

CHAPTER 5

POLYHEDRA AND TILINGS

Chapters 5-7 are devoted to a description of simple geometrical structures that are frequently important components of crystal structures. They often arise in a purely mathematical context and we generally consider them from this point of view, deferring most of the crystallographic aspects until later. We believe that "knowing" these basic structures is essential to understanding crystal structures and structural relationships.

We start with a description of some simple polyhedra, most of which are encountered in crystal chemistry. Finite polyhedra are closed figures with polygonal faces. The polygons are in general not regular and in fact only a very small subset of all polyhedra can be made with regular polygonal faces. In crystal chemistry the interest in polyhedra arises mainly (but not entirely) because their vertices represent the positions of atoms in the coordination sphere of a central atom. For this reason we generally place small spheres (which appear as circles in the drawings) at the vertices for emphasis. We use the terms "large" and "small" polyhedra in a relative sense to mean those having many or few vertices respectively.

There is a sense in which a tiling of the plane by polygons is a special case (with an infinite number of vertices) of a polyhedron so we consider such patterns in this chapter also. The vertices of such tilings often correspond to the positions of atoms in a plane of a crystal structure.

5.1 Polyhedra

A number of polyhedra have been met already in Chapter 2. A more systematic listing of common convex polyhedra is now given. Convex polyhedra are those for which all dihedral angles (angles between faces) are less than 180° when viewed from inside. The discussion is by no means complete; other (coordination) polyhedra will be met subsequently. Some large polyhedra have attracted interest as molecular forms of carbon ("fullerenes") and as the shapes of viruses; these polyhedra are discussed in Appendix 4.

5.1.1 Regular polyhedra

Most important and well known are the *regular* polyhedra. These are polyhedra with all vertices related by symmetry and with all faces congruent regular polygons.¹ It is trivial to show that there are at most five of these and that all possibilities can be realized. The faces must have fewer than six edges, as three regular hexagons meeting at a point must all lie in the same plane. In fact if n regular N -gons meet at a point the angles of the polygons must be less than $360^\circ/n$. The possibilities are given in Table 5.1. In the table the symbol N^n is

¹We restrict the discussion to convex polyhedra and thus exclude the four beautiful Kepler-Poinsot polyhedra which are constructed with intersecting faces.

the *Schläfli symbol* for the polyhedron. The regular polyhedra are also known as the Platonic solids.

Table 5.1 The regular convex polyhedra

n is the number of faces meeting at a vertex and V , E and F are the numbers of vertices, edges and faces.

faces	n	name	symbol	V	E	F	symmetry
triangles	3	tetrahedron	3^3	4	6	4	$\bar{4}3m$
triangles	4	octahedron	3^4	6	12	8	$m\bar{3}m$
triangles	5	icosahedron	3^5	12	30	20	$m\bar{3}\bar{5}$
squares	3	cube	4^3	8	12	6	$m\bar{3}m$
pentagons	3	dodecahedron	5^3	20	30	12	$m\bar{3}\bar{5}$

We have already met the tetrahedron, cube and octahedron but they are illustrated again in Fig. 5.1. In the figure a cube is shown on the left. Next an octahedron is shown inscribed in a cube; the vertices of the octahedron center the faces of the cube. A second polyhedron obtained by centering the faces of a polyhedron is said to be the *dual* of the first so the octahedron is the dual of the cube. It should be apparent that the polyhedron with vertices centering the faces of the octahedron is a cube (now smaller) so the cube (4^3) and octahedron (3^4) are the duals of each other. In general p^q is the dual of q^p . The right half of Fig. 5.1 shows a tetrahedron inscribed in a cube in two different ways. It should be apparent that the dual of the tetrahedron on the left is a (smaller) tetrahedron with the same orientation as the one on the right so that the tetrahedron (3^3) is *self dual*.

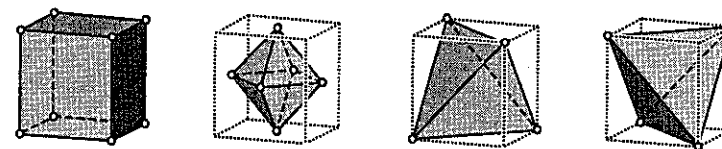


Fig. 5.1. From left to right: a cube, an octahedron and tetrahedra in two different orientations. Broken lines are edges obscured by the front faces, and dotted lines outline a cube.

The relationship to a cube allows an easy determination of some useful metrical properties of the octahedron and tetrahedron. Recall first that for a cube of unit edge, the length of a face diagonal is $\sqrt{2}$ and the length of a body diagonal is $\sqrt{3}$. The reader should verify that for a tetrahedron of unit edge, the distance from the center to a vertex is $\sqrt{3}/8$. The distance from a vertex to the center is $3/4$ of the distance from a vertex to the center of the opposite face, so the perpendicular distance from a vertex to its opposite face (the "height" of the tetrahedron) is $\sqrt{2/3} = 0.8165$. This last result is sufficiently useful that it (including the numerical value) is worth committing to memory. The volume of a

tetrahedron of unit edge is $1/(6\sqrt{2})$.

For an octahedron of unit edge, the distance from the center to a vertex is $1/\sqrt{2}$, and the distance between opposite vertices is twice that, i.e. $\sqrt{2}$. Less obvious is that the perpendicular distance between opposite faces is the same as the height of a tetrahedron with unit edge which, we repeat, is $\sqrt{(2/3)} = 0.8165$. The octahedron volume is $\sqrt{2}/3$, four times that of a tetrahedron with the same (unit) edge length.

