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SECTION 1: TUTORIAL

Frameworks for Extended Solids: Geometrical Design Principles

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> "...it [is] clear that practically any structure which seems topologically reasonable can be made, and that increased symmetry, *ceteris paribus*, imparts increased stability." A. R. von Hippel (1)

> "The synthesis of new structures requires not only chemical skill but also some knowledge of the principal topological possibilities." G. O. Brunner (2)

The basic geometries for three-dimensional low-connectivity nets are described. Examples of open framework solids with these topologies are adduced for illustration. Attention is drawn to methods of producing open frameworks by decoration and expansion of simple nets. © 2000 Academic Press

INTRODUCTION

In this tutorial article we present the basic topologies (nets) that underlie most low-density ("open") structures. For illustration we give some examples, often from our own work, of clusters and linkages that are assembled into frameworks, but the main emphasis is on the topologies that can be expected to form and which might reasonably be the target of a designed synthesis. It is our thesis that a few (about a dozen) simple high-symmetry topologies are of paramount importance, and we describe these.[1] It is our objective to outline the important connections existing between simple nets and extended structures that are assembled from molecular building blocks.

NOMENCLATURE AND DEFINITIONS

Nets and vertex symbols. Following common usage we define an N-connected net to be one in which all vertices are linked to N neighbors (note that the term "N-connected" has a quite different meaning in mathematics). In an (N,M)-connected net some vertices are connected to N neighbors and some to M neighbors. A special geometry of the net is one in which all edges (links between vertices) are of equal length and this corresponds to the shortest distance between vertices. The structure is often referred to an N-coordinated sphere packing in this special configuration, which often (by no means always) is the one of most interest in crystal chemistry. Nets with just one kind of vertex (all vertices related by symmetry) are called *uninodal*: the corresponding sphere packing is sometimes referred to as *homogenous.*

3- and 4-connected nets, particularly uninodal ones, are conveniently characterized by a vertex symbol (3, 4); in this symbol a number specifies the size of the smallest ring contained in an angle, and a subscript if present indicates that more than one ring of specified size is contained in that angle and gives their number. For example, in the 4-connected diamond structure every angle contains two 6-membered rings (Fig. 1) and, as in a 4-connected net there are six angles at a vertex, the symbol is $6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2$. In a 3-connected net there are three angles and the symbol for the most-symmetrical such net (named after $SrSi_2$) is $10_5 \cdot 10_5 \cdot 10_5$. There may be, indeed there often are (but not in these examples), larger rings in the structure. Note that, in contrast to some earlier workers, we use "ring" in a sense consistent with chemical usage ("benzene ring") and distinguish it from a circuit which may contain "shortcuts" (3). In anthracene $C_{10}H_8$, which may be considered as formed from two edge-sharing benzene rings, there is a 10-membered circuit around the molecule, but this is not a ring in our sense.

Nets in which all vertices, edges, and angles are equivalent by symmetry are referred to as *regular*. Those that have all edges, but not all angles, equal are referred to as *quasi-regular*. We argue that these are of special importance in crystal chemistry.

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[1] Recall that very many coordination polyhedra can, and do, appear in molecules and crystals, but a few simple, high-symmetry figures such as tetrahedra and octahedra predominate.

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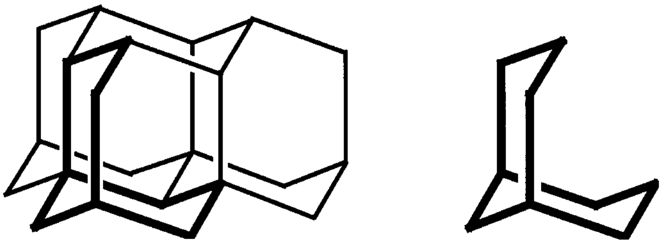

FIG. 1. Left: a fragment of the diamond net with two 6-membered rings emphasized. On the right the same two rings are shown; note that one angle is common to both rings.

Porous frameworks produced by decoration, augmentation, and expansion of nets. The term *decoration* was introduced (5) to describe the process of replacing a vertex by a group of vertices. It was earlier pointed out by Hansen (6, 7) that processes of this sort can lead to low density structures. For example, condensing ten indium sulfide tetrahedra produces a *T*3 supertetrahedron, $In_{10}S_{20}^{10-}$ (presented below in Fig. 8), and when these are further condensed, indium sulfide frameworks with giant cavities are produced (8). One of these adopts a decorated diamond topology where each vertex in the diamond net has been replaced by a *T*3 $In_{10}S_{16}^{2-}$ tetrahedral unit. In other words, each of the vertices in the 4-connected diamond net has been replaced by ten indium sulfide tetrahedra. A special case of decoration is *augmentation*; this is replacement of the vertices of an *N*-connected net by a group of *N*-vertices as in the CaB_6 framework. Here, B_6 units augment the 6-connected vertices on the simple cubic net. In the $MnGe_4S_{10}^{2-}$ framework, Ge_4 units augment half the 4-connected vertices on the diamond net: the other half are occupied by Mn (9).

Another strategy for producing porous frameworks is to increase the spacing between vertices in a net by using longer links, which in principle means that a bond is replaced by a sequence of bonds—a process we call *expansion.* In a strict sense, the $MnGe_4S_{10}^{2-}$ example just discussed is also expanded, since vertices (metal atoms) on the partly augmented diamond net have been spaced apart by –S– atom links. Framework aluminosilicates and zeolites are familiar examples of expanded 4-connected nets with edges of the underlying 4-connected net replaced by –O– links.

In metal-organic frameworks, the use of longer links such as 4,4′-bipyridine (bpy) has resulted in greatly expanded 3-D nets, albeit interpenetrated, as in $Cu(bpy)_2$ (10, 11), where the ditopic bpy spacers link Cu(I) atoms that define the 4-connected vertices of the diamond net. The bis(adiponitrile) copper(I) nitrate compound is an earlier example of an expanded diamond network (12).

Porous cyanides have been studied extensively, and we give a number of examples below. The familiar Prussian blue framework has ideal composition $MM'(CN)_6$ (13). This an example of an expanded simple cubic net, now with –C–N– links replacing the original edges of the net (notice that in actual fact the ordering of *M* and *M′* produces a face-centered cubic structure of double the cell edge).

An increasing number of assembled frameworks have as components polytopic grouping of linkers, which in themselves may act to decorate a vertex in an assembly. For example, 1,3,5-benzenetricarboxylate (BTC) (the anion of trimesic acid) is a tritopic linker with a central triangular unit which can in turn be linked to three cationic units as in $Zn_2(BTC)(NO_3)$ network of MOF-4 (14). The central C_6 unit of BTC is linked to three $Zn_2(-CO_2)_3$ units, which decorate the Si net of the $SrSi_2$ extended structure. Polytopic links can thus be employed both to decorate and to expand a net. This strategy has been used to good effect (15, 16) with 2,4,6-tri(4-pyridyl)-1,3,5-triazene (TPT), where three pyridyl units NC_4H_4– are linked to the three C atoms of a central C_3N_3 (pyrazine) ring; again there is a central triangular unit with attached linkers, which can join to cationic units. Many other examples will be found in the pages of this volume and in Refs. (17–19).

Molecular building blocks and secondary building units. Given the relevance of cluster and coordination polyhedron entities in determining the topology of the resulting extended assembly, it is useful to make a distinction between such entities based on whether they are employed as starting points in the synthesis or whether they form *in situ.* For example, the tetrahedral $Ge_4S_{10}^{4-}$ cluster is considered a molecular building block (MBB) since it was employed as a synthetic unit which was copolymerized with Mn(II) to form the extended network $MnGe_4S_{10}^{2-}$. When polytopic units are copolymerized with metal ions, it is common to recognize linked cluster entities in the assembled solid. Each such cluster is considered a secondary building unit (SBU), in that it is a conceptual unit which was not employed in the synthesis as a distinct molecular entity in the same manner described for tetrahedral germanium sulfide cluster.

We cite a recent example (20) that illustrates the utility of SBUs in the design of a framework with exceptional low density and high stability. Copolymerization of Zn(II) with linear terephthalate anions (ditopic linker), $[OOC–C_6H_4–COO]^{2-}$ (abbreviated to BDC for 1,4-benzenedicarboxylate) yields a framework formulated as $Zn_4O(BDC)_3$. Here, Zn_4O^{6+} clusters are linked by six BDC anions to form an octahedral geometry (Fig. 2) having the same topology as that of the B network in CaB_6 (described below). From the point of view of the topology we like to think of this structure as composed of octahedral $[Zn_4O](O_2C)_6$ SBUs that are joined by $–C_6H_4–$ links. The role of MBBs and SBUs in the design of robust porous frameworks with functionalized pores has been described (21).

FRAMEWORK TOPOLOGIES

There is a large literature on enumeration and description of low-coordination structures (nets), work that is

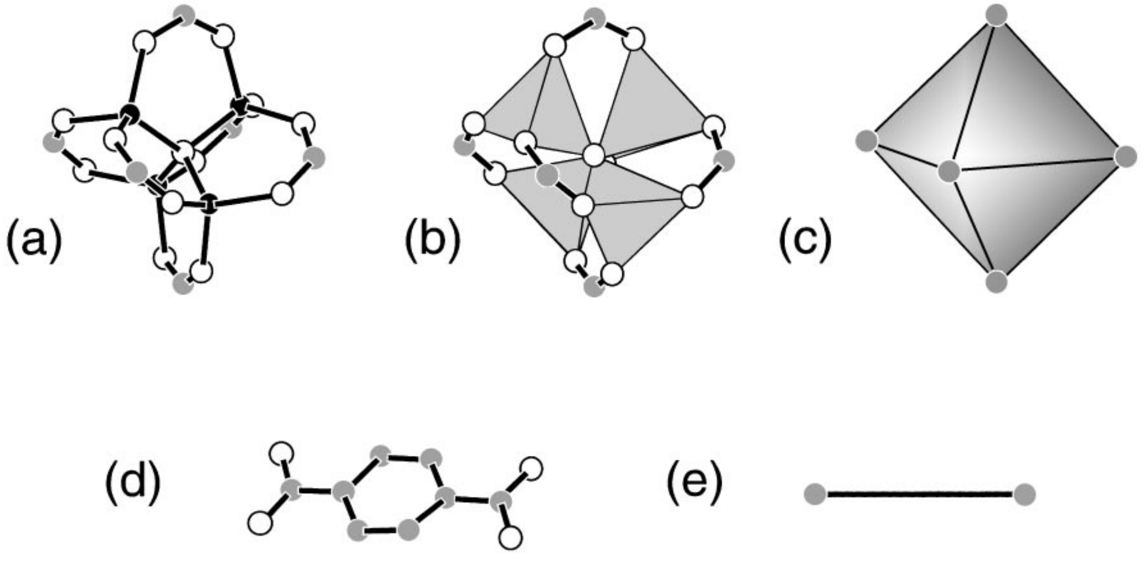

FIG. 2. The building units of $Zn_4O(BDC)_3$: (a) A central OZn_4 unit (filled circles are Zn) linked to six CO_2 units of BDC groups (shaded circles are C). (b) The same with four ZnO_4 tetrahedra shaded. (c) The same with the C_6 octahedron shaded. (d) The BDC anion (open circles are O and shaded circles are C). (e) The same with just the carboxylate C atoms joined by a link. Joining the octahedra with the links produces the CaB_6 topology (shown in Fig. 19 below).

associated particularly with Wells (22, 23) and Smith (24). However, as mentioned above, it is our thesis that in general only a small number of simple, high-symmetry structures will be of overriding general importance,[2] and these are described here. Some of the material can be found in Wells' books (22, 23) or in O'Keeffe and Hyde (3). For simplicity we restrict ourselves to three-dimensional structures: it must be part of the designer's art to avoid formation of lower-dimensional structures such as layer structures, unless of course (as may be), such a structure is the target of the synthesis.

