represents the structure of the anion in $K(Cu_4S_3)$, each tetrahedron shares five edges.

10. TETRAHEDRAL A_3X_2 STRUCTURES

The single solution ($v_6 = 4$) of our equations for this composition implies structures of 4.6 coordination. A thorough investigation of tetrahedral A_3X_2 structures would require the examination of all structures based on four- and six-connected nets which can be built with regular tetrahedral coordination of A and acceptable distances between X atoms of different

AX_4 tetrahedra. This has not been carried out; we restrict ourselves here to the structures of table 10. The omission from this table of an important A_3X_2 structure of 4.6 coordination, the corundum structure of α-O_3Al_2 and other sesquioxides, calls for comment because the structure may be represented as a connected three-dimensional system of *either* octahedral AlO_6 *or* tetrahedral OAl_4 groups. The metal ions occupy octahedral interstices in a hexagonal close packing of oxide ions. The (idealized) structure may be built of regular octahedra (hence its inclusion in a survey of octahedral structures (Wells 1984*c*), but because the tetrahedral coordination of O is very irregular (Al–O–Al angles 85°, 94° (two), 120°, and 132° (two)) it is necessary to show that the framework *cannot* be built from regular tetrahedra. This can be done by examining the way in which the tetrahedral OAl_4 groups are joined together. It is found that the group of six OAl_4 tetrahedra which meet at each vertex (Al) consists of a group of three with a common edge plus three which have only one vertex in common. This arrangement is not possible for regular tetrahedra if we insist on acceptable distances between Al atoms of different tetrahedra.

TABLE 10. STRUCTURES OF COMPOUNDS A_3X_2

Nitrides M_3N_2, phosphides M_3P_2 and arsenides M_3As_2

	Be[a]	Mg	Zn	Cd	Ca(α)
N	A	A	A	A	A
P	A	A	B	B	—
As	—	A	B	B	—

[a] Also a high-temperature form (Hall *et al.* 1969) A, 'anti-Mn_2O_3' structure; B, Zn_3As_2 or closely related structure.

Sesquioxides O_3M_2 of Mn, Sc, Y, In, Tl and some 4f and 5f metals.

In contrast to the hexagonal closest packing of A atoms (ions) in the corundum structure, the *positions of the X atoms* in the structures of table 10 are those of cubic closest packing. We shall describe the idealized CP structures, it being understood that in actual structures there may be considerable departures from perfect closest packing of the X atoms.

The formation of an A_3X_2 structure with tetrahedral coordination of A in a closest packing of X atoms results from occupancy of three quarters of the tetrahedral interstices. Filling of more than one half of these interstices in hexagonal closest packing leads to pairs of face-sharing tetrahedral AX_4 groups, and therefore the HCP A_3X_2 structures are not found. However, occupancy of three quarters of the tetrahedral interstices in cubic closest packing gives a family of structures which includes those of table 10. The sharing of faces between AX_4 groups can also be avoided in *hc* (ABAC...) packing of X atoms, as in the high-temperature form of Be_3N_2 (Hall *et al.* 1969). In the nitrides, phosphides, and arsenides, A_3X_2, the metal atoms (ions) are four-coordinated and N (P, As) close-packed; in the sesquioxides the oxygen atoms are four-coordinated and the metal atoms are in the positions of cubic closest packing.

The structure in which all tetrahedral interstices are occupied by A atoms in a cubic closest packing of X atoms is the antifluorite structure A_2X, in which X has eight A neighbours arranged at the vertices of a cube. The projection of this structure is the same as that of one layer of the structure (figure 61), where it can be seen that along any horizontal or vertical row successive tetrahedra are related by a rotation through 90°. Along a cubic axis therefore *alternate* tetrahedra are in the same orientation, that is, the pattern repeats after two tetrahedra. In the three-dimensional A_2X structure the smallest cubic (face-centred) unit cell contains eight tetrahedrally coordinated A atoms and 4 X atoms the latter having 8 A neighbours situated at the vertices of a cube (figure 64). The A_3X_2 structures arise by removal of one quarter of the A atoms from the A_2X structure, leaving X with six neighbours at six of the vertices of a cube. The missing atoms are those at the ends of an edge (E), a face diagonal (F), or a body-diagonal (B). These coordination groups are illustrated in figure 65, in which the lower diagrams show how these groups appear in the projections of figure 66. The A atoms in the A_2X structure lie at the nodes of a primitive cubic lattice with unit translation equal to one half that of the tetrahedral structure, and therefore the positions of the A atoms in the A_3X_2 structures may be found by removing in a regular way one quarter of the points of a primitive cubic lattice. Of the four ways of doing this (figure 66), one (F_1) is referable to a unit cell containing three A and the others to cells containing six A. Apparently there are no examples of compounds with these simple structures. All the structures E, F_2 and B (but not F_1) of figure 66 may be formed by stacking the layer of figure 67*a*, which has the simplest possible arrangement of vacancies. (As an isolated layer this has the composition A_3X_4; it is not included with A_3X_4 structures of class I ($v_3 = 4$) because some tetrahedra share two and others four edges.)

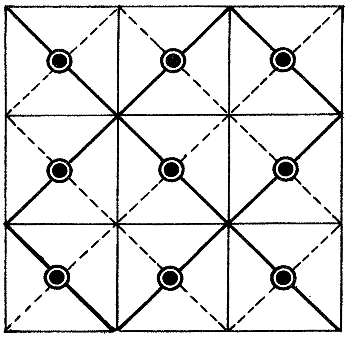

FIGURE 64. Projection of the CCP antifluorite A_2X structure shown as a system of edge-sharing tetrahedral AX_4 groups.

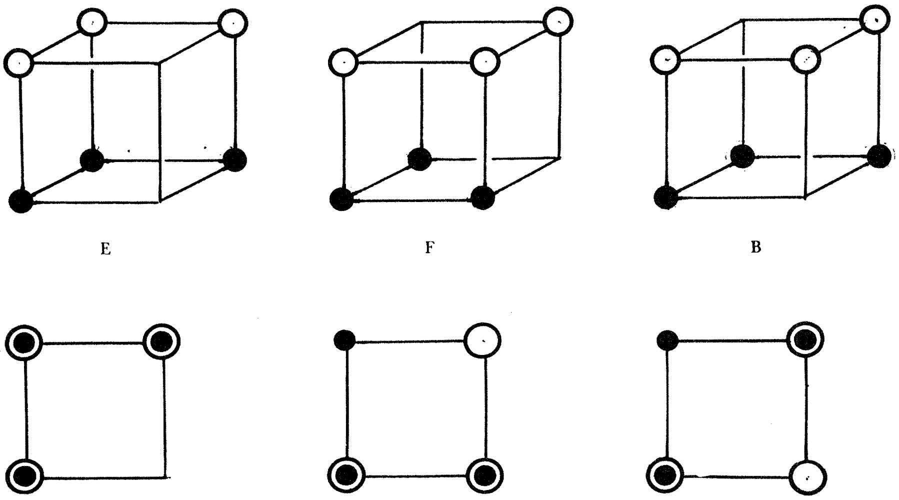

FIGURE 65. The (idealized) coordination groups E, F and B in A_3X_2 structures.

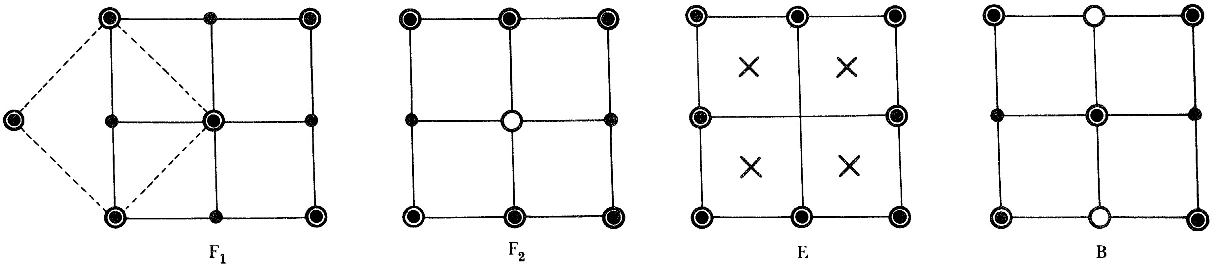

FIGURE 66. The four simplest A_3X_2 structures derived from the antifluorite structure (figure 64) by removing one quarter of the tetrahedrally coordinated A atoms. ● and ○ represent A atoms at heights 0 and $\frac{1}{2}$, and X (shown only in E) mark the positions of the CCP X atoms at heights $\frac{1}{4}$ and $\frac{3}{4}$.