The angle between the faces of a tetrahedron (the dihedral angle) is $\cos^{-1}(1/3) = 70.53^\circ$ and that between adjacent faces of an octahedron is the supplementary angle $\cos^{-1}(-1/3) = 109.47^\circ$. Opposite faces of an octahedron are parallel.

An icosahedron and a dodecahedron are illustrated in Fig. 5.2. Both have the same symmetry: $m\bar{3}5 = I_h$. We already remarked that $m\bar{3}$ is a cubic subgroup of $m\bar{3}5$ and illustrated that point using the icosahedron in Fig. 2.25. In the illustration of the dodecahedron, eight of the twenty vertices are shown as filled circles—these lie on the vertices of a cube. Of course all the vertices are equivalent, and four other sets of eight vertices forming a cube could have been picked out. Note an important distinction. The operations of $m\bar{3}$ relate all the vertices of an icosahedron to each other, but only sets of eight of the twenty vertices of the dodecahedron are so related. This is because the vertices of the icosahedron are on 5-fold axes, but in the dodecahedron the 5-fold axes run through the centers of pairs of opposite faces and vertices on a given face are related by a 5-fold axis which does not exist in $m\bar{3}$. In the dodecahedron the vertices are on $\bar{3}$ axes.



Fig. 5.2. An icosahedron, 3^5 (left), and a dodecahedron, 5^3 (right). Broken lines are edges obscured by the front faces.

Figure 5.2 should also make it apparent that the icosahedron (3^5) is the dual of the dodecahedron (5^3). Likewise the dual of the icosahedron is a (smaller) dodecahedron. For an icosahedron of unit edge, the distance from the center to a vertex is $5^{1/4}\sqrt{[(1 + \sqrt{5})/8]} = 0.9511$; i.e. slightly less than the edge length.

A note on terminology: The term “tetrahedron” refers to any polyhedron with four faces (which are triangles but not necessarily *equilateral* ones). Sometimes the term is used to refer specifically to a regular tetrahedron; this is particularly the case in such usage as “tetrahedral symmetry” which usually refers to the point group $\bar{4}3m (T_d)$ which is the

symmetry of a regular tetrahedron, but strictly refers also to $23 (T)$ and $m\bar{3} (T_h)$.¹

Similarly, the term “octahedron” strictly refers to any solid with eight faces, of which there are 257 (!) distinct examples, but it is often used only for the polyhedron with all triangular faces.² “Octahedral symmetry” likewise usually refers to $m\bar{3}m (O_h)$ which is the symmetry of a regular octahedron, but strictly should refer also to $432 (O)$. We will sometimes use terms such as “distorted octahedron” when we wish to emphasize the departure from regularity of the polyhedron with all triangular faces (3^4).

For many chemists the term dodecahedron refers, not to the regular dodecahedron, but to a polyhedron with twelve triangular faces (for which we prefer the term “bisdisphenoid”).³ The dodecahedron with twelve rhombic faces appears conspicuously later (we call it the rhombic dodecahedron). A regular dodecahedron is often called the pentagonal dodecahedron to distinguish it from the millions of other dodecahedra.

5.1.2 Combinations of octahedra and tetrahedra

Capping two opposite faces of a regular octahedron with two tetrahedra with equal edge lengths will produce a rhombohedron as shown in Fig. 5.3. The angles of the faces are 60° and 120° and three angles of 60° meet at two of the vertices. We note that a rhombohedron has symmetry $\bar{3}m$ and that the two opposite vertices where three equal angles α meet are on the $\bar{3}$ axis. If $\alpha < 90^\circ$ the rhombohedron is called *acute* (or *prolate*), and if $\alpha > 90^\circ$ the rhombohedron is termed *obtuse* (or *oblate*). If $\alpha = 90^\circ$ the rhombohedron is a cube of course. The rhombohedron with $\alpha = 60^\circ$ will be met many times; it is the primitive cell of the face-centered cubic lattice.

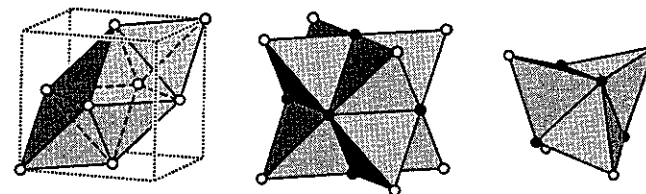


Fig. 5.3. Left: a 60° rhombohedron produced by capping two opposite faces of an octahedron with tetrahedra (compare with Fig. 5.1). Middle: a stella octangula produced by capping all the faces of an octahedron with tetrahedra—filled circles are the octahedron vertices. Right: a stella quadrangula obtained by capping all the faces of a tetrahedron—filled circles are the vertices of the central tetrahedron.

¹Please note that T_d refers to a symmetry group and is *not* shorthand for the word “tetrahedral”. Thus an atom at a site with T_d symmetry may, or may not, be four-coordinated; and conversely an atom with four neighbors at the vertices of a tetrahedron may, or may not, be at a site of T_d symmetry.

²Some readers will be familiar with “Dürer’s octahedron” which is a conspicuous feature of the celebrated engraving *Melencolia I* (1514). This polyhedron is an acute rhombohedron with the two acute vertices truncated and has two triangular faces and six pentagonal ones. Truncated tetrahedra and hexagonal prisms, discussed below, are other familiar examples of octahedra in this general sense.

³Another polyhedron with twelve triangular faces is the hexagonal bipyramid (see § 5.1.5).

Similarly capping *all* the faces of an octahedron with tetrahedra will produce the polyhedron known as a *stella octangula* shown in the middle of Fig. 5.3.¹ As the shading in the figure suggests, the stella octangula can also be considered as two interpenetrating larger tetrahedra.