3-Connected nets. A rigorous enumeration of all homogenous 3-coordinated sphere packings has been made by Koch and Fischer (25). There are only 52 of them, of which 46 remain 3-coordinated in their maximum volume form. Of these structures only one has site symmetry at a vertex that contains a 3-fold axis and this is therefore the only structure in which the three angles are equivalent (related by symmetry) and thus the only regular 3-connected net (Table 1). This is illustrated in Fig. 3. The structure is often named for $SrSi_2$ as the Si arrangement in that compound has that topology. In its maximum symmetry form the net has symmetry $I4_132$ and the vertices are either at positions 8 a (1/8,1/8,1/8 etc.) or at positions 8 b (7/8,7/8,7/8) and the vertex point symmetry is 32 (D_3). Notice that the net is chiral and that the two sets of positions refer to enantiomorphic forms (often symbolized $^{+}Y^{*}$ or $^{-}Y^{*}$, respectively). It is interesting, even astonishing, that the simplest and most symmetrical three-dimensional way of assembling (generally

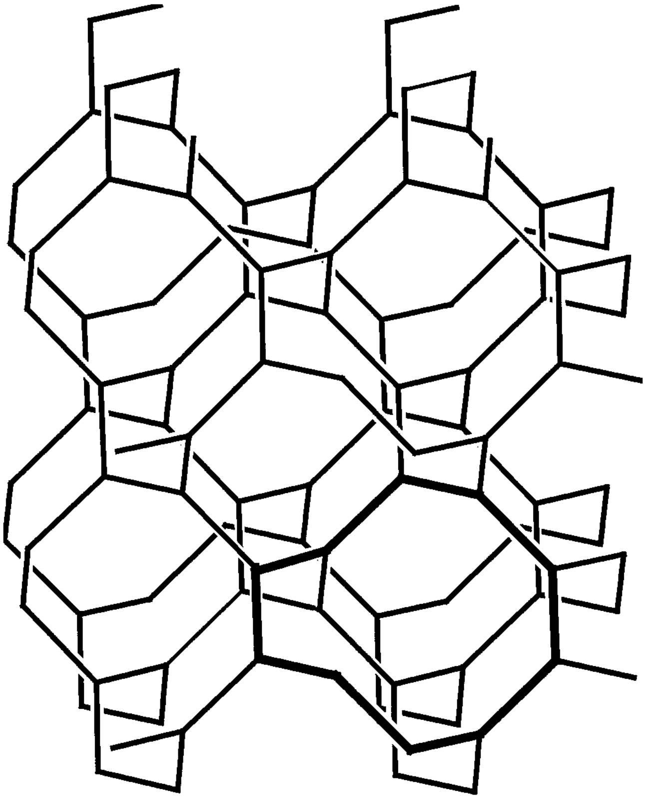

FIG. 3. A sketch of the $SrSi_2$ net. A 10-membered ring is outlined. See also Fig. 6.

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[2] We know of no systematic survey of the occurrence of structural topologies, and when we say that a particular topology is very common we really mean that it occurs very frequently in structures that we are likely to have examined and analyzed the geometry of.

TABLE 1
The Two Most-Important 3-Connected Nets

Name	s.g.	Wyckoff	p.g.	Z	Vertex symbol	s.g. (AB)
$SrSi_2$	$I4_132$	a or b	32 (D_3)	4	$10_5 \cdot 10_5 \cdot 10_5$	$P2_13$
$ThSi_2$	$I4_1/amd$	e	$mm2$ (C_{2v})	4	$10_2 \cdot 10_4 \cdot 10_4$	$I4_1md$

Note. s.g. is space group, p.g. is point group, Z is the number of vertices in the topological unit, and s.g. (AB) is the space group for the ordered AB structure with two kinds of vertex.

achiral) modules with 3-fold symmetry (and the only way that preserves local 3-fold symmetry) leads to a chiral structure. As mentioned above, this structure is adopted by $Zn_2(BTC)NO_3$ framework, in which $Zn(-CO_2)_3$ SBUs and benzene units alternately decorate the vertices of the Si net of $SrSi_2$.

Only two of the remaining nets have site symmetry with order greater than 2; these both have site symmetry $mm2$ (C_{2v}). They are the one named for $ThSi_2$ (Fig. 4) and a third with vertex symbol $4 \cdot 12_2 \cdot 12_2$ (Fig. 9, below). The minimum number of vertices in the repeat unit of a 3-connected net is four (22), and only the $SrSi_2$ and $ThSi_2$ nets have this number of vertices in the repeat unit (this is the same as the number of vertice in the primitive cell of the structure in its most symmetrical conformation). We therefore consider these two nets to be the basic 3-connected three-dimensional nets. (The familiar honeycomb or graphite layer, 6^3, is of course the simplest two-dimensional 3-connected net.) They account for the topology of the great majority of all known structures that are based on 3-connected nets and are the most likely targets for a successful designed synthesis. In both these structures all the rings are 10-rings and the vertex symbols are for $SrSi_2$: $10_5 \cdot 10_5 \cdot 10_5$ and for $ThSi_2$: $10_2 \cdot 10_4 \cdot 10_4$.

The $ThSi_2$ net is particularly common in structures where there are two distinct kinds of link arranged as a T (often with the arms different length from the upright) (26–28) although examples of open structures with triangular coordination are known (22). We consider it to be the basic net formed from T-shaped SBUs.

A uninodal net with vertex symbol $12_4 \cdot 12_7 \cdot 12_7$ and symmetry $P6_222$ is known (3); in Wells' (16) terminology it is (12, 3). An elegant variation of this net with symmetry $P3_221$ has been described by Abrahams *et al.* (10) in which one half of the vertices have three equal angles of 120° and the other

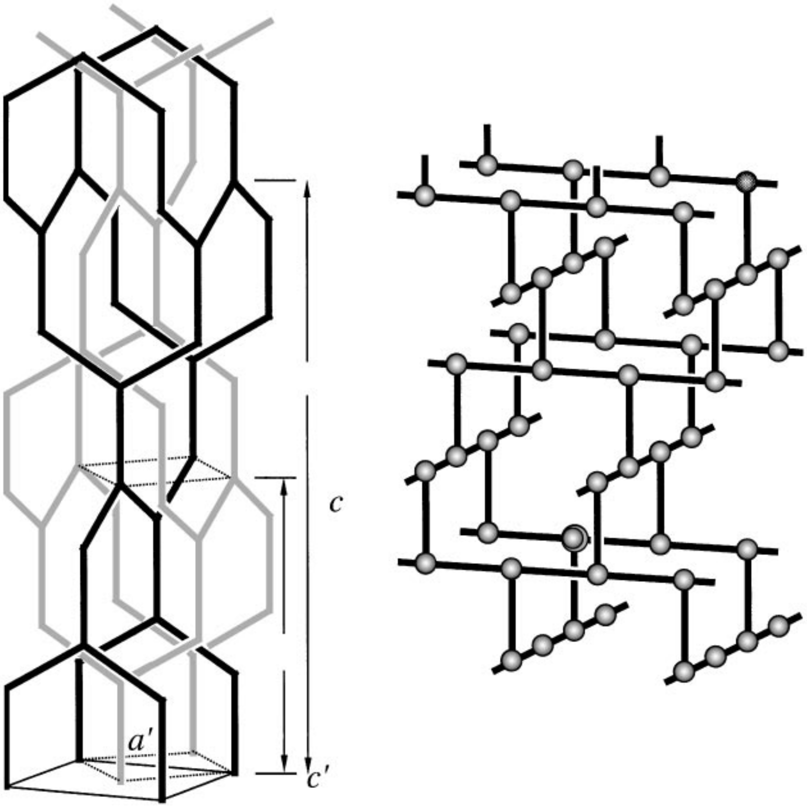

FIG. 4. Left: a fragment of the $ThSi_2$ net (heavy lines); a unit cell (edges a and c) is shown. A second interpenetrating net is shown in lighter shading. The unit cell for the interpenetrated structure has edges a' and c'. Right: the same $ThSi_2$ topology with edges meeting at vertices (shaded circle) in a T configuration.

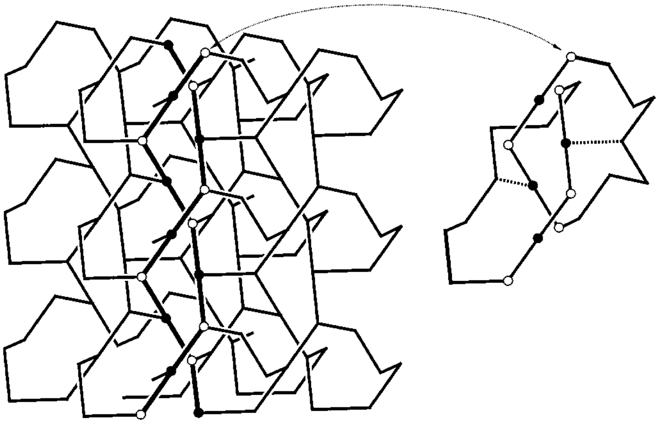

FIG. 5. A conformation of the 12^3 net. Open circles are on 120° vertices and filled circles are on T vertices. Only those on two intertwined 3_1 screws (heavier lines) are shown. Two catenated 12-rings are shown on the right.

half have a T configuration. Although this is only one example of this net to date, it provides an attractive target for a designed synthesis. There are several other points of interest: (a) In the configuration with alternating equilateral triangular and T vertices and equal edges, the distance between some pairs of vertices that are not directly linked is the same as the edge length. (b) In addition to 12-rings, the net contains 14-rings. An extended vertex symbol that shows the complete ring count is $12_4 14_{12} \cdot 12_7 14_8 \cdot 12_7 14_8$. (c) As Abrahams *et al.* point out, the 12-rings are catenated (pass through each other). We illustrate this net in Fig. 5—the reader will probably agree that enumerating rings is not easy. As it is the only uninodal net with 12-rings, we identify it by the short symbol 12^3.

The structure in which two enantiomorphous $SrSi_2$ nets are intergrown is of interest (Fig. 6). The symmetry is now $Ia\bar{3}d$ (centrosymmetric) with vertices in positions 16 *b*. The closest distance of approach of vertices of different nets is $\sqrt{(3/2)} = 1.225$ times the edge length. The *G* minimal surface, which is one of the three basic cubic minimal surfaces (29), separates the two networks. This *G* surface occurs in many contexts, for example, as the cubic surface of bicontinuous phases in water–lipid and water–surfactant systems. In the cubic mesoporous material MCM-48, which is formed from a water–surfactant template (30) the polycrystalline matrix follows the shape of the *G* (gyroid) surface (31, 32). The structure of γ-Si (a metastable high-pressure phase) is derived from the two intergrown $SrSi_2$ nets by a small distortion (lowering the symmetry to $Ia\bar{3}$) such that the nearest approach of Si atoms on the two nets becomes equal to the bond length in each net and the structure becomes 4-connected (3). Other examples of intergrowths are given by Batten and Robson (33).