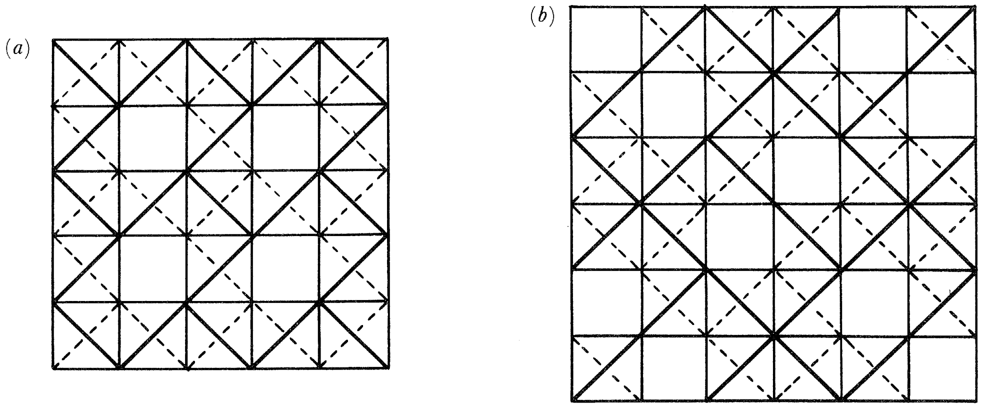

FIGURE 67. Two arrangements, (a) and (b), of vacancies in a layer of tetrahedra in A_3X_2 structures.

In O_3Mn_2 the pattern of vacancies in a (100) layer is that of figure 67*b*, and four layers of this kind form the repeat unit. Because there are many ways of arranging the vacancies in the tetrahedral positions there is an indefinitely large number of structures with E-, F- or B-type six-coordination groups or combinations of these, but observed structures favour F or B types. The majority of A_3X_2 compounds of table 10 adopt the O_3Mn_2 structure, in which the unit cell contains 16 formula-masses and there is F-type coordination of three quarters of the metal atoms and B-type coordination of the remainder. In Cd_3As_2 on the other hand there is F-type coordination of the metal atoms in a complex structure with 32 Cd_3As_2 in the (tetragonal) unit cell. Owing to the arrangements of vacant A sites and also to small distortions from the ideal CCP structure few A_3X_2 compounds have cubic symmetry, including O_3Mn_2 itself, though the mineral bixbyite, $O_3(Fe, Mn)_2$, is cubic, as also is O_3In_2. There has been some difference of opinion concerning the structures of Zn_3P_2, Zn_3As_2, Cd_3P_2, and Cd_3As_2, which have closely related structures or possibly essentially the same structure. The latest single crystal study of Cd_3As_2 (Steigmann & Goodyear 1968) led to a tetragonal structure referable to a unit cell containing 32 Cd_3As_2 in which the arrangement of vacancies in the tetrahedral interstices of a CP assembly of As atoms is consistent with the space group $I4_1\,cd$. The structure is more complex than that of O_3Mn_2 though the arrangement of vacancies in any one of the eight layers is the same as that in O_3Mn_2 (figure 67*b*). In all these A_3X_2 structures there are departures from the ideal structure with CP X atoms and the six-coordination groups described above.

TABLE 11. EDGE-SHARING STRUCTURES OF THE ANTIFLUORITE FAMILY

number of edges shared	1	2	3	4	5	6
formula	AX_3	AX_2	A_2X_3	AX	A_4X_3	A_2X
type of structure	finite (dimer)	chain	double chain	layer	double layer	three-dimensional

11. TETRAHEDRAL A_2X STRUCTURE

The solution $v_8 = 4$ is realized if all the tetrahedral interstices in a cubic closest packing of X atoms are occupied by A atoms when each X is surrounded by eight A atoms at the vertices of a cube. This is the antifluorite structure of, for example, the oxides M_2O of Li, Na, K and Rb. A model can be constructed by stacking the AX layers of figure 61 so that the two remaining edges of each tetrahedron are shared; this is the last member of the family of structures of table 11.

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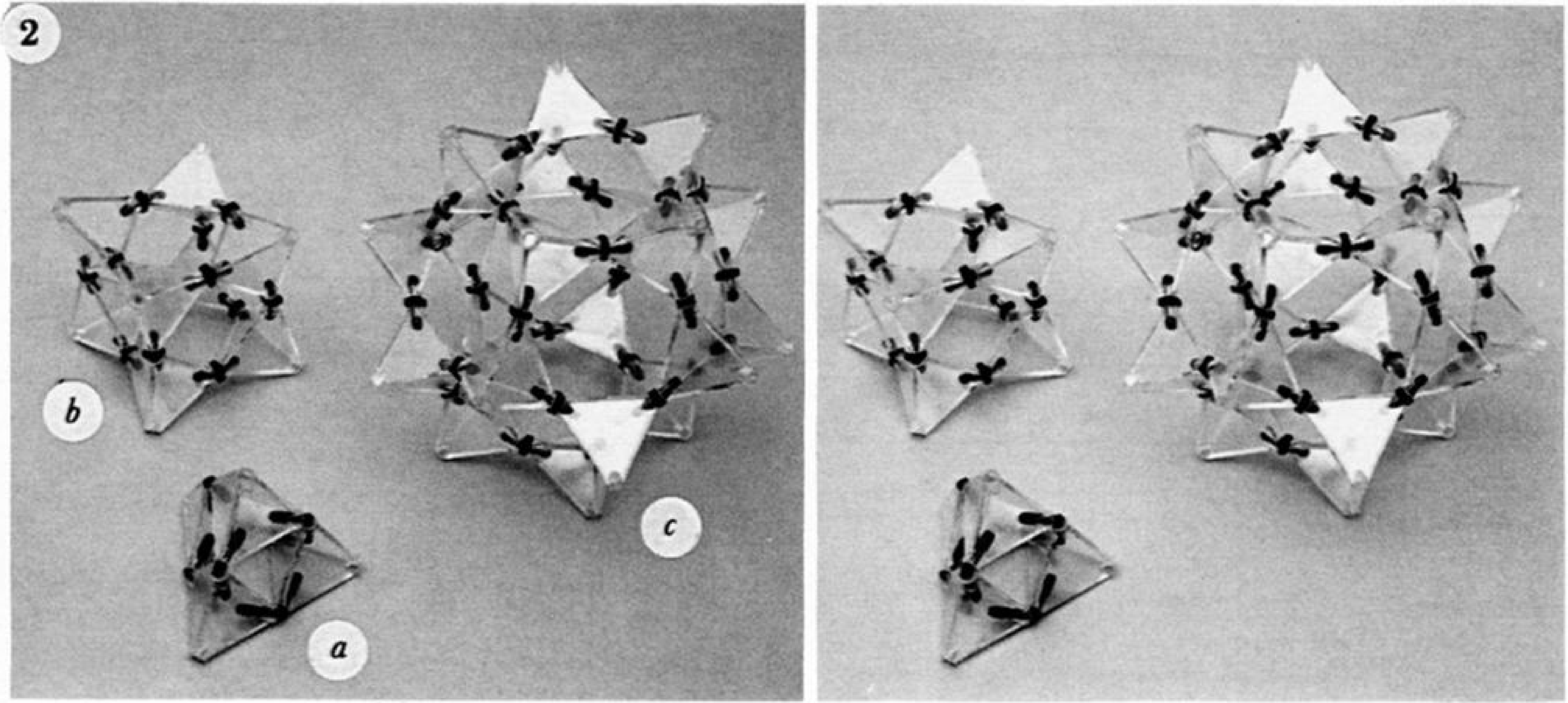
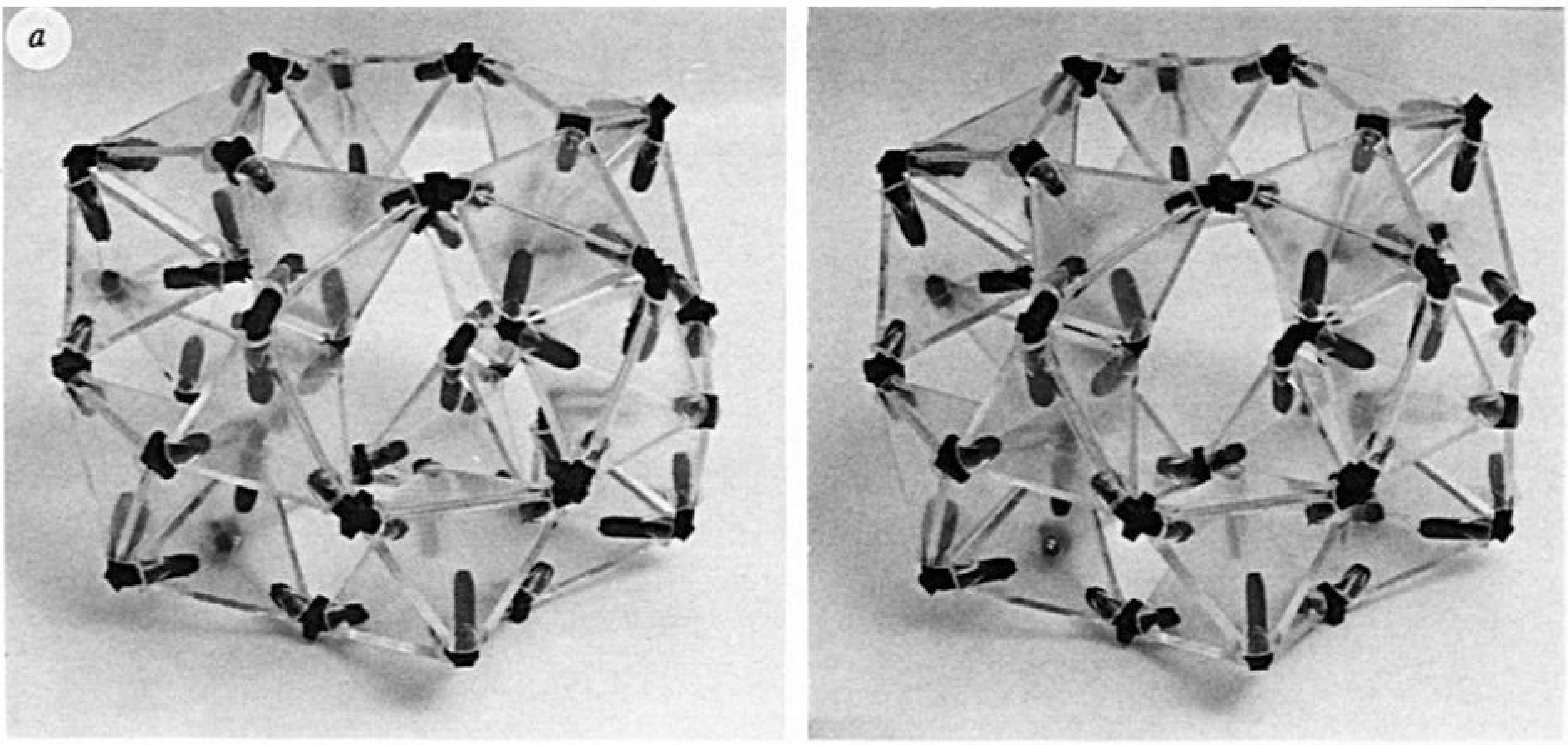