Also shown in Fig. 5.3 is the polyhedron obtained by capping the four faces of a tetrahedron with tetrahedra. By analogy it is called a *stella quadrangula*; it is of some interest in crystal chemistry.² See § 5.2.4 and § 5.6.8 for some examples of its occurrence.

Other combinations of tetrahedra and/or octahedra will be met subsequently (§ 5.2). Of great importance in crystal chemistry is the fact that regular octahedra and tetrahedra with equal edges and in the number ratio of 1:2 can be packed together to fill space; this is a topic covered in Chapter 6.

5.1.3 Archimedean polyhedra

Table 5.2. The Archimedean polyhedra other than prisms and antiprisms.

V , E and F are the numbers of vertices, faces and edges. The numbers N in the Schläfli symbol represent in cyclic order the polygons (N -gons) meeting at a vertex.

Schläfli symbol	name	V	E	F	symmetry
3.6 ²	truncated tetrahedron	12	18	8	$\bar{4}3m$
3.4.3.4	cuboctahedron	12	24	14	$m\bar{3}m$
4.6 ²	truncated octahedron	24	36	14	$m\bar{3}m$
3.8 ²	truncated cube	24	36	14	$m\bar{3}m$
3.4. ³	rhombicuboctahedron	24	48	26	$m\bar{3}m$
3 ⁴ .4	snub cube	24	60	38	432
3.5.3.5	icosidodecahedron	30	60	32	$m\bar{3}\bar{5}$
4.6.8	truncated cuboctahedron	48	72	26	$m\bar{3}m$
3.10 ²	truncated dodecahedron	60	90	32	$m\bar{3}\bar{5}$
5.6 ²	truncated icosahedron	60	90	32	$m\bar{3}\bar{5}$
3.4.5.4	rhombicosidodecahedron	60	120	62	$m\bar{3}\bar{5}$
3 ⁴ .5	snub dodecahedron	60	150	92	235
4.6.10	truncated icosidodecahedron	120	180	62	$m\bar{3}\bar{5}$

Polyhedra with equivalent (i.e. symmetry-related) vertices but with more than one kind of regular polygonal face are referred to as *semi-regular* or *Archimedean*. These consist of the infinite families of regular prisms and antiprisms together with thirteen others. Prisms and antiprisms are discussed in the next section; the remaining polyhedra, all of which have either cubic or icosahedral symmetry, are listed in Table 5.2, together with the number of vertices (V), edges (E) and faces (F). These quantities are related by the Euler condition for

finite polyhedra $V - E + F = 2$. Of the polyhedra in the table, the cubic ones are the most important in crystal chemistry, but some of the others are also met. Some are conveniently derived by cutting off (truncating) vertices of simpler polyhedra in a symmetrical way and hence their names.

The rhombicuboctahedron (3.4.³) is sometimes called the *small* rhombicuboctahedron and the truncated cuboctahedron (4.6.8) is sometimes called the *great* rhombicuboctahedron. We find it easier to remember, and to recall mentally, these polyhedra from their Schläfli symbols rather than from their often cumbersome names.¹

The cuboctahedron (3.4.3.4) was introduced in Fig. 2.25 (p. 54) where we saw that it was simply related to the regular icosahedron. It is illustrated again in Fig. 5.4 together with its dual, the rhombic dodecahedron, which we will describe in § 5.1.5 below. The cuboctahedron and its relative the "twinned cuboctahedron" are discussed further when we consider sphere packings in Chapter 6. An important property of the cuboctahedron is that distance from the center to a vertex is equal to the edge length. It is also an example of a *quasiregular* polyhedron, which is one in which all edges and vertices (but not faces) are equivalent. (3.5.3.5 is the other quasiregular polyhedron.) As the edges are all equivalent, there is only one dihedral angle which is $\cos^{-1}(-1/\sqrt{3}) = 126.26^\circ$.

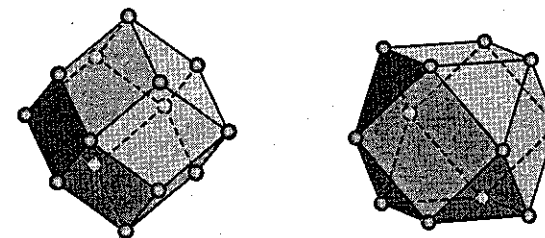


Fig. 5.4. Right: a cuboctahedron (3.4.3.4). Left: a rhombic dodecahedron, the dual of the cuboctahedron. Broken lines are edges obscured by the front faces.

The remaining cubic Archimedean polyhedra are illustrated in Fig. 5.5. They are sufficiently important that it is worth learning their names and shapes.

The truncated tetrahedron (3.6²) is an important 12-coordination polyhedron. It occurs particularly in structures of intermetallic compounds (see § 5.2.5). The reader with polyhedra at hand may like to verify that four regular octahedra and seven regular tetrahedra (all with equal edge length) can be combined to make a truncated tetrahedron.

The snub cube (3⁴.4) occurs in left and right-handed forms; Fig. 2.26 (p. 54) illustrates both and their relationship to the rhombicuboctahedron (3.4.³).

Truncated octahedra (4.6²) have the interesting property that they can be packed together

¹A reminder that the numbers N in the Schläfli symbol represent in cyclic order the polygons (N -gons) meeting at a vertex. Schläfli symbols are most useful for polyhedra with just one kind of vertex and we do not use them for polyhedra such as the rhombic dodecahedron (Fig. 5.4) with two different kinds of vertex (4³ and 4⁴).