It should be mentioned that Wells (23) devoted a chapter (which appears not to have been widely read) to interpenetrating nets. He points out, for example, that cubic closest packing (fcc) can be subdivided into four $SrSi_2$ nets either of the same hand or two of each hand, so the structure as a sphere packing has exactly 1/4 the density of closest sphere packing.

Intergrowths of $ThSi_2$ nets are also common. In the simplest case, two interpenetrating nets are displaced by half the *c* repeat distance of the tetragonal unit cell. There are several points of interest. (i) The symmetry of the two intergrown structures is different; it is now $P4_2/nmm$ and the unit cell is smaller with $a' = a/\sqrt{2}$ and $c' = c/2$ so the volume is 1/4 of the body-centered unit cell for the single net and again contains just 4 vertices in the repeat unit

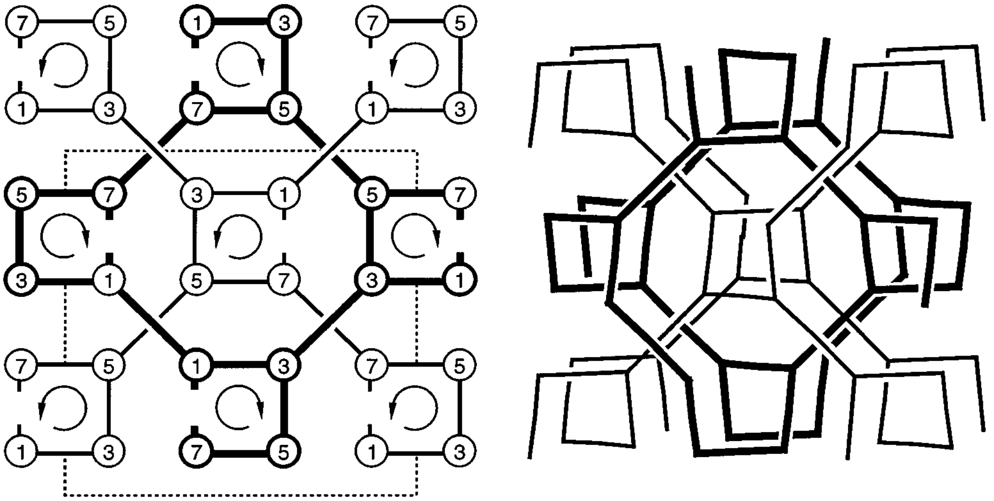

FIG. 6. Left: intergrowth of two Y^* ($SrSi_2$) nets of opposite hand shown in projection on [001]. Numbers are elevations in multiples of $c/8$. Right: the same in clinographic projection.

(see Fig. 6). (ii) With edges all of unit length, the vertices on one net have two vertices of the other net the same distance away as vertices on the same net, so considered just as a packing of equidistant vertices (i.e., as a sphere packing) the structure is 5-coordinated (we see the same sort of behavior in intergrown diamond nets below) and the symmetry is actually *I*4/*mmm* (see Fig. 15, below).

In many instances, particularly with long linkers, there are multiple intergrowths and the distance between vertices on different intergrown nets are shorter than in the same net. For examples see Ref. (33).

4-Connected nets. There is no treatment of 4-connected structures analogous to that of Koch and Fischer (25) for 3-coordinated sphere packing, but we can easily enumerate the uninodal ones with all edges related by symmetry (regular or quasiregular). For all edges to be equivalent the vertex site symmetry must be 222 (D_2) or higher (i.e., a supergroup of 222) and thus have point symmetry with an invariant point (rather than invariant line or plane). As the vertices are all related by symmetry it follows that the structure must correspond to an invariant lattice complex (i.e., all coordinates are 0 or a simple fraction, rather than variable *x*, *y*, or *z*). These lattice complexes have been known since the early days of crystallography, and are listed in, for example, the "International Tables for Crystallography" (34). Those corresponding to 4-connected nets are listed in Table 2.

For all angles to be related by symmetry, the point group must be $\bar{4}\,3m$ (T_d). It may be seen, therefore, that the *diamond* net is the only regular 4-connected net (Fig. 7). It is of course ubiquitous in crystal chemistry. The form of silica based on the expanded diamond net is cristobalite, and there are many materials, including nitrides, chalcogenides, phosphides, halides, and ice I_c, based on this topology (35), far too many compounds to be listed here. The net of all the atoms in the sphalerite (ZnS) structure is diamond, so it is an *AB* derivative. The diamond net is unique in that expanded TX_2 compounds ("cristobalites") can be made with that topology with regular TX_4 tetrahedra and with a very wide range of X–T–X angles (3, 35). When this angle is 180° the structure has maximum volume and the symmetry is $Fd\bar{3}\,m$. The angle can be reduced by concerted tilts of the TX_4 tetrahedra in a number of ways which reduce the symmetry. In two special tilt systems, when the T–X–T angle is 109.5° the X arrangement corresponds to close packing. In one, which has symmetry $I\bar{4}\,2d$, the packing is cubic (ccp) and in a second, with symmetry $Pna2_1$, the packing is hexagonal (hcp). It is this ability to accommodate a wide range of T–X–T angles that allows the topology to occur for such different materials as SiO_2 (Si–O–Si $\approx$ 145°) and $ZnCl_2$ (Zn–Cl–Zn $\approx$ 109°).

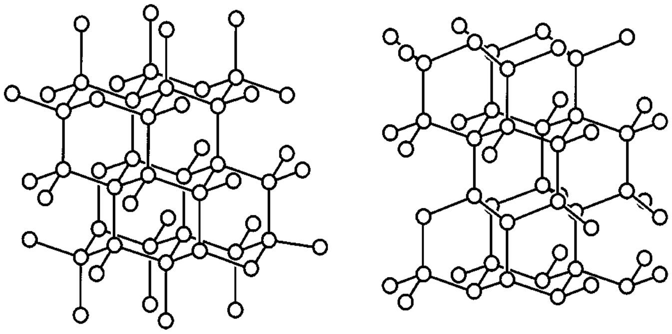

FIG. 7. Comparison of the diamond (left) and lonsdaleite (right) nets.

TABLE 2
Some Important 4-Connected Nets

Symbol	Name	s.g.	Wyckoff	p.g.	Z	Vertex symbol
D	Diamond	$Fd\bar{3}m$	*a*	$\bar{4}\,3m$ (T_d)	2	$6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2$
*J**	NbO	$Im\bar{3}\,m$	*b*	$4/mmm$ (D_{4h})	3	$6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}8_2{\cdot}8_2$
Q	Quartz	$P6_222$	*a*	222 (D_2)	3	$6{\cdot}6{\cdot}6_2{\cdot}6_2{\cdot}8_7{\cdot}8_7$
*W**	Sodalite	$Im\bar{3}\,m$	*d*	$\bar{4}\,m2$ (D_{2d})	6	$4{\cdot}4{\cdot}6{\cdot}6{\cdot}6{\cdot}6$
V		$I4_132$	*c*	222 (D_2)	6	$3{\cdot}3{\cdot}10_2{\cdot}10_2{\cdot}10_3{\cdot}10_3$
*S**		$Ia\bar{3}\,d$	*d*	$\bar{4}$ (S_4)	12	$6{\cdot}6{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2$
	Lonsdaleite	$P6_3/mmc$	*f*	$3m$ (C_{3v})	4	$6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}$
	$CdSO_4$	$P4_2/mmc$	*a*	mmm (D_{2h})	2	$6{\cdot}6{\cdot}6{\cdot}6{\cdot}6_2{\cdot}*$
	CrB_4	$I4/mmm$	*g*	$mm2$ (C_{2v})	4	$4{\cdot}6_2{\cdot}6{\cdot}6{\cdot}6{\cdot}6$
	$SrAl_2$	$Imma$	*i*	m	4	$4{\cdot}6{\cdot}4{\cdot}6{\cdot}6{\cdot}8_26_2$
	Moganite	$Cmmm$	*a*	mmm	1	$4{\cdot}4{\cdot}6_2{\cdot}6_2{\cdot}8_4{\cdot}8_4$
			h	$mm2$	2	$4{\cdot}8_6{\cdot}6{\cdot}6{\cdot}6{\cdot}6$
	PtS	$P4_2/mmc$	*c*	mmm (D_{2h})	2	$4{\cdot}4{\cdot}8_2{\cdot}8_2{\cdot}8_2{\cdot}8_2$
			f	$\bar{4}\,m2$ (D_{2d})	2	$4{\cdot}4{\cdot}8_7{\cdot}8_7{\cdot}8_7{\cdot}87$

Note. The first listed is the only regular net and the next five are quasiregular. These six correspond to invariant lattice complexes and their symbols (25) are given. The last net has two vertices and has entries on two lines.

The decorated diamond net commonly occurs in structures with two intergrown nets. Recall that the cristobalite TX_2 (derived from diamond) has lowest density with T–X–T = 180° and that the combination of two such nets intergrown leads to ccp X (for example, the Cu in Cu_2O). In the collapsed single net with symmetry $I\bar{4}\,2d$ with T–X–T = 109.5° the X atoms are again in ccp. In compounds with the ZnI_2 structure (36) (one form of GeS_2 is another example) there are four ZnI_4 tetrahedra condensed into a $T2$ supertetrahedron Zn_4I_{10} (Fig. 8); corner sharing of the supertetrahedra produces stoichiometry T_4X_8, i.e., TX_2. Two collapsed decorated nets with T–X–T = 109.5° interpenetrate (the symmetry is now $I4_1/acd$) and again the X arrangement is ccp so an "open" structure is not achieved. Other examples of interpenetrated networks of the same structure are β-$Ca_3Ga_2N_4$ (37) and Na_2SnAs_2 (38), in which Ca or Na are in the interstices between the interpenetrating nets.

Condensing eight tetrahedra produces a $T3$ supertetrahedron (Fig. 8) and when these are condensed into

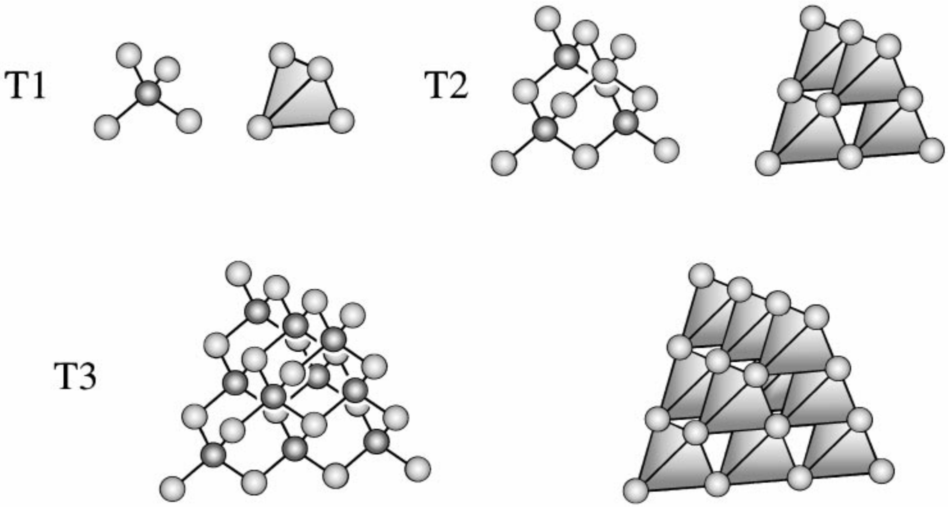

FIG. 8. Left: a $T2$ supertetrahedron T_4X_{10} formed by condensing four TX_4 tetrahedra, Right: a $T3$ supertetrahedron T_8X_{20}.

a framework the stoichiometry is, per unit, $T_{10}X_{18}$. Indium sulfide frameworks with the diamond topology have been made both with two interpenetrating nets (39) and without (40); the choice of base neutralizing the $In_{10}S_{18}^{6-}$ framework is critical in determining whether there is interpenetration or not. The uninterpenetrated structure has very large cavities.