FIGURE 2. The polyhedral $(A_2X_5)_n$ complexes A_4X_{10}, A_8X_{20}, and $A_{20}X_{50}$. In models illustrated by stereo-pairs rubber connectors represent X atoms.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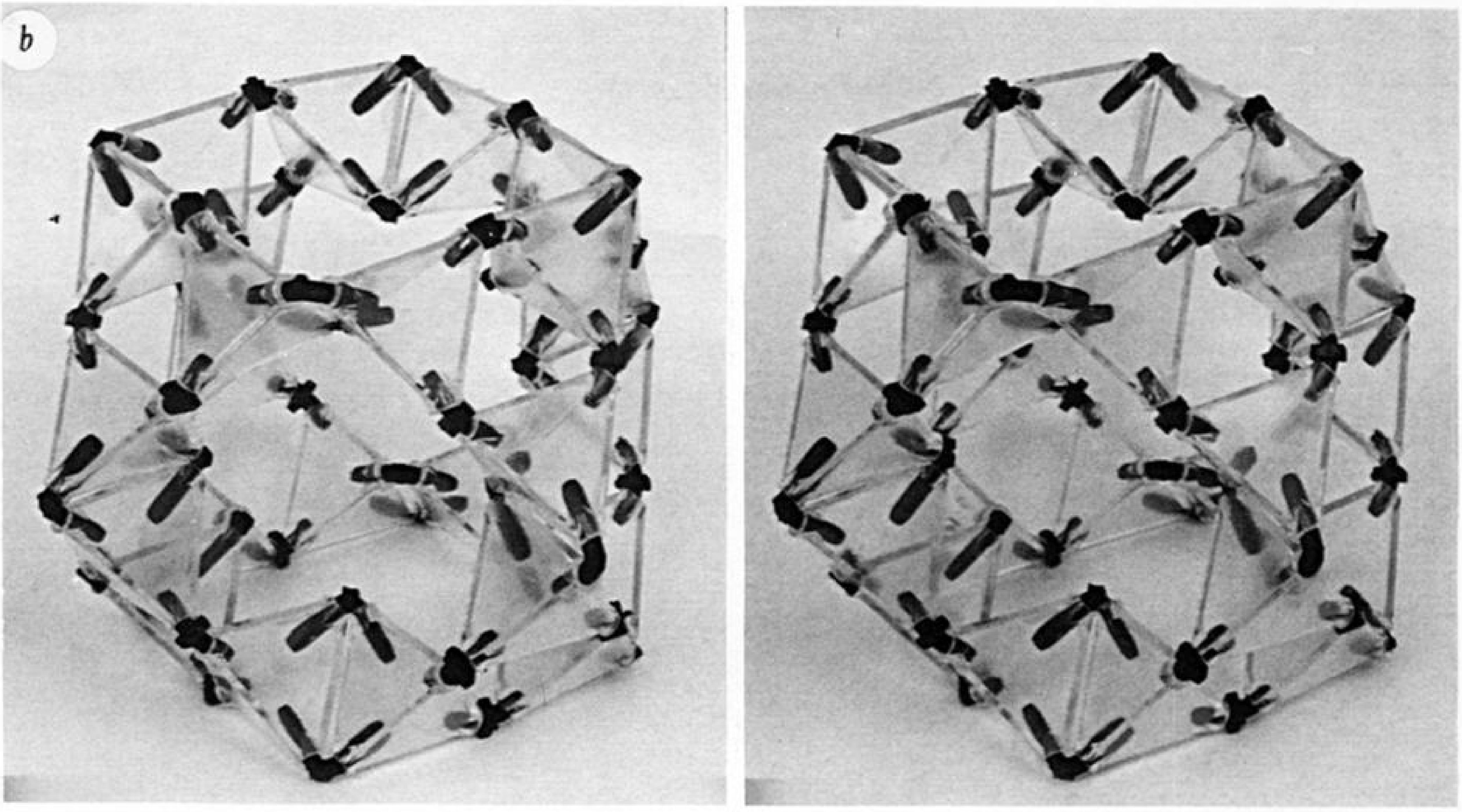