¹So christened by the great geometer, astronomer and mystic, Johannes Kepler (1571-1630).

²See Hyde & Andersson (Book List) p. 342.

to fill space as discussed in Chapter 7. In such an array the centers of the polyhedra fall on a body-centered cubic lattice and the surface of a polyhedron encloses all points in space closer to the lattice point at its center than to any other lattice point, so it is the *Voronoi polyhedron* associated with the lattice point. In a terminology used by physicists, it is the *Wigner-Seitz cell* of the body-centered cubic lattice. The dihedral angles are $\cos^{-1}(-1/3) = 109.47^\circ$ between square and hexagonal faces and $\cos^{-1}(-1/\sqrt{3}) = 125.26^\circ$ between hexagonal faces.

We meet the truncated cuboctahedron (4.6.8) later also in connection with polyhedron packings and in zeolite structures. It is the largest polyhedron with equivalent vertices and cubic symmetry (the number of vertices is 48—equal to the order of group $m\bar{3}m$).

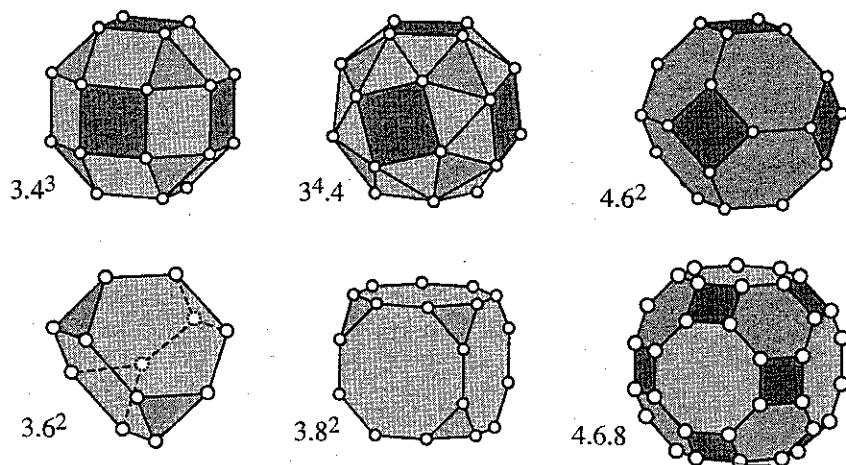


Fig. 5.5. Six of the cubic Archimedean polyhedra. Top left: rhombicuboctahedron (3.4^3). Top middle: snub cube ($3^4.4$). Top right: truncated octahedron (4.6^2). Bottom left: truncated tetrahedron (3.6^2). Bottom middle: truncated cube (3.8^2). Bottom right: truncated cuboctahedron ($4.6.8$). In each polyhedron faces related by symmetry have the same depth of shading. For 3.6^2 (only) edges obscured by the front faces are shown as broken lines.

The six beautiful icosahedral Archimedean polyhedra are illustrated in Fig. 5.6. It will be found that models of them are useful aids to appreciating icosahedral symmetry. Most familiar will be the truncated icosahedron (5.6^2) which represents the structure of C_{60} ¹; it may also be familiar as the structure of a soccer ball (balls based on $3.5.3.5$ are also sometimes seen). It should be apparent that $3^4.5$ is related to $3.4.5.4$ in the same way as $3^4.4$ is related to 3.4^3 . Note that $3^4.5$ with symmetry $235 (= I)$ is enantiomorphic.

¹Note that there two distinct edges in the truncated icosahedron; one (66) that is common to hexagons and a second (65) common to a hexagon and a pentagon. In C_{60} the 66 bond is significantly shorter than the 65 bond. The symmetry remains icosahedral of course.

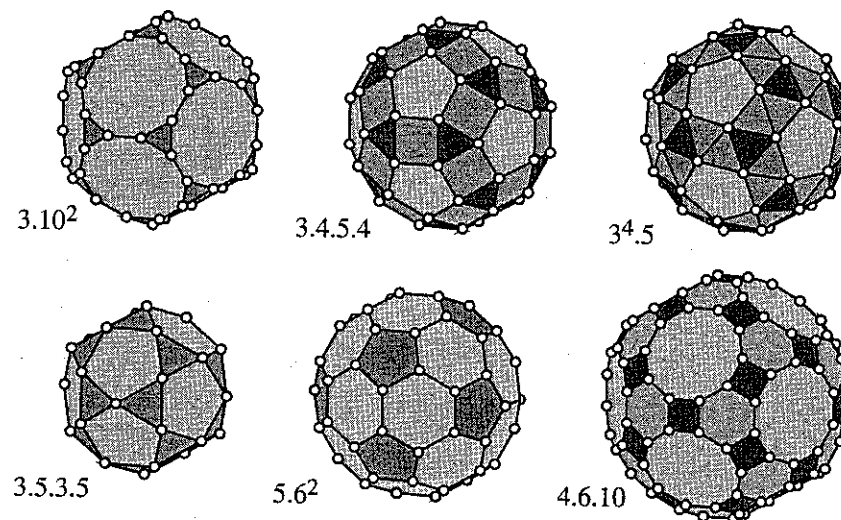


Fig. 5.6. The icosahedral Archimedean polyhedra. Top left: truncated dodecahedron (3.10^2). Top middle: rhombicosidodecahedron ($3.4.5.4$). Top right: snub dodecahedron ($3^4.5$). Bottom left: icosidodecahedron ($3.5.3.5$). Bottom middle: truncated icosahedron (5.6^2). Bottom right: truncated icosidodecahedron ($4.6.10$). In each polyhedron, faces related by symmetry have the same depth of shading.