Lonsdaleite is a rare form of 4-coordinated carbon with a structure (3) that is related to, but distinct from, that of diamond (the two structures are compared in Fig. 7). The AB derivative is the familiar wurtzite form of ZnS and the SiO_2 polymorph with the *lonsdaleite* topology is tridymite. Unlike cristobalite, tridymite cannot be made in any simple way with all T–X–T angles equal and less than 180°, and tridymite forms of silica have complex structures; for this reason too, corresponding halides, sulfides, etc., are not known.

Considerable confusion has arisen because in the many compounds with the $NaFeO_2$ structure (35) the net of all the atoms is lonsdaleite, but materials of this class are better considered as stuffed "FeO_2" (the strong bonds are Fe–O) and the FeO_2 is in fact the $Pna2_1$ form of cristobalite, which is of course based on the diamond net.

Of the other 4-connected nets, the two most important are the ones with high point symmetry, viz. NbO and sodalite. The *NbO* net (Fig. 9) is the structure of all the atoms in NbO. It provides a rare example of a 4-connected net with square-planar coordination of vertices. Its importance is mainly as a basic topology underlying more complex structures, although it does occur, very slightly deformed from cubic symmetry, as the Te net in $AgTe_3$ (41).

The remaining net with high-symmetry vertices is the *sodalite* net (Fig. 10). It is the net of the tetrahedral atoms

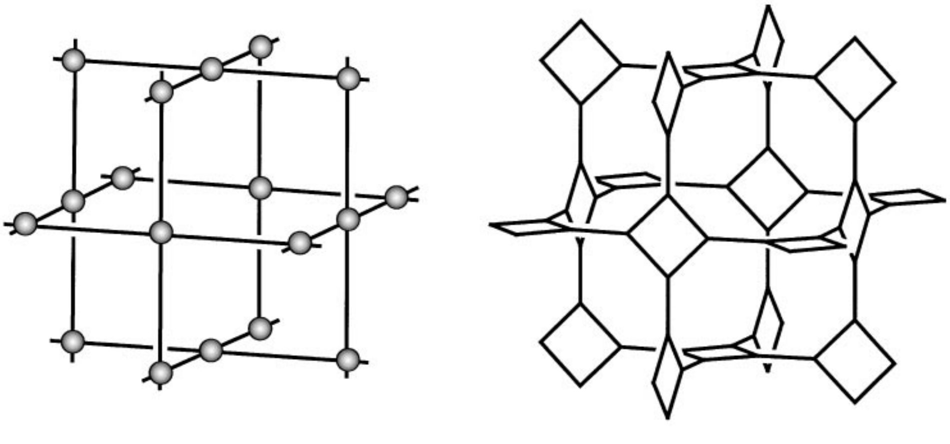

FIG. 9. Left: a fragment of the NbO net. Right: the 3-connected net 4.12.12 derived by replacing the vertices of the NbO net (shaded circles on the left) by squares.

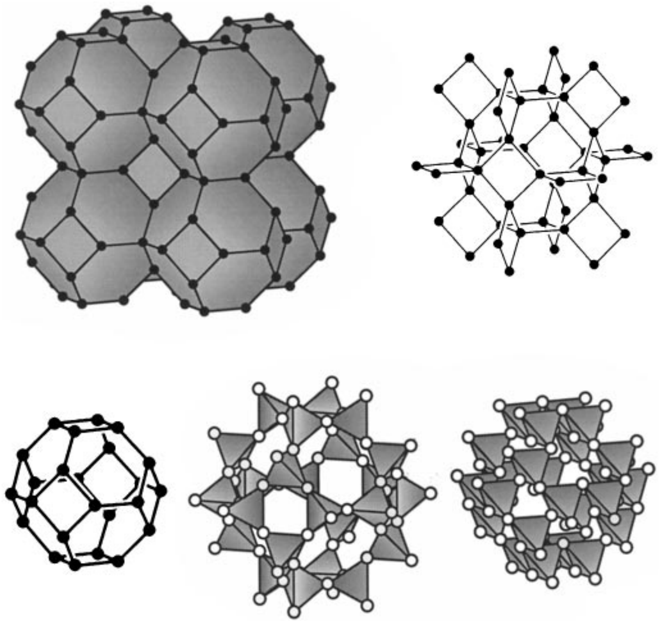

FIG. 10. Aspects of the sodalite net. Top left: a packing of truncated octahedra. Top right: the net of the vertices and edges of this packing. Bottom left: an outline of one truncated octahedron. Bottom middle and right: part of a framework of corner-connected TX_4 tetrahedra (open circles are X atoms) with T–X–T = 160.6° (middle) and 109.5° (left).

(Al and Si) in sodalite, ideal formula $Na_4Al_3Si_3O_{12}Cl$. An enormous number of compounds are known with structures based on this expanded topology, including oxides, sulfides (tetrahedrites) (42), nitrides (43, 44), halides (45), clathrate hydrates, and intermetallic structures (α-Mn structure type) (30). Like diamond, the net can accommodate a range of T–X–T angles (3, 46) and this accounts for its widespread occurrence. However the maximum angle and maximum symmetry is for 160.6°. For a structure with regular tetrahedra, there appears to be only one way to reduce the T–X–T angle and when it is 109.5° the X arrangement is incomplete (3/4) ccp. For the symmetry of derived structures see Ref. (3). In aluminosilicates and related materials the T–X–T angle is about 145°, but in materials such as sulfides and halides it is close to 109°. Recently a sodalite-derived sulfide based on supertetrahedral clusters (again with T–X–T angles close to 109°) with giant pores has been described (8). We should note that so far virtually all the occurrences of this topology are based on corner-sharing tetrahedral clusters such as TX_4 with T–X–T links, rather than with extended links that occur so often for the diamond topology.

The augmented sodalite structure is of special interest as it represents the position of the vertices in the least dense stable sphere packing (5, 47) (in a stable sphere packing, each sphere is surrounded by at least four other spheres with points of contact not all on the same hemisphere). We have already mentioned indium sulfide structures (8) with giant pores in which the vertices of a sodalite net are decorated with $In_{10}S_{20}$ supertetrahedra.

If the original 4-connected net had square coordination then the augmentation process is the replacement of vertices by squares. The simplest example of augmentation by squares is the conversion of the NbO net into a 3-connected net (Fig. 9). This net was referred to above in connection with high-symmetry 3-connected nets. An example (48) of its occurrence is in the structure of zinc squarate (the squarate anion is $C_4O_4^{2-}$) in which ZnO_4 squares and C_4 squares are linked by the C–O bonds. Large cavities in the reported structure are filled by water and acetic acid molecules.

We list the remaining quasiregular 4-connected nets in Table 2; the *quartz* net is perhaps the most important of these, as it represents the topology of the most stable form of silica, the second most common crystalline material on the surface of the earth, and a material of considerable technological importance. The structure is not found for sulfides or chlorides, as small T–X–T angles are not possible without unreasonably small $X \cdots X$ distances, although a form of BeF_2 has the quartz structure. A nice example (49) of an expanded version of the quartz structure is found in $ZnAu_2(CN)_4$: here tetrahedral Zn atoms are linked by approximately linear –N–C–Au–C–N– groups. The Zn atoms are ≈ 10 Å apart (compare Si $\cdots$ Si ≈ 3 Å in quartz). Alternatively, and equivalently, we could describe the structure as a decorated quartz net (see below) in which ZnN_4 tetrahedra are joined by –C–Au–C– links. In the actual structure, six such nets interpenetrate to make a dense material. Interestingly the same structure had been found earlier (50) in $CoAu_2(CN)_4$ but the connection to quartz had not been recognized.

A variant on the quartz structure is the *moganite* structure (Fig. 11), which in its simplest conformation with symmetry *Cmmm* also has only three vertices in the repeat unit (two square and one tetrahedral, so they are of two kinds (3)). This net also occurs in a cadmium cyanide framework (51) although the authors referred to it a "new honeycomb net." Part of the difficulty in recognition is that the expanded moganite structure appears with different symmetries in different contexts: *I*2/*a* in SiO_2 and *Ibam* in BeH_2. Notice that the quartz net does not contain 4-rings (the apparent 4-rings in Fig. 11 are 8-rings seen in projection). The vertex symbol is $6\cdot6\cdot6_2\cdot6_2\cdot8_7\cdot8_7$. The moganite net (which has two different kinds of vertex) does have 4-rings.

Three other simple structures are listed in Table 2. The structure named for *SrAl*$_2$ is found in a number of different contexts that illustrate the range of materials that can have a given simple topology. Thus it is the 4-connected net of the nearest neighbors of α-Np (52). It is the Al_2 or MgSi framework of compounds with the $SrAl_2$ and SrMgSi structures (53) (the latter is claimed to be the largest ternary structure

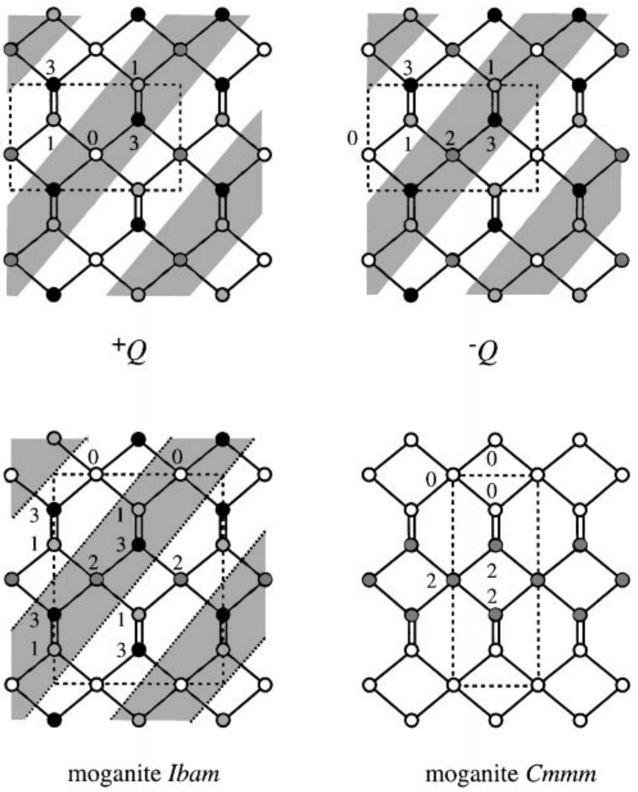

FIG. 11. Top: The two enantiomers of the quartz net projected on $(11\bar{2}0)$. Numbers are elevations in multiples of $|\mathbf{a}+\mathbf{b}|/4$. Bottom left: the moganite net projected on (010), numbers are now elevations in multiples of $b/4$. Notice the alternating bands of ^+Q (unshaded) and ^-Q (shaded). Bottom right: a simpler conformation of the moganite net with symmetry *Cmmm* and three vertices in the repeat unit.

type). It is the AlSi framework of compounds such as $RbAlSiO_4$ and $LiAlSiO_4 \cdot H_2O$ (the latter is known as zeolite Li–A and has zeolite code ABW (54)). Structures with interpenetrating $SrAl_2$ nets have also been described (55) in frameworks of Ag ions linked by long-chain aliphatic dinitriles $[NC\text{–}(CH_2)_{10}\text{–}CN]$.