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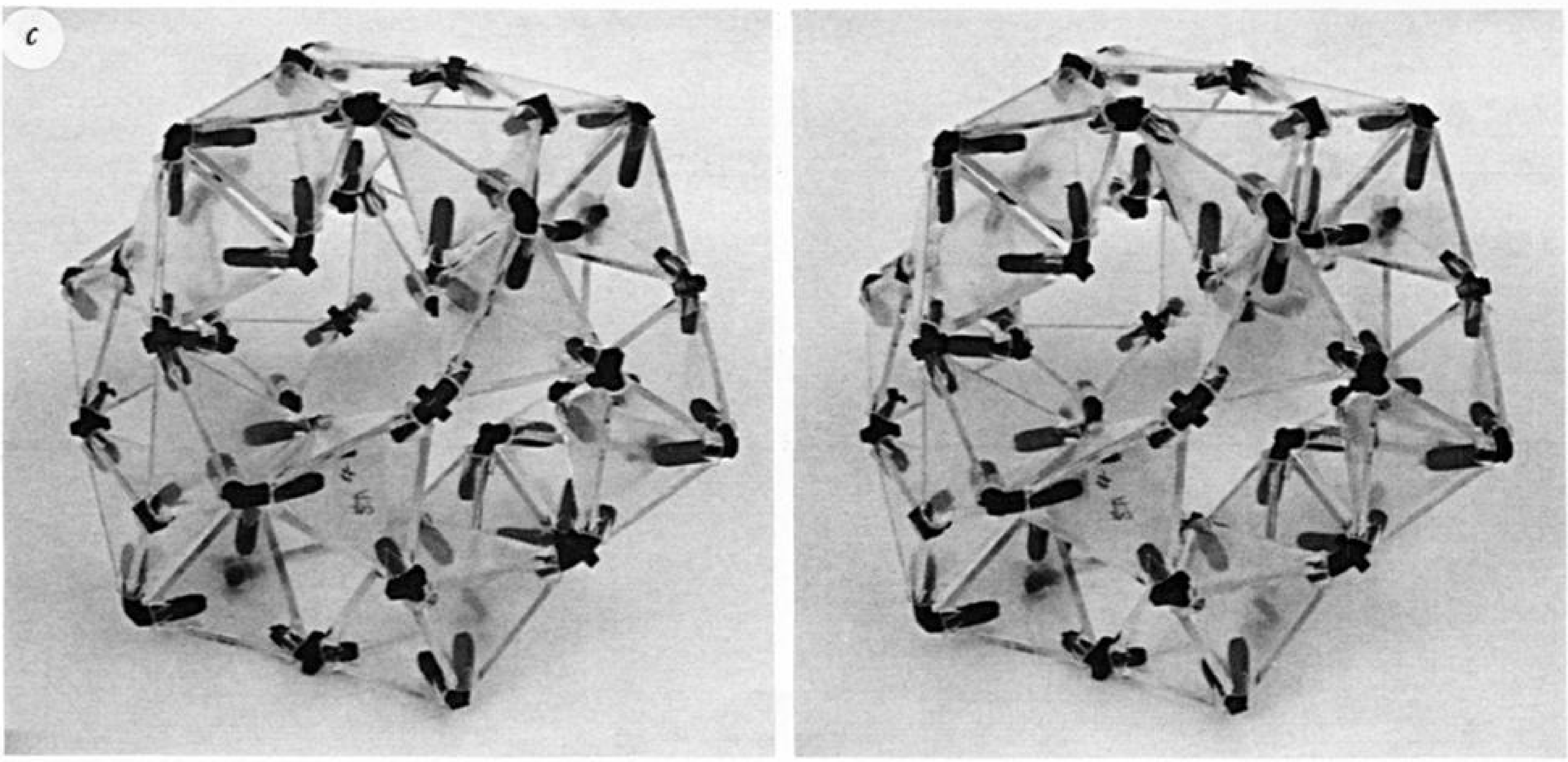
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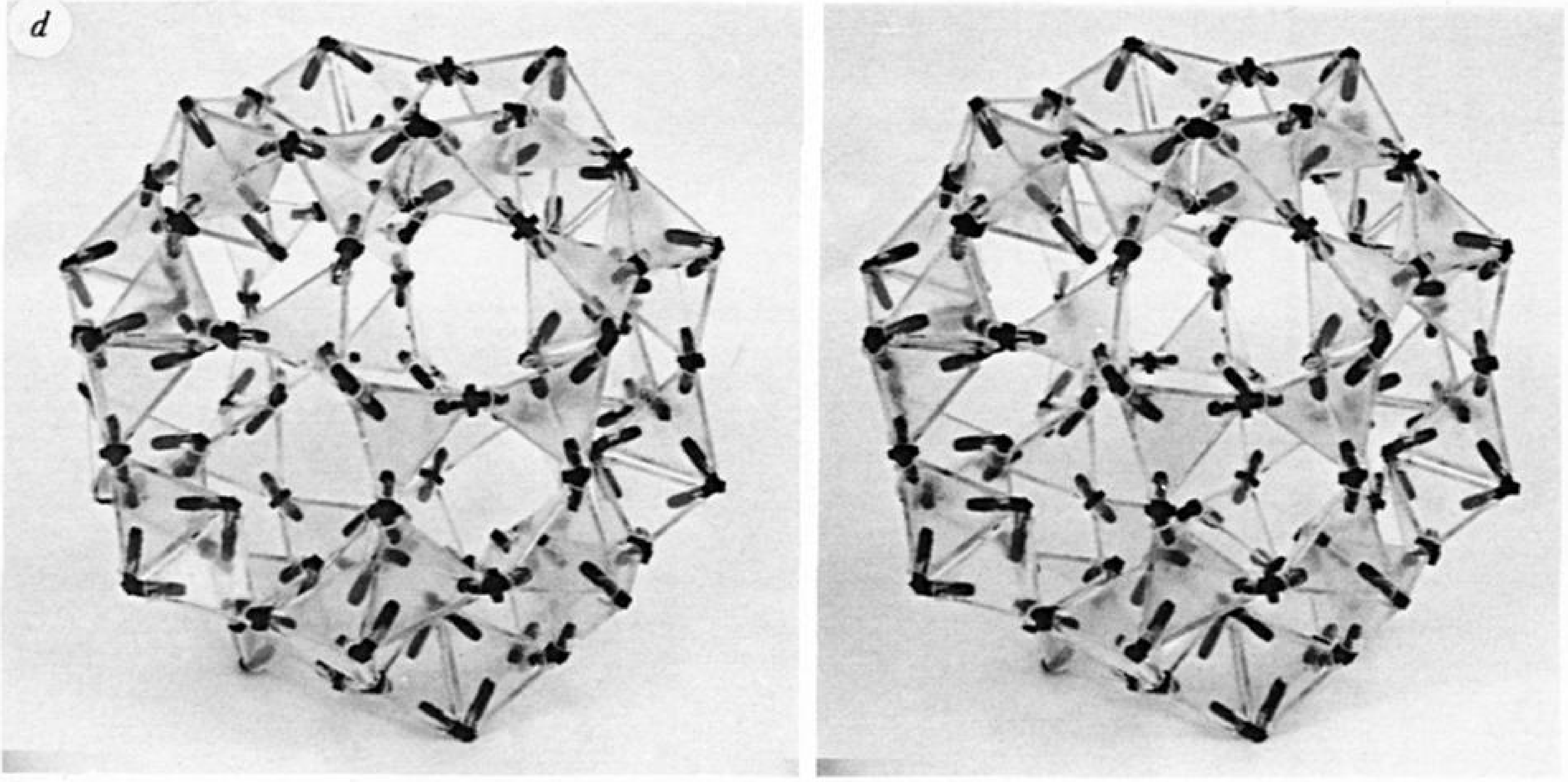
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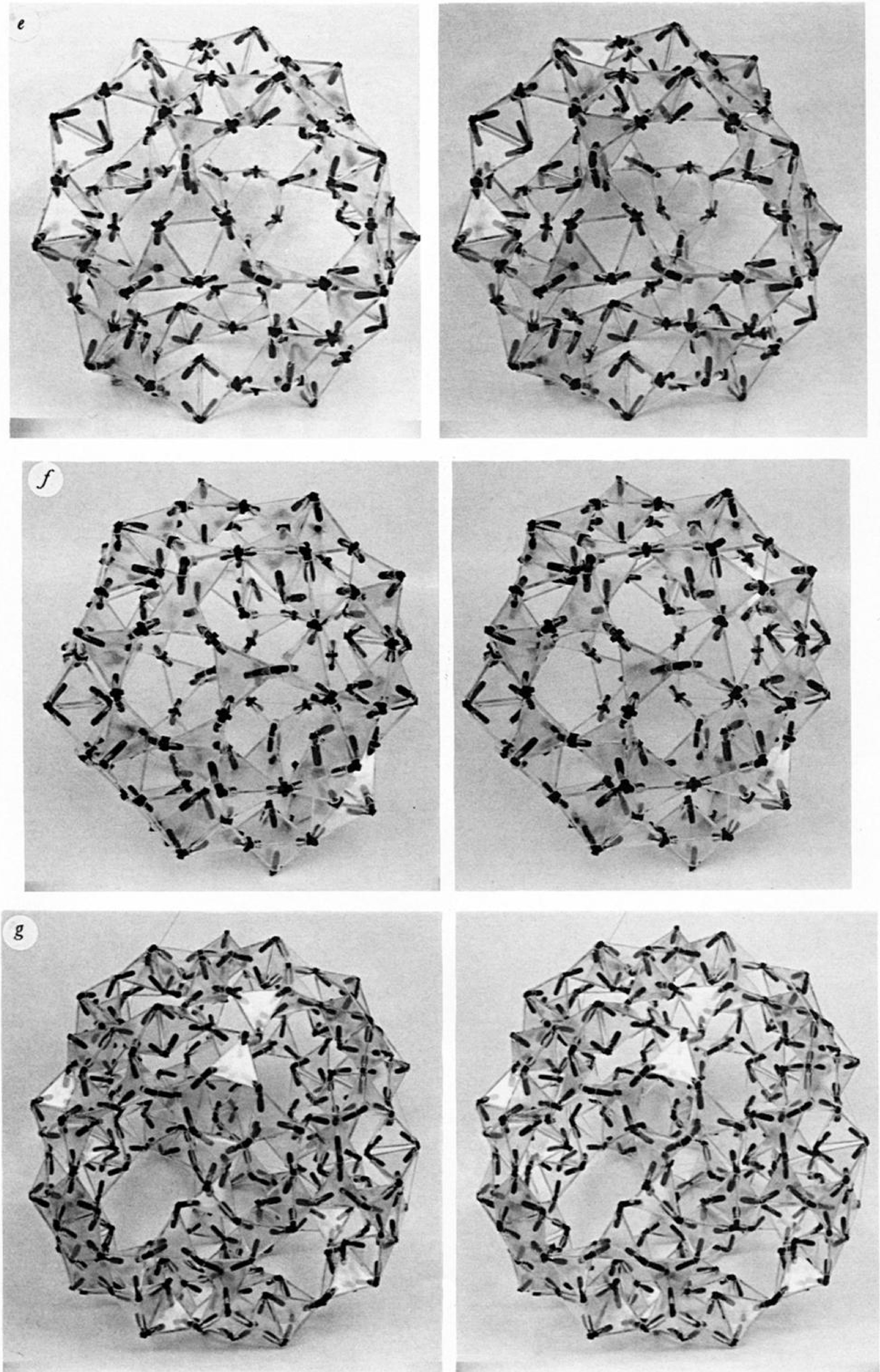
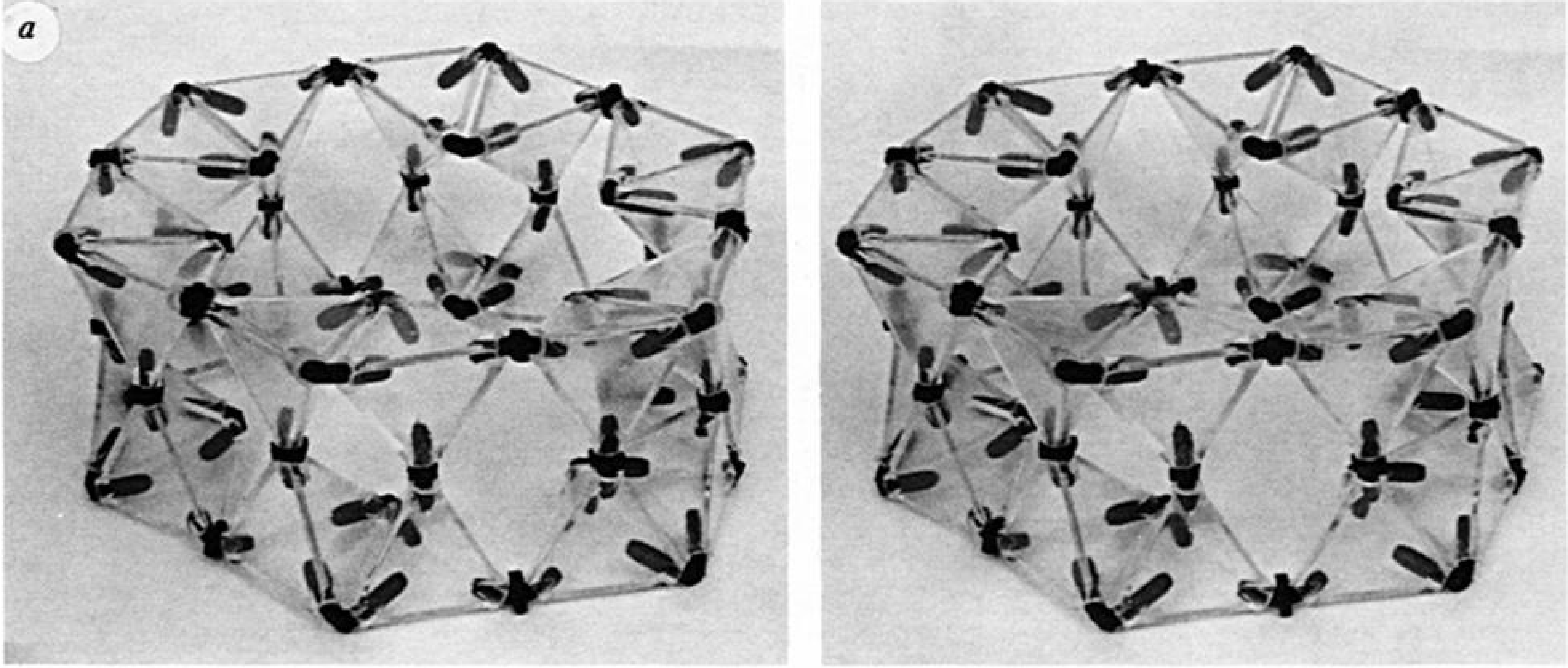