5.1.4 Prisms, antiprisms and capped prisms

The remaining semiregular solids are prisms and antiprisms. The semiregular prisms are right prisms with two faces that are N -gons and N square faces (symbol $4^2.N$). The triangular (or *trigonal*) prism should be familiar. It has Schläfli symbol 3.4^2 . Note that the triangular prisms encountered as coordination figures in solids usually have rectangular faces that are not square (see the Note § 5.6.2 at the end of this chapter). A cube is a square prism. The term “prism” is almost invariably used by crystal chemists to mean “right prism” (i.e. that *all* the quadrangular faces are rectangles).

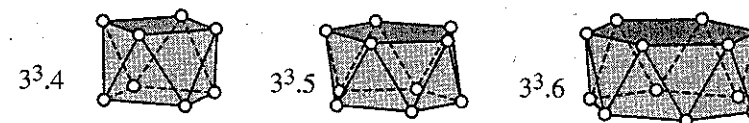


Fig. 5.7. From left to right: a square antiprism ($3^3.4$), a pentagonal antiprism ($3^3.5$) and a hexagonal antiprism ($3^3.6$). Edges obscured by the front faces are shown as broken lines.

Antiprisms conclude the enumeration of the semiregular solids. They have two N -gon

faces and $2N$ triangular ones (symbol $3^3.N$). The regular octahedron is a triangular antiprism. The square antiprism ($3^3.4$), pentagonal antiprism ($3^3.5$) and hexagonal antiprism ($3^3.6$) are illustrated in Fig. 5.7. Note that they have non-crystallographic symmetries (see § 2.5.6, p. 52). The symmetry of a square antiprism is $\bar{8}m2 = D_{4d}$, that of a pentagonal antiprism is $\bar{5}2/m$ (short symbol $\bar{5}m$) = D_{5d} and that of a hexagonal antiprism is $\bar{12}m2 = D_{6d}$.

Sometimes coordination figures (particularly for 6- or 8-coordination) are encountered that are intermediate between prisms and antiprisms. We refer to such solids as *metaprisms*. Fig. 5.8 illustrates the case of 6-coordination. Square metaprisms are also common coordination figures. The symmetry of metaprisms with $2N$ vertices is $N2$ for N odd and $N22$ for N even.

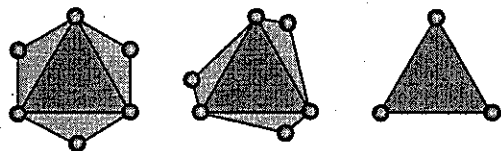


Fig. 5.8. Left: a trigonal antiprism (symmetry $\bar{3}m$) with the bottom face the same as the top one but rotated by 60° . Middle: a trigonal metaprism (symmetry 32) with bottom face the same as the top one but rotated by 30° . Right: a trigonal prism (symmetry $\bar{6}m2$).

The process of adding an extra vertex outside a polyhedron is usually known as *capping*. Examples of particular interest in chemistry are coordination figures obtained by capping the rectangular faces of trigonal prisms. According to whether there are one, two or three such extra vertices, the polyhedra are referred to as monocapped, bicapped or tricapped trigonal prisms respectively. A tricapped trigonal prism is illustrated in Fig. 5.9 in two ways; first as the full polyhedron and secondly with the "capping" vertices treated separately, as is often done for clarity in crystal structure drawings. As already remarked, the rectangular faces are generally not square, but elongated along the direction of the $\bar{6}$ axis. The symmetry is $\bar{6}m2$.

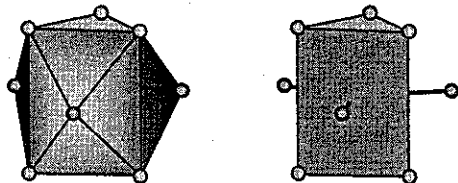


Fig. 5.9. Two illustrations of a tricapped trigonal prism with all distances from the vertices to the center equal and with all edges not parallel to the $\bar{6}$ axis equal.

Capping the two pentagonal faces of a pentagonal antiprism results in an icosahedron.

5.1.5 Catalan polyhedra: the rhombic dodecahedron, bipyramids and pyramids

The *Catalan* solids (named after the Belgian mathematician) are the duals of the Archimedean polyhedra. The Archimedean polyhedra have all *vertices* equivalent, so the Catalan polyhedra have all *faces* equivalent. The Archimedean polyhedra are generally of interest as symmetrical coordination polyhedra, whereas the Catalan polyhedra are more relevant to the external shapes of symmetrical crystals. As our interest is mainly in the internal structure of crystals we only mention here some Catalan polyhedra of special interest.¹

The most interesting to us is the dual of the cuboctahedron. This is the rhombic dodecahedron (Fig. 5.4, p. 137) which has twelve faces that are rhombuses with alternating angles of $\cos^{-1}(-1/3) = 109.47^\circ$ and $\cos^{-1}(1/3) = 70.53^\circ$. The cuboctahedron has 14 faces and 12 vertices whereas the rhombic dodecahedron has 12 faces and 14 vertices. Both polyhedra have 24 edges that are all equivalent in each case. The dihedral angles of the rhombic dodecahedron are thus all the same (and equal to 120°), and it is another a space-filling polyhedron. When packed together to fill space, the polyhedron centers fall on the points of a face-centered cubic lattice. It is the Voronoi polyhedron (Wigner-Seitz cell) of the face-centered cubic lattice.