The $SrAl_2$ topology has also been found for the linkage of tetrahedral MnS_4 and supertetrahedral Ge_4S_{10} units in a form of the $MnGe_4S_{10}^{2-}$ framework (56). Interestingly (as mentioned above) the same composition with a diamond topology had been previously synthesized (9); this emphasizes that the composition of the building units is insufficient to determine the topology achieved (this is, of course, a commonplace observation for aluminosilicates). Indeed an important part of the designer's task, and one which we do not address here, is the recognition of appropriate templates (57).

The *CrB₄* net is the structure of the boron framework in that compound. It is also the net of all the atoms in β-BeO and related ternary materials (35). Examples of framework oxides in which it occurs in an expanded form are a form of $CaAl_2Si_2O_8$ and metavariscite $AlPO_4 \cdot 2H_2O$ (see (3)). A supertetrahedral sulfide with the same topology is also known (8). The CrB_4 and $SrAl_2$ nets are illustrated in Fig. 12.

The *CdSO₄* net is the second example (the first was diamond) of a 4-connected net with the minimum number (2) of vertices in the repeat unit; it is illustrated in Fig. 13 in its most symmetrical conformation (symmetry $P4_2/mmc$). For examples of the occurrence of it, and related nets, see references (58, 59).

As discussed below there is interest in nets with both tetrahedral and square planar vertices. Clearly there must be at least two different types of vertex, but if these occur in equal numbers it is possible for there to be just one kind of edge. The only net of this kind of which we are aware is that named for *PtS* (cooperite) in which Pt forms PtS_4 rectangles and S forms SPt_4 tetrahedra (Fig. 14). It is not possible to have simultaneously perfect squares and regular tetrahedra (but such groups can be linked into a network as described below). Data for this net are also given in Table 1. Examples of nanoporous extended solids with structures based on this topology are given in Refs. (60, 61). We list another example here: the augmented PtS net is the simplest way to connect

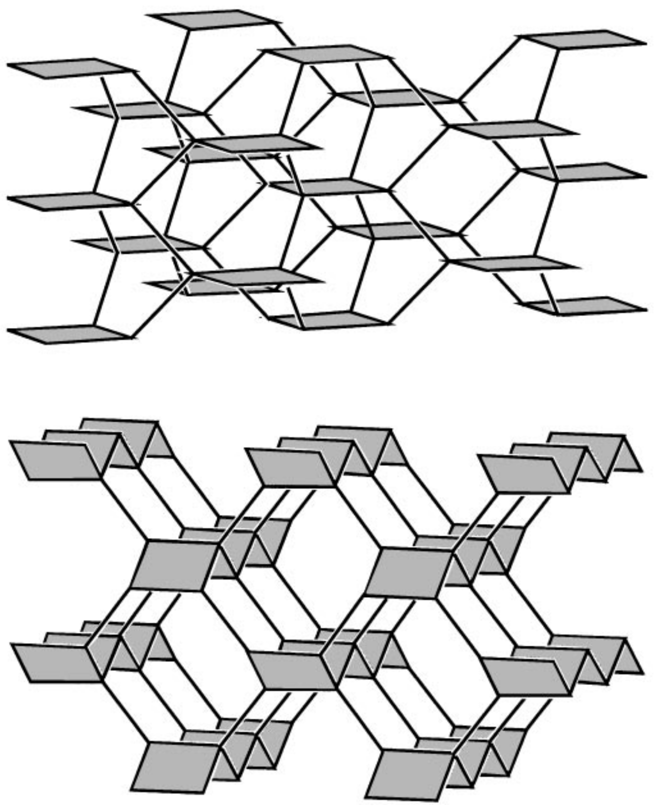

FIG. 12. Top: the CrB_4 net; 4-rings (squares) are shaded. Bottom: The $SrAl_2$ net: zigzag rods ("double zigzags") of edge-sharing squares are shaded.

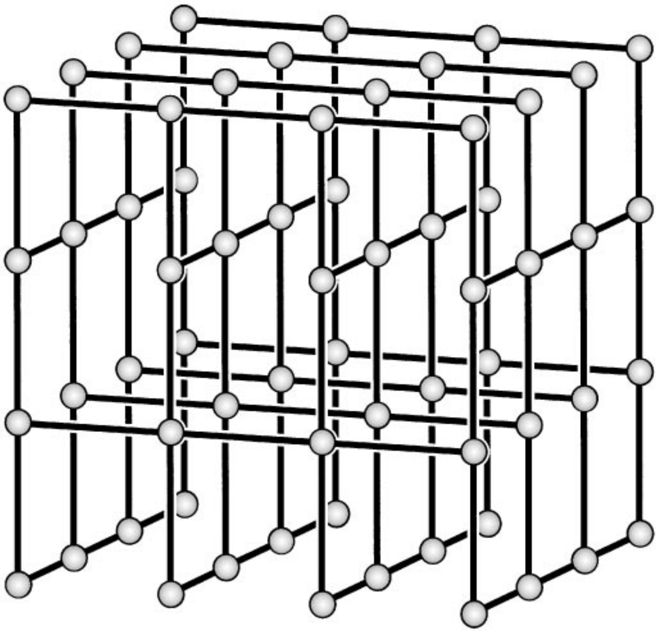

FIG. 13. The $CdSO_4$ net.

tetrahedra and squares (Fig. 14). An elegant example (62) of its occurrence is in $CuPt(CN)_4 \cdot NMe_4$ in which CuN_4 tetrahedra are linked to PtC_4 squares by N–C bonds, although we could equally describe the net as expanded PtS with Pt on Pt sites and Cu on S sites and –C–N– linkers expanding the original net.

Interpenetrating diamond nets. Two interpenetrating (intergrown) diamond nets occur very commonly. One of the first "Zintl" phases prepared was NaTl in which the Na and Tl atoms each form a diamond net displaced relative to each other by 1/2,1/2,1/2. If the two nets are composed of identical atoms, the arrangement in bcc and each vertex has eight nearest neighbors and the arrangement of vertices alone has symmetry $Im\overline{3}m$ (i.e., bcc)—see Fig. 15. But if just the four bonds of the original nets are maintained, the symmetry is $Pn\overline{3}m$. The *D* minimal surface (29) separates the two diamond nets and also has this symmetry. In cuprous oxide, again with the same symmetry, Cu atoms link tetrahedrally coordinated O atoms (i.e., the structure consists of corner-connected OCu_4 tetrahedra) into two interpenetrating (anti-) cristobalite structures. In the $Zn(CN)_2$ structure disordered linear –C–N– links join the tetrahedrally coordinated metal atoms, again forming two interpenetrating networks (63).

Notice that the two interpenetrating diamond nets combined have only two vertices in the repeat unit (the positions 2*a* of $Pn\overline{3}m$, viz. 0,0,0 and 1/2,1/2,1/2) just like the single net (cf. the discussion of the $ThSi_2$ net above). For some of the very many examples of multiply intergrown diamond nets see ref. (33).

4-Connected nets and polyhedral tilings. The vertex symbol of the *sodalite* nets has no subscripts, indicating that each angle contains just one ring. This is because the structure is made up of a packing of *simple* polyhedra (polyhedra with three edges meeting at each vertex) (Fig. 10).

Structures made up of packings of simple polyhedra such that two polyhedra meet at each face, three meet at each edge, and four meet at each vertex are of importance in several contexts, other than as the frameworks of crystal structures, such as in foams of bubbles or as the grain

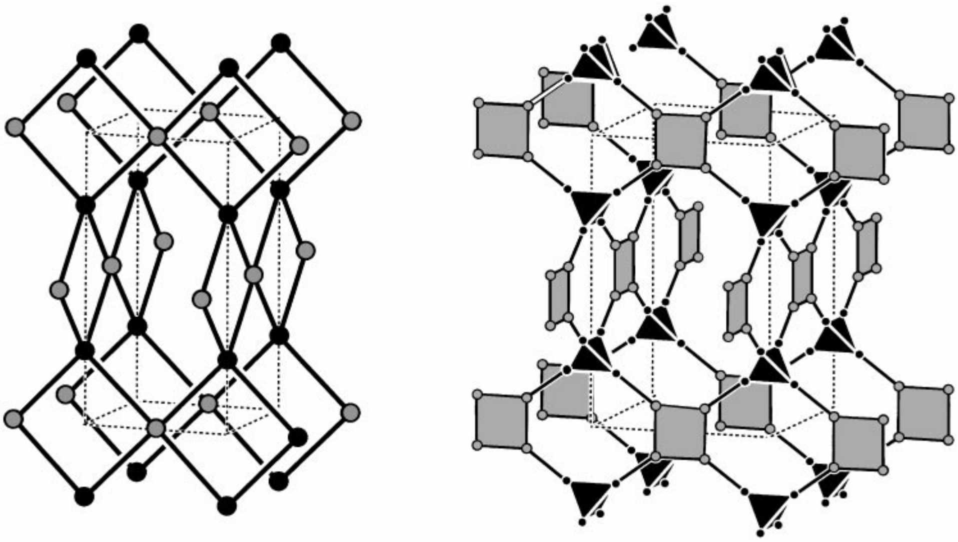

FIG. 14. Left: the PtS (cooperite) net (S, filled circles; Pt, shaded circles). Right: the augmented PtS net.

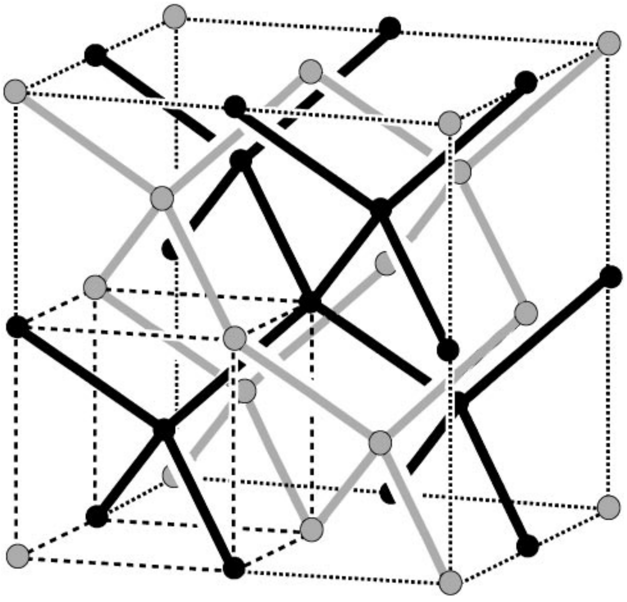

FIG. 15. Two interpenetrating diamond nets. The larger ($Fd\bar{3}\,m$) cell is for the case of two different nets (e.g., NaTl). The smaller ($Pn\bar{3}\,m$) cell is for the case of two identical nets. The smaller cell (now $Im\bar{3}\,m$) is the unit cell for just the vertices.

structure in a polycrystalline material. Most of the low density zeolite structures such as that of faujasite (zeolite code FAU (54)) are based on tilings of 3-D space by simple polyhedra. The polyhedra correspond to the cavities in the structure and their faces correspond to the pores connecting the cavities.