FIGURE 10. The polyhedral structures $(AX_2)_n$ of table 3 based on (*a*) pentagonal dodecahedron, (*b*) truncated cube, (*c*) truncated octahedron, (*d*) truncated cuboctahedron, (*e*) truncated dodecahedron, (*f*) truncated icosahedron, (*g*) truncated icosidodecahedron.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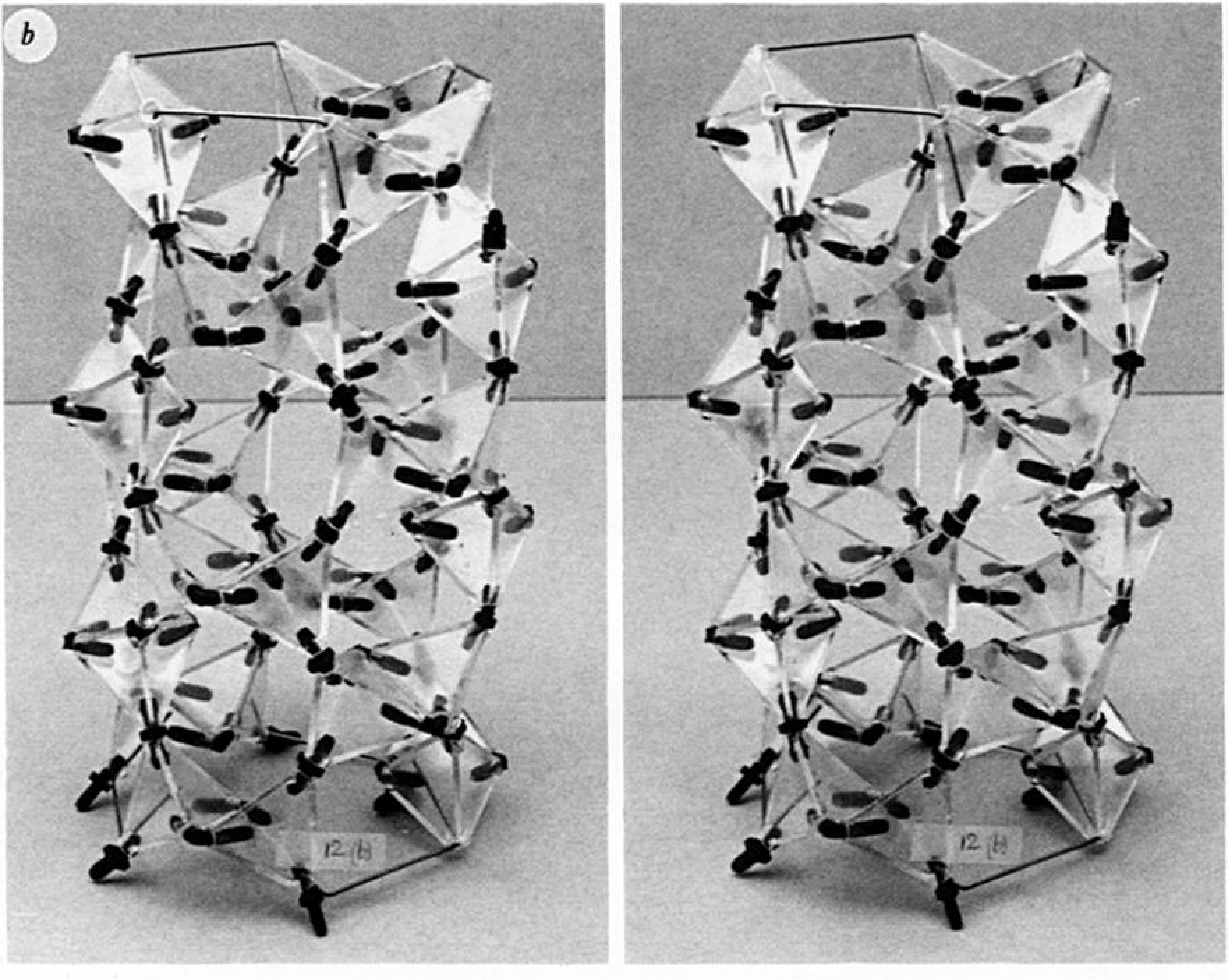
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12 (b)
12 (b)