The duals of the right prisms are the bipyramids. A cube is a special case of a square prism and an octahedron is a square bipyramid. A pyramid is of course half of a bipyramid. Pyramids are self dual (a tetrahedron is a triangular pyramid). The two distinct polyhedra with five vertices are the trigonal bipyramid and the square pyramid; Fig. 5.10.

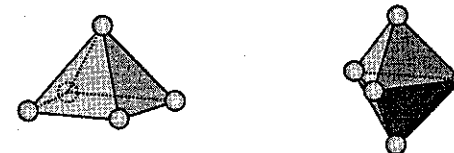


Fig. 5.10. The two polyhedra with five vertices. Left: a square pyramid. Right: a trigonal bipyramid.

5.1.6 Deltahedra and the bisdisphenoid

Another class of polyhedra that we consider in this chapter is that of *deltahedra*. These are convex polyhedra in which all faces are equilateral triangles. Some have been met before. The maximum number of triangles meeting at a vertex is five and the minimum is three. The minimum number of vertices is four (in the regular tetrahedron) and the maximum number is twelve (in the icosahedron). In Table 5.3, V_3 , V_4 and V_5 are the numbers of vertices at which 3, 4 or 5 triangles meet.

¹The Catalan polyhedra are described in detail by Cundy & Rollett (Book List). A good account in the context of crystal shapes is given by J. V. Smith (Book List).

Table 5.3. The eight convex deltahedra

vertices	V_3	V_4	V_5	faces	edges	name
4	4	0	0	4	6	tetrahedron
5	2	3	0	6	9	trigonal bipyramid
6	0	6	0	8	12	octahedron
7	0	5	2	10	15	pentagonal bipyramid
8	0	4	4	12	18	bisdisphenoid
9	0	3	6	14	21	tricapped trigonal prism
10	0	2	8	16	24	bicapped square antiprism
[11?]	0	1?	10?	18?	27?	impossible!]
12	0	0	12	20	30	icosahedron

The reader should observe the regularity of the numbers of vertices, edges and faces, and is invited to prove the impossibility of the deltahedron with eleven faces (not an entirely trivial task). The polyhedron with ten vertices is obtained by capping each of the two square faces of a square antiprism with a square pyramid.

The boron atom skeletons of the *closo* borane anions $B_nH_n^{2-}$ are close to ideal deltahedra for $6 \leq n \leq 12$, except for $n = 11$; however $B_{11}H_{11}^{2-}$ does exist, as a polyhedron with irregular triangular faces in which $V_4 = 2$, $V_5 = 8$, and $V_6 = 1$. The isoelectronic carboranes $B_{n-2}C_2H_n$ are isostructural.

The *bisdisphenoid* is an interesting polyhedron with symmetry $\bar{4}2m$ that is illustrated in Fig. 5.11. We will use this term for dodecahedra (= 12 faces!) with this symmetry even when the faces are not *equilateral* triangles. It is a rather common 8-coordination figure.

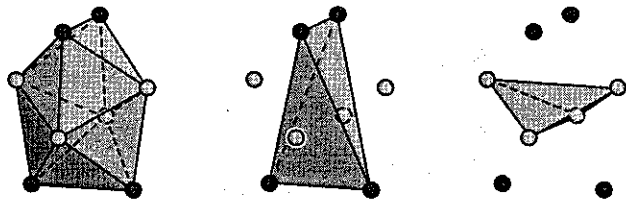


Fig 5.11. Left: A bisdisphenoid. The $\bar{4}$ axis is vertical and the faces are equilateral triangles. In the center and on the right the two sets of four vertices on "elongated" and "squashed" tetrahedra are indicated.

The term *sphenoid* (which comes from the Greek word for a wedge) refers to a figure with inclined planes meeting at an edge. A tetrahedron can be decomposed into two pairs of such sphenoids and is sometimes called a disphenoid. The origin of the term *bisdisphenoid* come from the fact that a bisdisphenoid can be decomposed into two

tetrahedra, one "elongated" and one "squashed" as indicated in Fig. 5.11. It should be apparent that the distance from the vertices of the squashed tetrahedron to the center is less than the distance from the vertices of the elongated tetrahedron to the center. In the bisdisphenoids occurring in crystal structures, the distances from the vertices to the center are often (approximately) equal; the faces can no longer be equilateral triangles in this case.

If we remove the restriction to *convex* polyhedra, there are many other possibilities for deltahedra; one of them is the polyhedron constructed from two inter-penetrating icosahedra (shown in Fig. 5.12) which has six triangles meeting at some of the vertices.

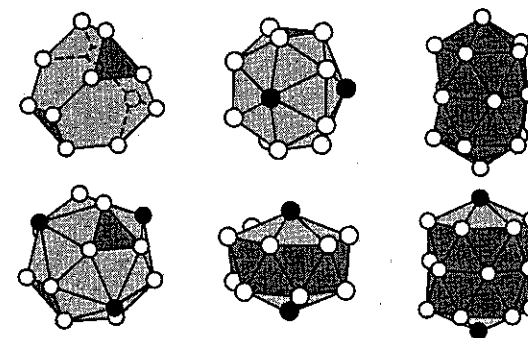


Fig. 5.12. Frank-Kasper and related polyhedra. On the left is shown on the top a truncated tetrahedron and on the bottom the Friauf polyhedron ($V_6 = 4$) obtained by capping the hexagonal faces of the truncated tetrahedron. In the middle on top is shown the 15 vertex polyhedron ($V_6 = 3$) and underneath it is the 14 vertex polyhedron ($V_6 = 2$) obtained by capping the hexagonal faces of a hexagonal antiprism. In these four drawings, 6-coordinated vertices are shown as filled circles and equilateral triangles are darker shaded. On the right are shown top: intergrown icosahedra (capped pentagonal antiprisms) and bottom: intergrown capped hexagonal antiprisms.