The sodalite structure is the only 4-connected net derived from a packing of simple polyhedra in which all the vertices and all the polyhedra are the same. In the context of foams it is known as the Kelvin structure, as Lord Kelvin conjectured that it was the lowest energy (minimum surface area) of a foam of equal bubbles. A number of other 4-connected nets derived from packings of identical polyhedra have been described (if one allows nonconvex polyhedra, there is an infinite number of these), but they generally have a number of different kinds of vertex and appear (so far anyway) to be of less importance in crystal chemistry. However, the enumeration of tilings of space by polyhedra turns out to be a very powerful method of enumerating crystalline frameworks especially when the algorithm proceeds by enumerating all uninodal, binodal, etc., structures (64). Thus it is known that there are just nine uninodal 4-connected nets derived from packings of simple polyhedra. Six of these correspond to known zeolite structures. The method is readily applied (65, 66) to tilings by polyhedra with vertices at which only two edges meet (see, for example, the diamond tile in Fig. 16 and also Refs. (3, 47)).

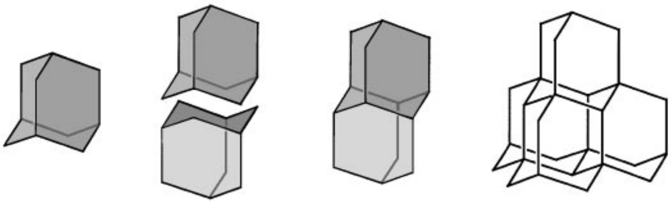

FIG. 16. The diamond net as a tiling of space. Left: one tile, an adamantane unit. Center: two tiles. Right a fragment of the net constructed from four tiles.

A set of structures of special interest is derived from tilings of space by simple polyhedra without 3- or 4-sided faces so that the corresponding nets have rings that are 5- or larger rings (47) (Fig. 16). It turns out that (at least as far as is known) only four polyhedra are possible and these can only combine in special ratios, so that as far as the relative numbers of polyhedra are concerned all structures can be considered as derived as intergrowths of three basic ones. The polyhedra (Fig. 17) have 12 pentagonal faces and either 0, 2, 3, or 4 hexagonal faces. The basic structures formed by packings of these polyhedra are those of the three common gas hydrate networks known as types I, II, and III (3, 47). The type I and II structures occur in clathrasils (framework silicas) with zeolite codes (54) MEP and MTN. Recently "expanded" forms of silicon, germanium, and tin with partial or complete filling of the polyhedra with atoms of metal such as Na have attracted considerable interest, recent papers (67, 68) give additional references. It is believed that there is more carbon in oceanic methane hydrate (with the type I structure) than in all known oil deposits (69).

(3,4)-Connected nets. In (3,4)-connected nets special interest attaches to those nets with all 4-connected vertices (A) attached to 3-connected vertices (B) and vice versa (for nets with links joining pairs of 3-connected or 4-connected vertices, see Wells (23)). The composition is then A_3B_4; Si_3N_4 provides a familiar example. We know of only four nets with all the links equivalent; two of them are rather important in crystal chemistry, but not very well known (Table 3).

The first is known as the *boracite* net (3) and is shown in Fig. 18. One way to consider this structure is as derived from the sphalerite structure AB by removing a quarter of

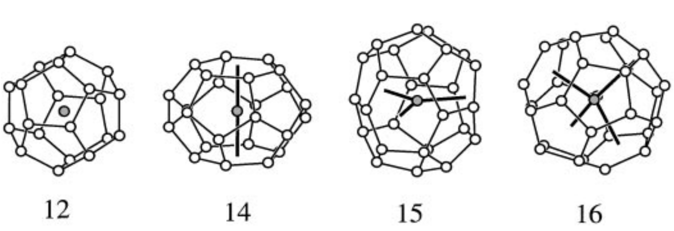

FIG. 17. The four polyhedra without 3- or 4-sided faces that can combine to tile space. The numbers are the numbers of faces.

TABLE 3
Some Simple (3,4)-Connected Nets

Name	s.g	4-vertex	3-vertex
Boracite	$P\bar{4}3m$	$d\bar{4}m2$ (D_{2d})	e $3m$ (C_{3v})
Twisted boracite	$Fm\bar{3}m$	d mmm (D_{2h})	f $3m$ (C_{3v})
Pt_3O_4	$Pm\bar{3}n$	$c\bar{4}m2$ (D_{2d})	e 32 (D_3)
	$I\bar{4}3d$	$a\,\bar{4}$ (S_4)	c 3 (C_3)

Note. s.g. is space group. Under "vertex" are listed Wyckoff position and site symmetry.

the *A* (or *B*) atoms. Note that one can have either 120° angles at the 3-connected vertex or 109.5° angles at the 4-connected vertex, but not both simultaneously. The symmetry is primitive cubic, space group $P\bar{4}3m$ and there are three 4-connected and four 3-connected vertices in the unit cell. The expanded framework in boracite, which is made up of linked BO_3 triangles and BO_4 tetrahedra, has stoichiometry B_7O_{12}. The pattern of 4-connected vertices is the same as in the ReO_3 (*J*) structure (Fig. 19) with the vertices in fixed (invariant) positions in the unit cell. Batten *et al.* (15) describe a structure with large cavities that is based on two intergrown boracite nets.

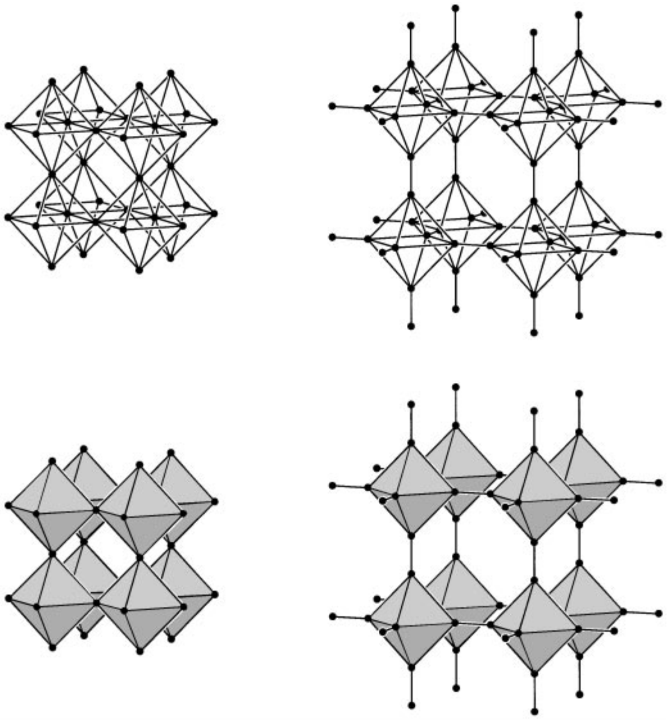

FIG. 19. Left: the ReO_3 arrangement of corner-sharing octahedra (*J* lattice complex). Right: The net of B in CaB_6 (The Ca atoms center the large cavities).

A variation on the boracite net, which is of lesser importance, but still known in crystal chemistry is what we call the "twisted" boracite net in which there is planar coordination at the 4-connected vertex (Fig. 18). This is derived by rotating alternate unit cells of the boracite structure by 90° along one of the cube directions (a $\bar{4}$ axis). The cubic unit cell edge is doubled and the symmetry is now $Fm\bar{3}m$.

Augmenting the boracite net produces a linkage of triangles and tetrahedra (Fig. 20), and augmenting the twisted boracite net produces another linkage of squares and tetrahedra (Fig. 21). We have found several examples of these nets in our recent work (to be published). Although not so described, the Cu salt of trimesic acid (1,3,5-benzene tricarboxylic acid) (70) is based on the augmented twisted boracite net. Again an obvious variation is to decorate (augment) just either one of the two kinds of vertex.

The *Pt_3O_4* net (3, 22) is the simplest 3,4-connected net in the sense that it is the only one in which both sets of vertices are in invariant positions. The 4-connected vertices are in square coordination and the 3-connected vertices are in equilateral triangular coordination (Fig. 22). The augmented net is the linkage of triangles and squares to form a very elegant and open 3-connected (Fig. 23).

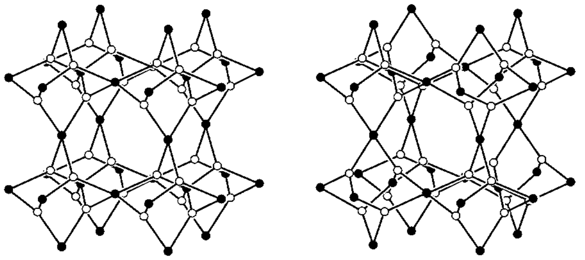

FIG. 18. Left: the boracite net. Right: the "twisted" boracite net.

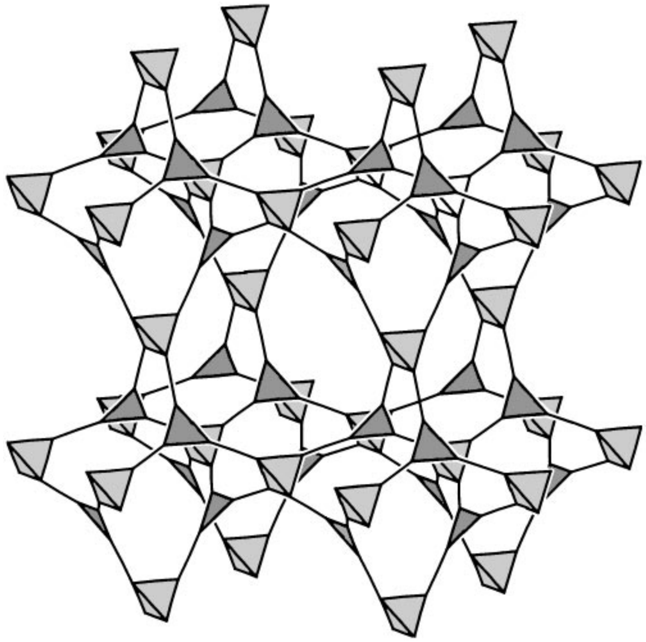

FIG. 20. The augmented boracite net.