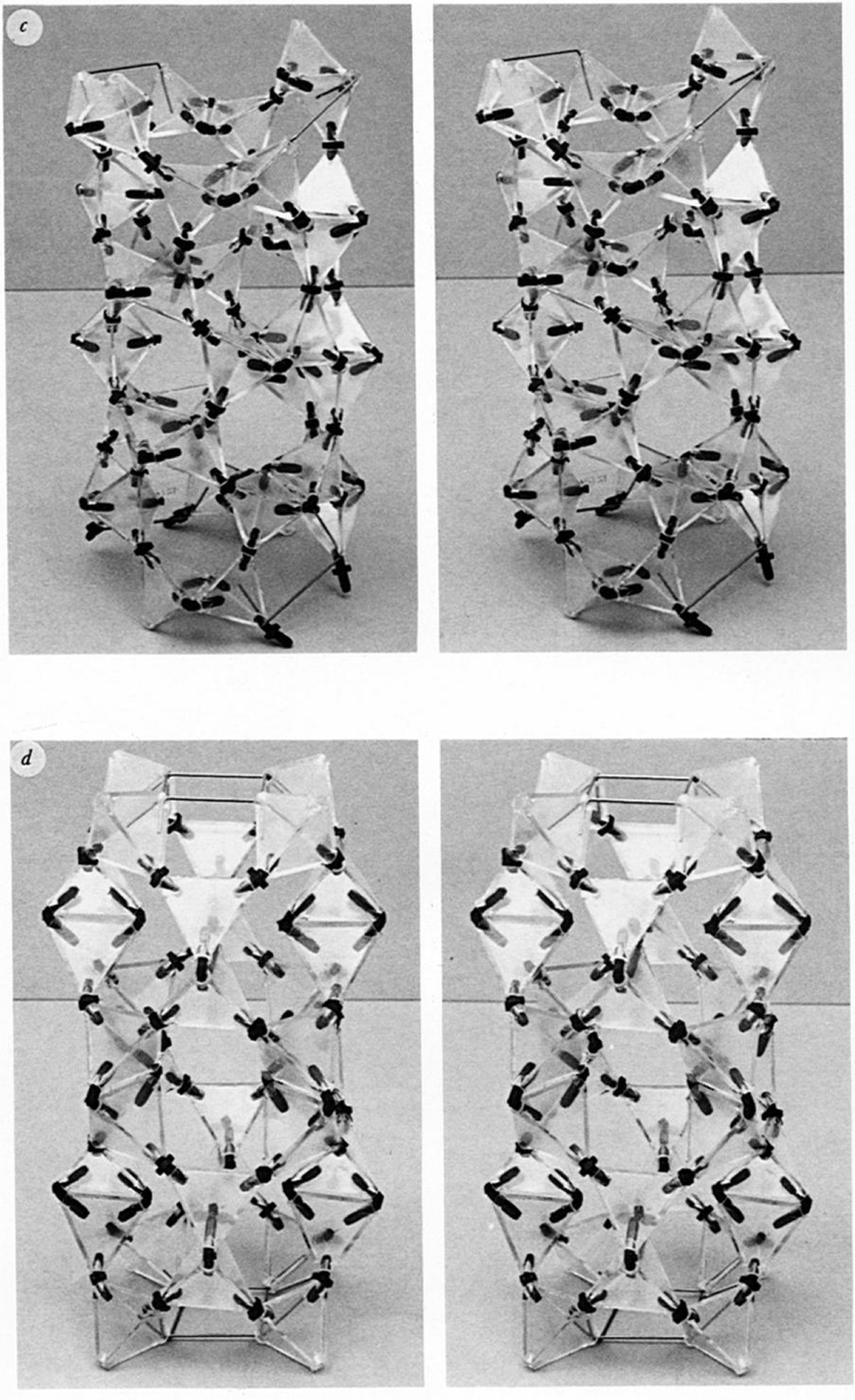
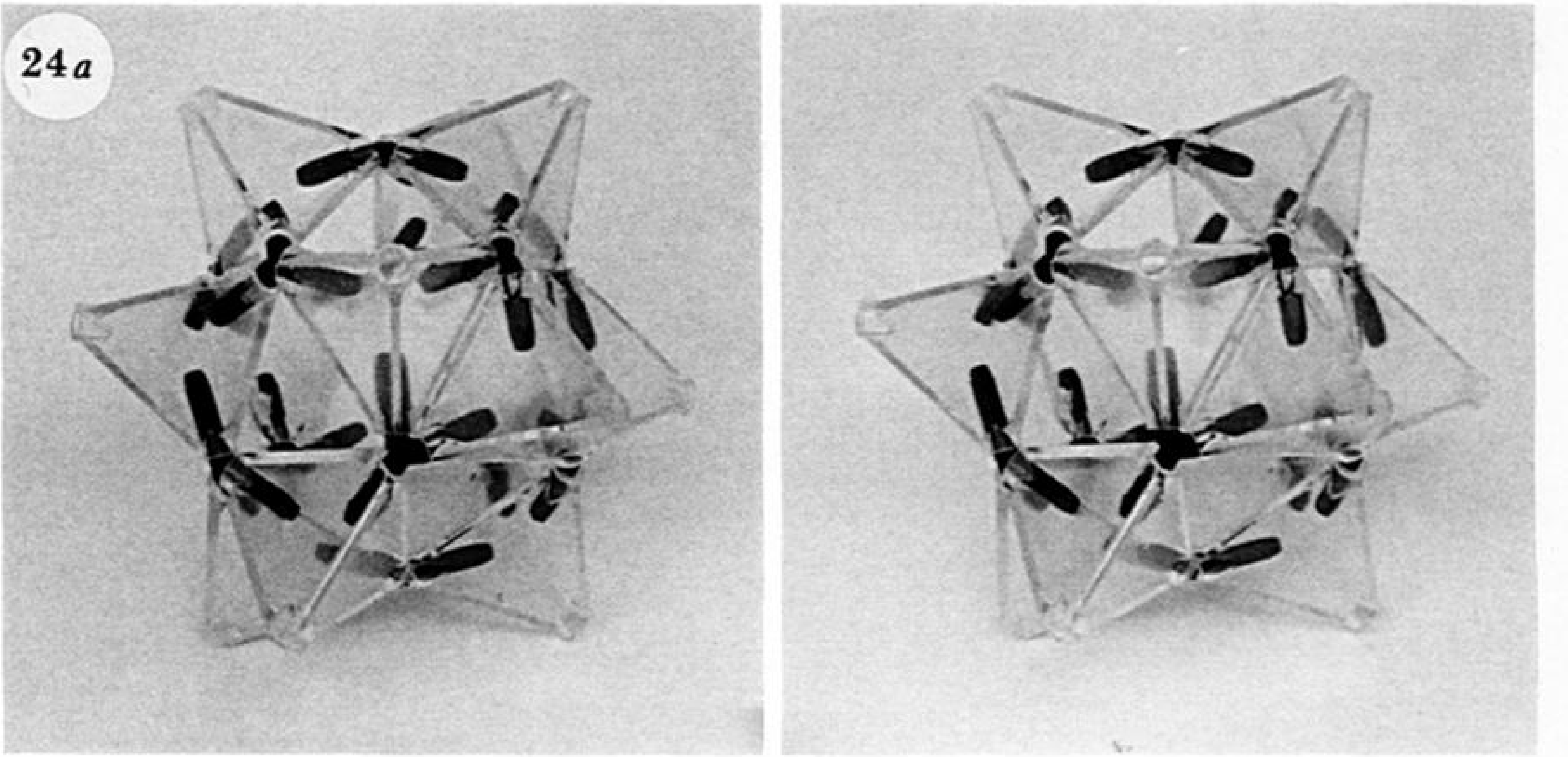
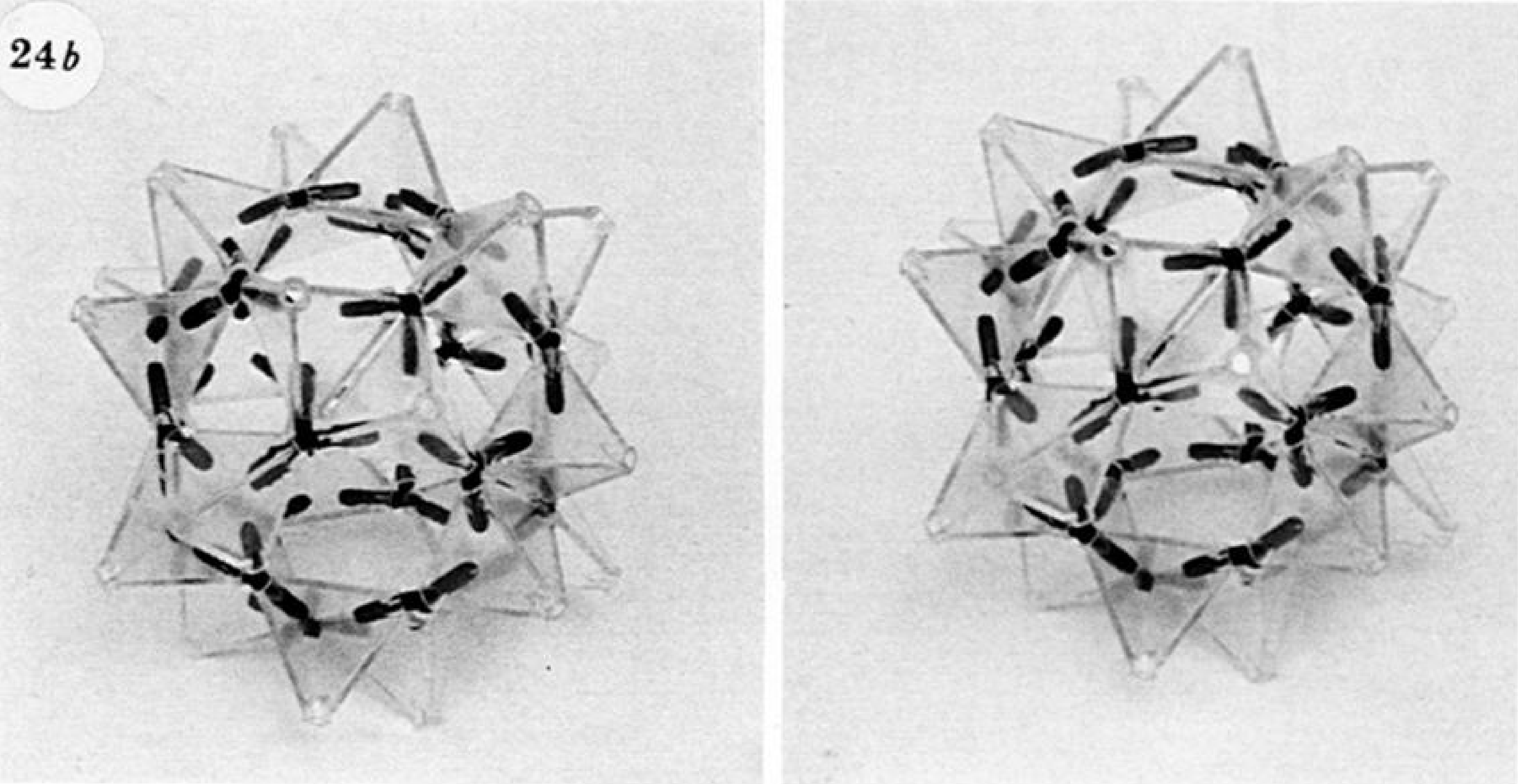