5.1.7 Frank-Kasper polyhedra and intergrown polyhedra

If the restriction to equilateral triangles is lifted, there is an infinite number of polyhedra with triangular faces. These are often referred to as *simplicial* polyhedra. Of special interest are those in which either five or six triangles meet at a vertex. Let the number of such vertices be V_5 and V_6 . It is easy to show that $V_5 = 12$ in every case. "Geodesic" domes are parts of such polyhedra. Their duals have faces that are either hexagons or pentagons, and three meet at every vertex; for these latter polyhedra there must be exactly twelve pentagonal faces—see Exercise 6 and Appendix 4.

The *Frank-Kasper* polyhedra (Fig. 5.12) are the four simplest simplicial polyhedra with $V_5 = 12$; they are found as coordination figures in dense intermetallic structures. $V_6 = 0$ corresponds to the icosahedron (12 vertices). As a periodic structure cannot have 5-fold symmetry axes, icosahedra in crystal structures will not be strictly regular, but they often come surprisingly close. The next case, $V_6 = 1$ cannot be realized. The next three

possibilities, $V_6 = 2, 3$, and 4 , can be realized and have $14, 15$, and 16 vertices respectively. They are the only possibilities not having contiguous 6-coordinated vertices. The edges meeting at a 6-coordinated vertex must be longer than the other edges if the polyhedron is to be convex.

The polyhedron with 14 vertices is made from a hexagonal antiprism by capping the hexagonal faces. The polyhedron with 16 vertices is similarly derived from a truncated tetrahedron (3.6^2) and is often called a Friauf polyhedron (it is a conspicuous feature of the structures of the intermetallic phases known as Friauf-Laves phases—see § 6.6.3). The polyhedron with 15 vertices (see Fig. 5.12) has $\bar{6}m2$ symmetry (the same as that of a trigonal prism) and is sometimes called the μ -phase polyhedron (after the structure in which it was first identified). The 16-, 15-, and 14-coordinated polyhedra are sometimes symbolized P, Q , and R respectively.

"Ionic" crystal structures are typified by the fact that generally the coordination of cations is entirely by anions and *vice versa*. These structures can be described in terms of catenated (vertex-, edge-, or face-sharing) coordination polyhedra. It may be recalled, for example, that we described the quartz structure in terms of corner-sharing $\{\text{Si}\}\text{O}_4$ polyhedra in § 3.6. These structures are characterized by generally low coordination numbers (average for all atoms < 8).

On the other hand, in intermetallic structures, coordination numbers are generally higher (≥ 12) and usually include coordination of like atoms by like. If they are to be described in terms of coordination polyhedra such as the polyhedra of this section, it will be found that the polyhedra must interpenetrate each other. Fig. 5.12 illustrates intergrowths of two icosahedra and also of two bicapped hexagonal antiprisms. The vertices in the interior of the intergrowths are (approximately) at the centers of icosahedra and bicapped hexagonal antiprisms respectively, and thus serve as both the *center* of one polyhedron and as the *vertex* of another. In intermetallic crystal structures there is a continuous intergrowth (rather than just the pairs discussed here) which makes such structures particularly difficult to illustrate satisfactorily. In MgCu_2 , for example (§ 6.6.3), there are intergrown $\{\text{Mg}\}\text{Cu}_{12}\text{Mg}_4$ Friauf polyhedra which produce, *mirabile dictu*, for the Cu coordination $\{\text{Cu}\}\text{Mg}_6\text{Cu}_6$ icosahedra.

Simplicial polyhedra can be considered as made up of (irregular) tetrahedra with one vertex at the center and the other three on a face of the polyhedron. In this way, the icosahedron can be decomposed into 20 tetrahedra and the Friauf polyhedron similarly decomposed into 28 tetrahedra. Structures which can be described as a packing of irregular tetrahedra are often described as "topologically close-packed."

5.1.8 Relationships between polyhedra with eight vertices

We mentioned earlier the fact that there are 257 topologically distinct octahedra. Their duals will be the 257 distinct polyhedra with eight vertices.¹ Some other symmetrical arrangements that we have met and that often occur in crystal (and molecular) structures are

¹A complete catalog of polyhedra with ≤ 8 vertices is given by D. Britton & J. D. Dunitz, *Acta Crystallogr. A* 29, 362 (1973).

the cube, square antiprism, bicapped trigonal prism and hexagonal bipyramid. Often in polyhedra representing coordination of a central atom, the distances from the vertex atoms to the central atom are approximately equal, so the vertices are approximately on the surface of a sphere. As the number of vertices increases, conversion from one polyhedron to another will generally involve smaller displacements of vertices. Because 8-coordination is rather common, and the possibilities large, the relationships between the possible coordination polyhedra have been the subject of some discussion.¹ We describe some important cases briefly here.

The relationship between a cube (square prism) and square antiprism should be obvious. The intermediate case, a square metaprisim, with point symmetry 422 , is commonly encountered in crystals.

The relationship between a cube and a hexagonal bipyramid is also very simple. Fig. 5.13 shows a cube viewed down a body diagonal. The six vertices not on the diagonal project as a hexagon; they are in fact on a skew hexagon with 90° angles. Converting these angles to 120° will produce a planar hexagon and the vertices will correspond to a hexagonal bipyramid. The "waist" edges of the hexagonal bipyramids must be shorter than the other edges; if the edges were all equal, the polyhedron would collapse to a two-dimensional figure. The $\{\text{Y}\}\text{O}_8$ coordination in the structure of $\text{Y}_2\text{Ti}_2\text{O}_7$ is an example of coordination intermediate between a hexagonal bipyramid and a cube.