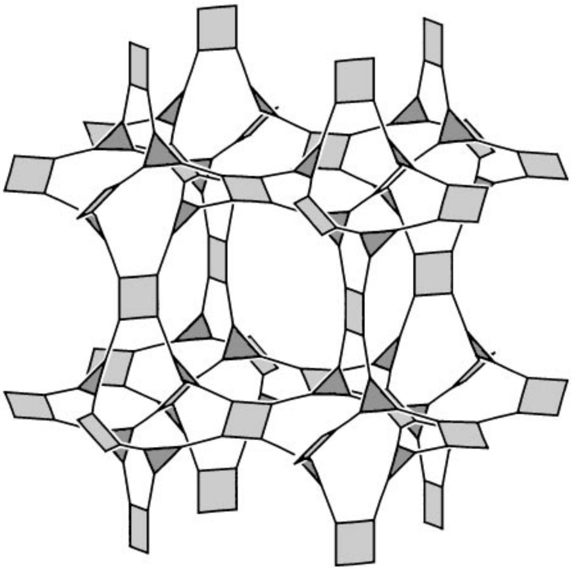

FIG. 21. The augmented twisted boracite net.

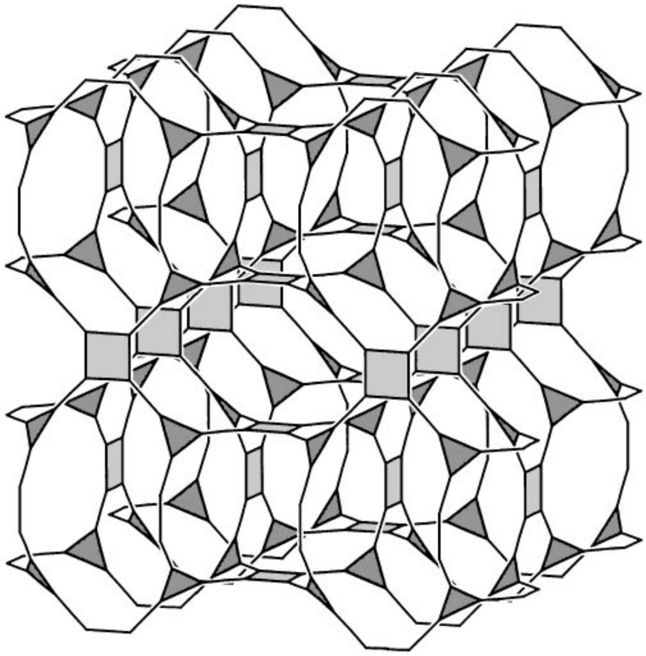

FIG. 23. The augmented Pt_3O_4 net.

We also list a *fourth* net (71), which appears to be of lesser importance, but is again rather simple with the 4-connected vertices in fixed positions and all edges equivalent. The 3-connected vertices are in positions *x*,*x*,*x*, etc.; when $x = 9/32$ they form a regular tetrahedron around the 4-connected vertices. The angles at the 3-connected vertices are then 119.6°. It does not appear to be possible for a 3,4-connected net to have simultaneously both regular tetrahedral coordination, with angles of 109.5°, and planar triangular coordination with angles of 120°. (The actual structures of materials such as Si_3N_4 are a compromise between these two conditions.)

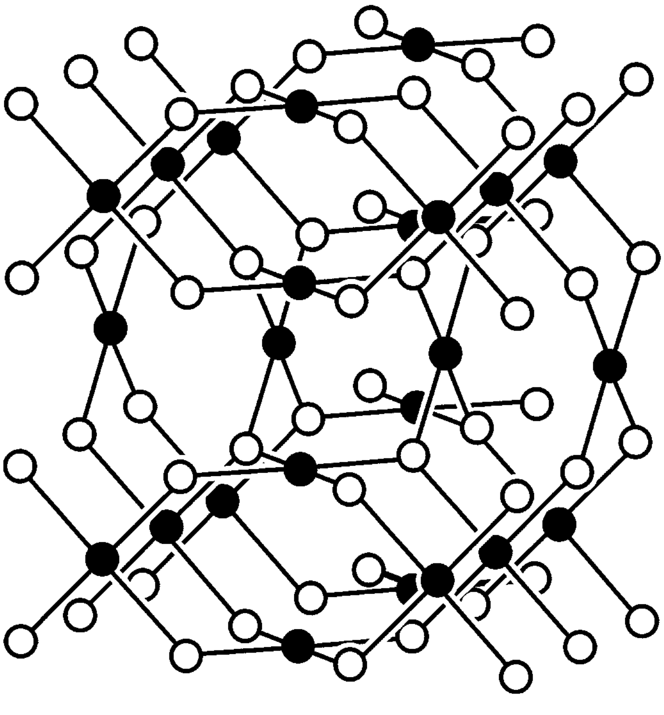

FIG. 22. The Pt_3O_4 net. (Filled circles are Pt).

5-, 6-, and 8-Connected nets. It is easy to show that there cannot be a 5-connected net with all edges equivalent (it would require the presence of 5-fold symmetry axes which are not possible in two- or three-dimensional periodic structures). The *CaB_6* net (Fig. 19) is very common in may contexts. In compounds such as $Ga(CN)_3$ (63), C and N atoms replace the B atoms and Ga centers the octahedra—there is disorder of the CN groups which may be CN or NC along any given bond. Structures based on octahedrally coordinated metal atoms joined by –C–N– links are generically referred to as "Prussian blue." As shown in Fig. 19, The CaB_6 structure may be considered as derived from a simple cubic structure of corner-connected octahedra (often named for the anion positions in ReO_3 and also known as the invariant lattice complex *J*). Alternatively it could be considered as the augmented primitive cubic (*P*) net. Clearly a large variety of other 5-connected nets can be derived similarly from other structures consisting of corner-connected octahedra (3). Another common boride structure with 5-connected B atoms forming a uninodal net is that of UB_{12} (3) which is made up similarly of linked B_{12} cuboctahedra. We may consider this structure to be an augmentation of the 12-coordinated face-centered cubic structure (symbol

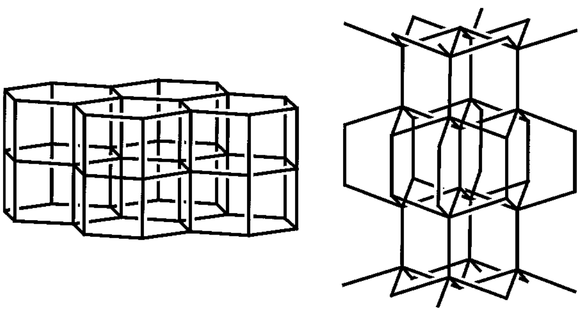

FIG. 24. Two simple 5-connected nets. Left: BN net, Right: the *bct* net (square pyramidal coordination).

TABLE 4
Some Simple 5-, 6-, and 8-Connected Nets

Name	Connectivity	s.g	Positions	Symmetry	*AB*
CaB_6	5	$Pm\bar{3}m$	6 *e*	$4mm\ (C_{4v})$	
BN	5	$P6/mmm$	2 *c*	$\bar{6}m2\ (D_{3h})$	$P6_3/mmc,\ c' = 2c$
bct	5	$I4/mmm$	4 *c*	$\bar{4}m2\ (D_{2d})$	$I4mm$
P	6	$Pm\bar{3}m$	1 *a*	$m\bar{3}m\ (O_h)$	$Fm\bar{3}m,\ a' = 2a$
T	6	$Fd\bar{3}m$	16 *c*	$\bar{3}m\ (D_{3d})$	(53)
I	8	$Im\bar{3}m$	2 *a*	$m\bar{3}m\ (O_h)$	$Pm\bar{3}m$
J	8	$Pm\bar{3}m$	3 *c*	$4/mmm\ (D_{4h})$	

Note. s.g. is space group. *AB* refers to the symmetry of the ordered binary derivative structure.

F). Expansion of the CaB_6 structure leads to a network of corner-sharing AX_5 square pyramids with stoichiometry A_2X_5. In Nb_2F_5 two such networks interpenetrate (3, 72).

Two 5-connected nets that contain only even rings (and can therefore be realized as alternating *AB* structures) are shown in Fig. 24. They contain the minimum number of vertices in the repeat unit (2). In the first there is trigonal bipyramidal coordination; hexagonal BN approximates this arrangement as an ordered *AB* variant; Li_4SeO_5 (73) has a structure that is in turn an ordered variant of the *BN* structure. The second net has square-pyramidal coordination. The arrangement of vertices is the same as in two interpenetrating $ThSi_2$ nets (Fig. 4). In Table 4 we refer to this net as *bct* (for the symmetry which is body-centered tetragonal).

Of course a prismatic stacking of planar 3-connected nets will generate 5-connected nets. The BN net with the stacking of graphite (6^3) layers is the simplest of these; other uninodal possibilities are stackings of 4.8^2, 4.6.12, and 3.12^2 nets.

There are two 6-connected nets of special importance. The simple cubic net (name *P* for primitive cubic) is the basic structure underlying all three-dimensional periodic structures (the combination of the six translations $\pm\mathbf{a}$, $\pm\mathbf{b}$, $\pm\mathbf{c}$ generate a lattice). In what should be entirely familiar, two intergrown *P* nets produce bcc (symbol *I*) and four intergrown *P* nets produce fcc (symbol *F*). In each of these structures (they are of course the cubic lattices) there is just one point in the primitive cell. Only if atoms fall on the points of one of these three lattices can they have octahedral ($m\bar{3}m = O_h$) symmetry.

The second 6-coordinated net can be considered a network of corner connected tetrahedra (Fig. 25). It occurs in many places in crystal chemistry. The vertices are in special positions of $Fd\bar{3}m$ and correspond to the invariant lattice complex *T*. The centers of the tetrahedra form a diamond network and, taken with the tetrahedron vertices, form the cubic conformation of the cristobalite (expanded diamond) network. The *T* arrangement also occurs as the position of the octahedral cations in spinel, and the ordering of two kinds of cation on these sites in so-called "inverse" spinels (such as magnetite) is a famous problem. For the two simplest solutions see Ref. (69). Notice that as it contains odd (3-) rings one cannot have alternating *A* and *B*, with *A* having only *B* neighbors and vice versa.

For completeness we include the two simplest 8-connected structures. One is of course the body-centered cubic lattice (symbol *I*). The ordered *AB* version is the CsCl or β-brass (CuZn) structure. The other well-known structure is the invariant lattice complex with symbol *J*, more commonly named for the anion array in ReO_3. It is illustrated in Fig. 19. In an arrangement of two intergrown *J* structures, each vertex has four nearest neighbors of the other net, and the pattern is in fact that of NbO. This is in fact an appropriate description of the NbO structure as there is surely strong Nb–Nb bonding. Augmentation of the body-centered cubic structure leads to a network of linked cubes, the *polycubane* structure (74) (zeolite code ACO (54)).

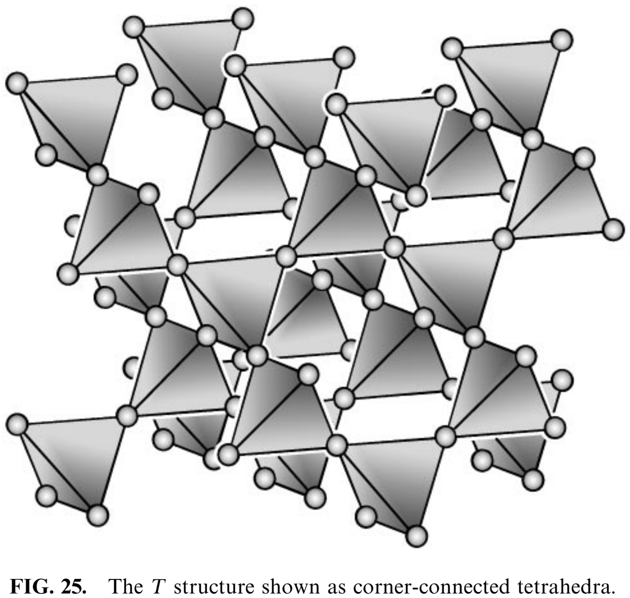

FIG. 25. The *T* structure shown as corner-connected tetrahedra.