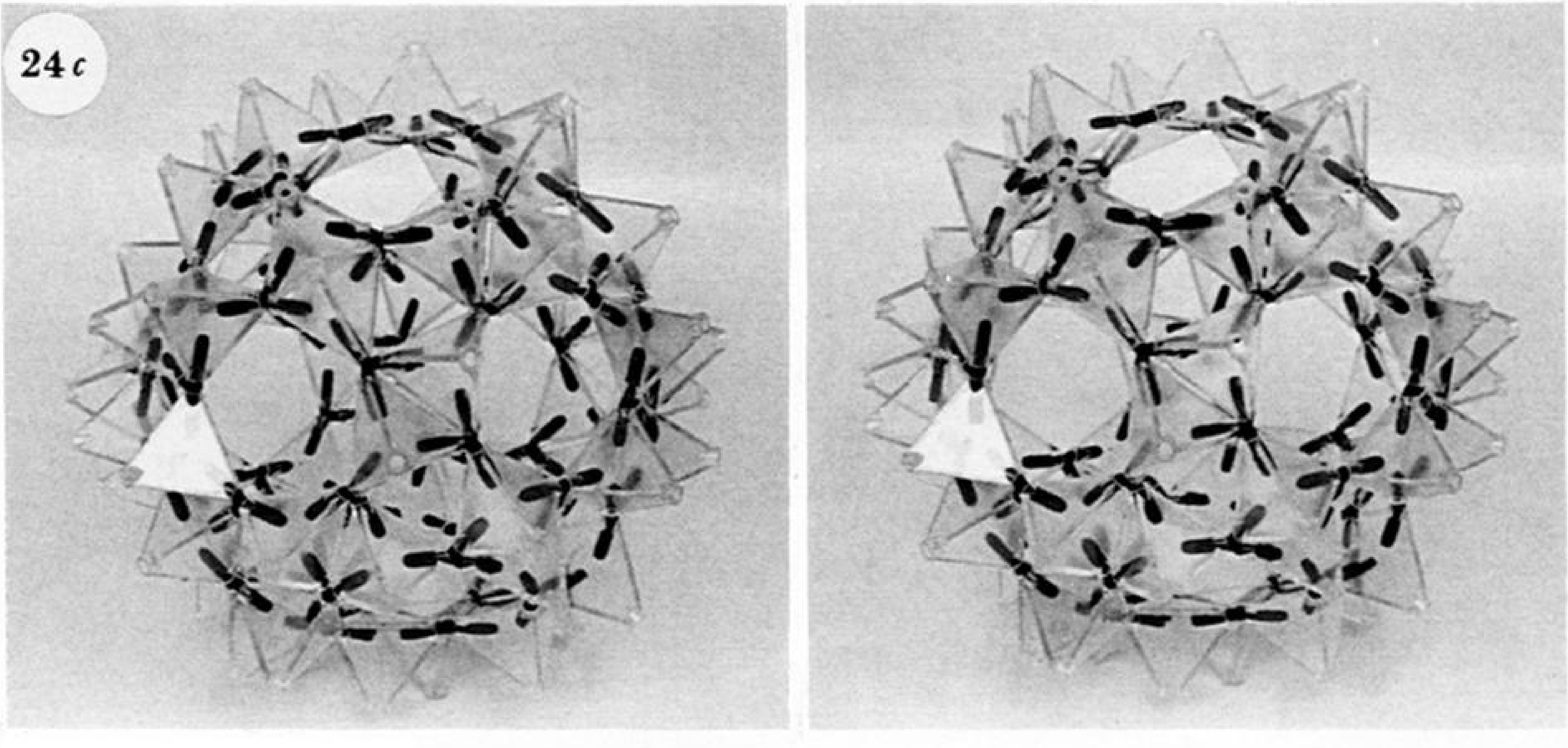
FIGURE 12. (*a*) Prismatic structure $A_{24}X_{48}$ formed from the chain **4**, (b)–(d) tubular chains (see text).