Intergrowth of T and D nets: The Cu_2O *and* $MgCu_2$ *structures.* As mentioned above in *Cu_2O* there are two interpenetrating OCu_4 tetrahedral frameworks of the cristobalite type. In each framework the Cu atoms are on a *T* net, and the two *T* nets combined form fcc (*F*). The two diamond (*D*) O nets combine to form a bcc (*I* lattice) and if the bonds were ignored, Cu_2O could be considered as an interpenetration of the *F* and *I* lattices (to produce a primitive cubic structure!) (75).

Another basic intergrowth of the *D* and *T* structures produces the *$MgCu_2$* structure (with Mg on the *D* net and Cu on the *T* net). This is of course the famous cubic Friauf phase (3) that is the most common binary structure known in chemistry (47).[3]

It should be clear that decorating the 6-connected primitive cubic lattice will produce a cubic structure of linked octahedra. This is just the CaB_6 framework already described (Fig. 19).

(3,6)- (4,6)-, and (4,8)-Connected nets. Little systematic study has been made of higher-coordination structures with mixed connectivity. Here we briefly mention our candidates for those most likely to be of importance in the design and synthesis of low density structures. We identify structures with high symmetry. In this regard we should mention the work of Brown (76) who has analyzed the possibility of occurrence of symmetrical structures with stoichiometries AB, AB_2, and A_2B_3.

It appears to be impossible to have equiangular triangular coordination combined with regular octahedral coordination; certainly it is impossible if octahedral symmetry is required at the 6-coordinated site. Perhaps the best compromise is achieved by the net of the familiar structure of the rutile form of *TiO_2*. It is probably the easiest target for a designed synthesis, despite the fact that there are two kinds of Ti–O bond. Indeed interpenetrating rutile structures have already been reported (77) in compounds $M(\text{tcm})_2$ [$M = 3d$ transition metal, $\text{tcm}^- =$ tricyanomethide, $C(CN)_3^-$]. Augmentation of the rutile net, resulting in a linkage of triangles and octahedra is shown in Fig. 26.

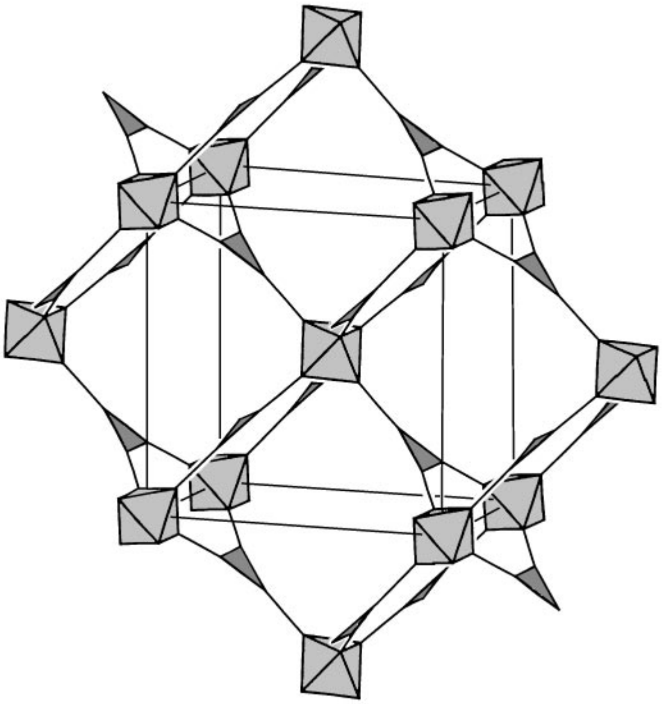

FIG. 26. The augmented rutile net.

Likewise it appears impossible to have regular tetrahedral and regular octahedral coordination in a (4,6)-connected structure; certainly not with tetrahedral and octahedral symmetry at the two sites. The best compromise appears to be the structure of the corundum form of *Al_2O_3* (α-alumina). The expanded structure derived from this with corner-sharing octahedra and tetrahedra is the rhombohedral $Fe_2(SO_4)_3$ structure (3). The same framework is found in the large group of compounds with the nasicon structure; typical compositions are $Na_4Zr_2Si_3O_{12}$ and $Na_3Sc_2P_3O_{12}$. The structure has also been known in open framework cyanides (referred to as "zeolitic cyanides") for more than 20 years. Examples of compositions are $K_2Fe_2Zn_3(CN)_{12}\cdot 5H_2O$, $Na_2Fe_2Zn_3(CN)_{12}\cdot 9H_2O$, and $Cs_2Fe_2Zn_3(CN)_{12}\cdot 6H_2O$ (78); in these compounds octahedrally coordinated Fe and tetrahedrally-coordinated Zn are joined by –C–N– links.

The augmented corundum net is of particular interest as a linkage of tetrahedra and octahedra (Fig. 27). Notice that in the cyanides just described, FeC_6 octahedra and ZnN_4 tetrahedra are linked by C–N bonds.

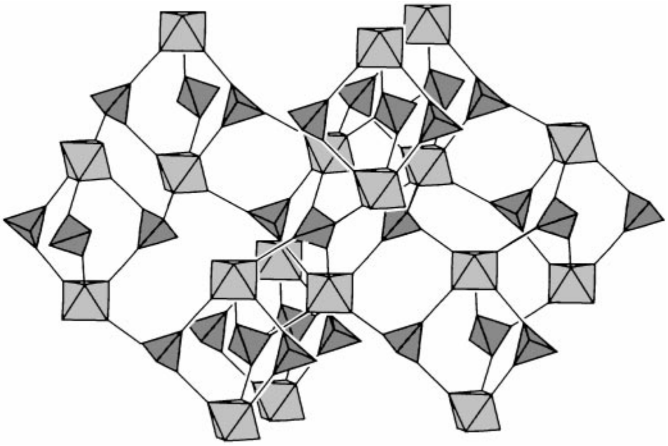

FIG. 27. The augmented corundum net.

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[3] Although, astonishingly, it is absent from most textbooks of inorganic chemistry!

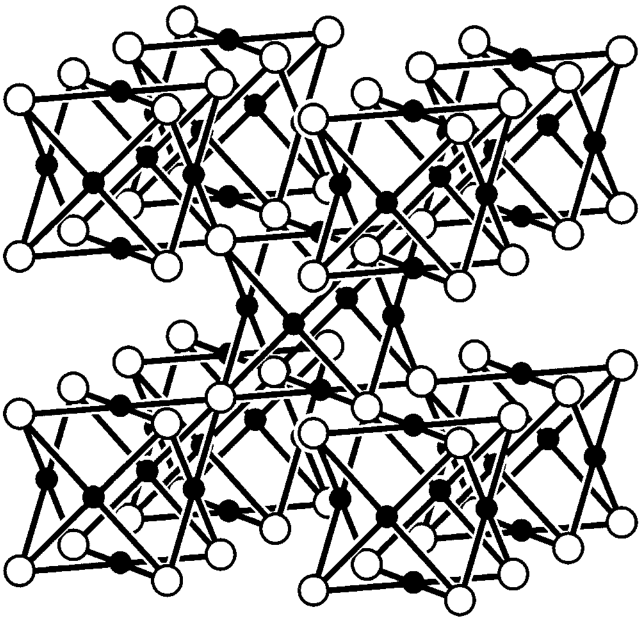

FIG. 28. A 4,6-connected net with square and octahedral coordination.

A second 4–6 connected net, this time with planar (square) 4-coordination is also of interest (Fig. 28). An elegant example of its occurrence is in the $Co_3[Re_6Se_8(CN)_6]_2$ framework with Co at the 4-connected sites, Re_6Se_8 clusters decorating the 6-connected sites, and –C–N– groups providing expanding links (79).

There is one (and only one) (4,8)-connected structure with regular tetrahedral and cubic coordination. This is the fluorite structure, and it is not surprising that it is nature's preferred structure for nonmetallic compounds of stoichiometry AB_2.

Decoration of the fluorite net will produce a linkage of tetrahedra and cubes. If only the 8-coordinated vertices are decorated, the result is a network of cubes linked by isolated tetrahedra. This is the framework of the common octadecasil structure (zeolite code AST (54)). For a discussion of how TX_2 structures based on this topology can adapt to different T–X–T angles, and for a discussion of how cubes can be linked together, see Ref. (74).

CONCLUSION

In this article we have described the simplest topologies of low-connectivity nets. There are of course, much more complicated topologies known. The most complicated zeolite described to date has 16 different kinds of tetrahedral vertex (54). Perhaps in trying to produce a simple 4-connected net with large structure building units, one might stumble upon a structure of this complexity by chance; but we believe the day is still long away when we will be able to *design* a synthesis to produce a previously specified structure of such complexity. Although we should mention in this connection that Iwamoto and co-workers (80–82) in particular have made an astonishing variety of what they term "mineralomimetic" structures largely based on $Cd(CN)_2$. Some of these are indeed "zeolite-like," at least in their structural aspects.

TABLE 5
The Basic Nets with One or Two Kinds of Vertex Figure

Coordination	Coordination figures		Net
3	Triangle	Triangle	Y^* ($SrSi_2$)
3	T	T	$ThSi_2$
3,3	Triangle	T	$12_4 \cdot 12_7 \cdot 12_7$
3,4	Triangle	Square	Pt_3O_4
3,4	Triangle	Tetrahedron	Boracite
3,6	Triangle	Octahedron	Rutile (TiO_2)
4	Square	Square	NbO
4	Tetrahedron	Tetrahedron	Diamond (C)
4,4	Square	Tetrahedron	Cooperite (PtS)
4,6	Tetrahedron	Octahedron	Corundum (Al_2O_3)
4,6	Square	Octahedron	See text
4,8	Tetrahedron	Cube	Fluorite (CaF_2)
6	Octahedron	Octahedron	Primitive cubic
8	Cube	Cube	Body-centered cubic

Indeed we repeat our main contention: most structures that can readily be *designed and synthesized* will have very simple basic topologies dictated by the shape (triangle, square, tetrahedron, etc.) and connectivity of the structure-building units. For convenience, Table 5 lists one basic structure for each kind of unit shape, or combination of two shapes. Targeting just these topologies should keep the synthetic chemist busy for some time to come.

A complete primer on designed synthesis will also dwell on topics such as ensuring that three-dimensional, rather than layer, structures are formed (assuming that is desired) and the prevention of interpenetration of open frameworks (again, assuming that is desired). In such considerations, the structure-directing role of guests and counterions is of paramount importance and careful attention will have to be placed on guest–host interactions. These will depend strongly on the specific chemistry, as opposed to the simple geometry which has been our concern in this paper.

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