24*a*



24*b*



24*c*

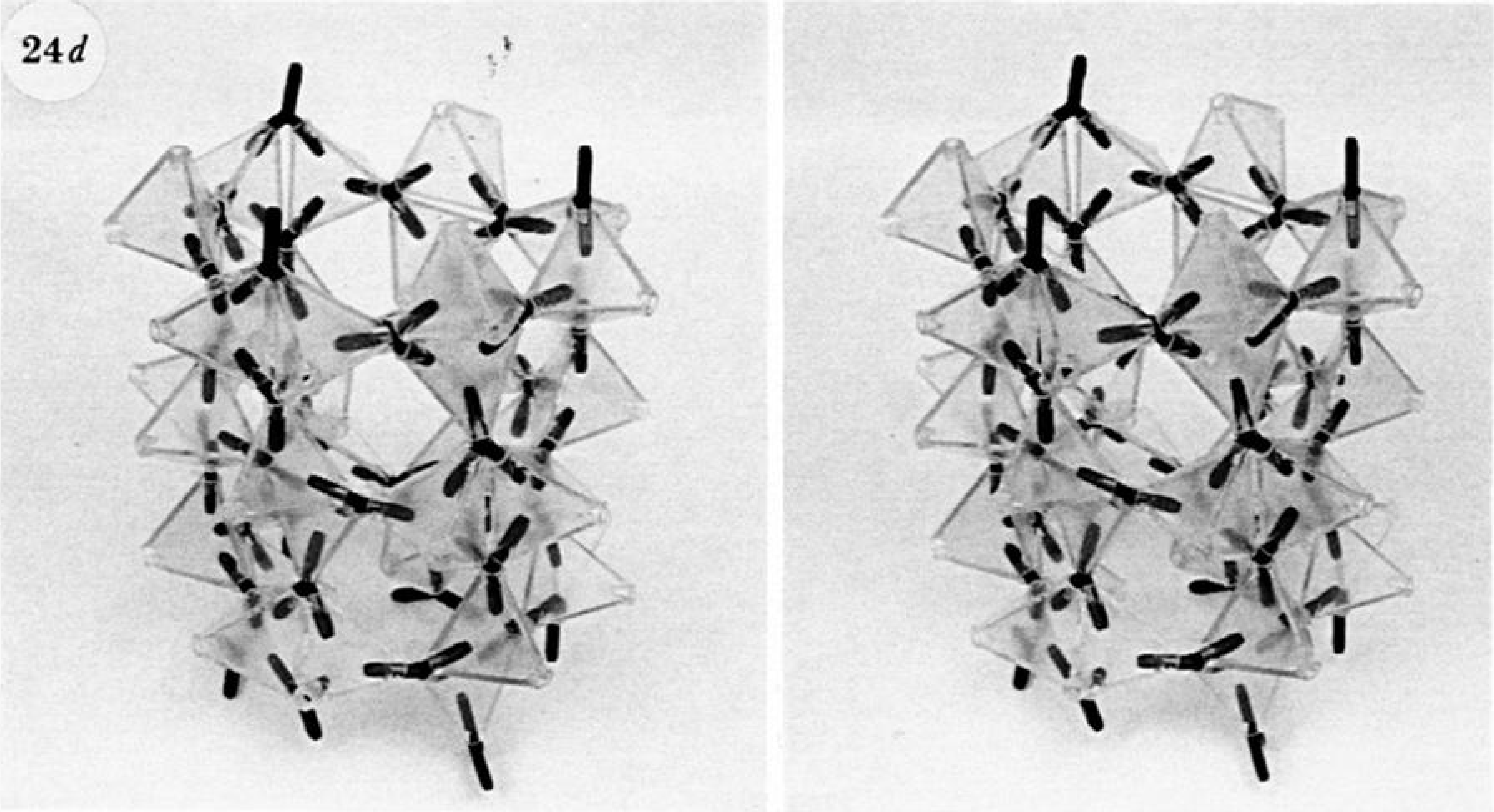


FIGURE 24. (*a*)–(*c*) Polyhedral AX_2 complexes of class II(*b*): (*a*) icosahedron $A_{12}X_{24}$, (*b*) snub cube $A_{24}X_{48}$, (*c*) snub dodecahedron $A_{60}X_{120}$, (*d*) tubular AX_2 chain of class II(*b*) (see text).

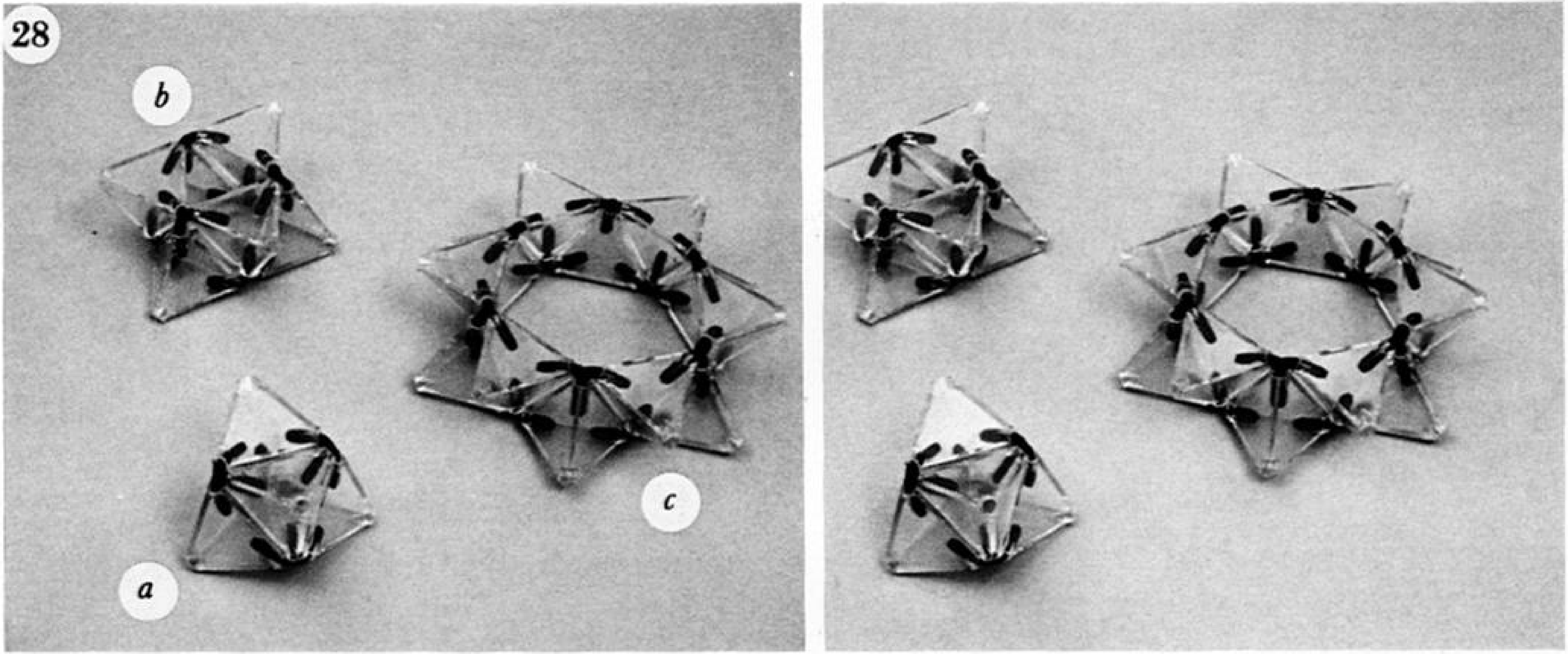


FIGURE 28. Three finite $(\mathrm{AX}_2)_n$ complexes: (*a*) $\mathrm{A}_4\mathrm{X}_8$ of class II(*d*), (*b*) and (*c*) $\mathrm{A}_6\mathrm{X}_{12}$ and $\mathrm{A}_{12}\mathrm{X}_{24}$ of class II(*c*).