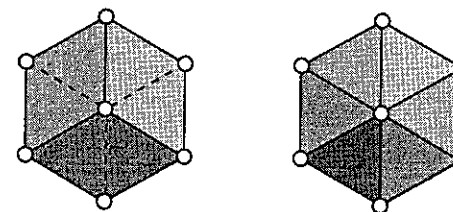


Fig. 5.13. The relationship between a cube and a hexagonal bipyramid.

Less obvious are the relationships between a square antiprism, a bisdisphenoid and a bicapped trigonal prism, but in fact these three polyhedra are very closely related as shown in Fig. 5.14. Converting the two square faces of the antiprism to pairs of triangles produces the topology of the bisdisphenoid and only small displacements of the vertices are necessary to produce $42m$ symmetry. Note that the $\bar{4}$ axis of the bisdisphenoid is parallel to one of the 2-fold axes of the antiprism. Similarly, converting just one of the faces of the square antiprism to a pair of triangles converts it into a bicapped trigonal prism.

The conversion directly from a cube to a bisdisphenoid is also important and should be obvious when it is recalled that the vertices of a cube are the same as the convex vertices of a stella quadrangula (Fig. 5.3) which can be considered as two interpenetrating regular tetrahedra. Converting one of these tetrahedra into a squashed tetrahedron and the other into

¹See especially D. L. Kepert, *Inorganic Stereochemistry* [Springer-Verlag, Berlin (1982)].

an elongated one will produce a bisdisphenoid (compare with Fig. 5.11).

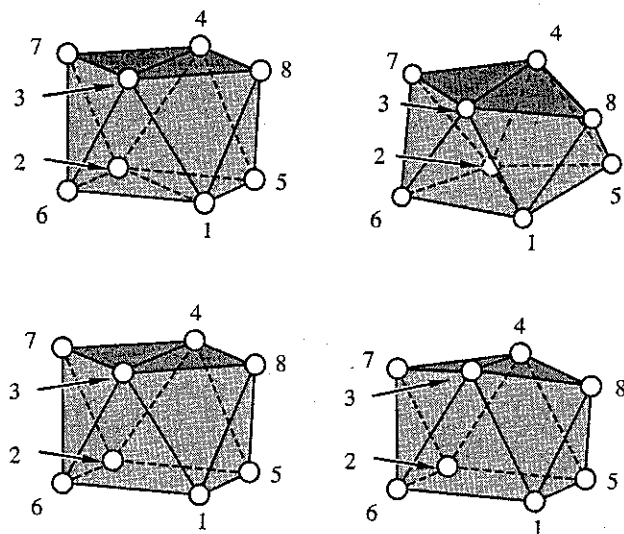


Fig. 5.14. Top: the relationship between a square antiprism (left) and a bisdisphenoid (right). Note that the 4 axis of the bisdisphenoid is horizontal. Bottom: the relationship between a square antiprism (left) and a bicapped trigonal prism (right).

It should be emphasized that, in the context of crystal or molecular structures, the use of polyhedra to describe the positions of atoms is purely for convenience. In a crystal there are only atoms and (less surely) bonds. On the other hand, the salient features of a polyhedron to the eye are its faces (hence the term *polyhedron*) which are really of little importance in the crystal structure.

In particular, to illustrate structural relationships, it is often fruitful to choose one or another polyhedron to describe a particular structure element, and even to describe the same coordination in more than one way. In the garnet structure, Ca is eight coordinated by O and has a site symmetry 222. This symmetry is a subgroup of that of a cube ($m\bar{3}m$), a square metaprisim (422), a bisdisphenoid ($\bar{4}2m$) and a bicapped trigonal prism ($mm2$). It is not surprising therefore, that different authors describe the coordination figure differently [as e.g. a "twisted cube," "distorted square antiprism," or "distorted dodecahedron" (meaning bisdisphenoid)].

5.1.9 Tamme's problem and coordination polyhedra

In his study of pollen grains (which are approximately spherical), the biologist P. M. L.

Tamme concluded that the orifices on their surfaces are arranged so that there is a maximum number, subject to the constraint that the distance between them is not less than some minimum amount. It might be supposed that similar considerations also apply to packing coordinating atoms around a central atom. The mathematical expression of Tamme's problem is to find the arrangement of points on the surface of a sphere so that the shortest distance between pairs of points is as large as possible. Solutions of Tamme's problem, particularly its generalization to arrangements of points in space, are here referred to as *eutactic* arrangements.¹

The general problem is difficult and most results have been obtained numerically.² For four points the solution is provided by the vertices of a regular tetrahedron, and for six points by the vertices of a regular octahedron.

The solution for five points is provided both by the vertices of a trigonal bipyramid and by the vertices of a square pyramid with all edges equal (i.e. half a regular octahedron). Note that in this case the shortest distance is $\sqrt{2}r$, where r is the radius of the sphere; the same result is obtained for an octahedron, so there might as well be six points on the surface of the sphere rather than five.³ It is noteworthy that 4- and 6-coordination are much more commonly found than 5-coordination of cations in crystals. When 5-coordination is found, the square pyramid and trigonal bipyramid occur with comparable frequencies.⁴

For eight points the solution to Tamme's problem is provided by the vertices of an Archimedean square antiprism (not, as is occasionally claimed, a cube). For nine points the figure obtained is that of a tricapped trigonal prism. We may note also that for twelve points the solution to Tamme's problem is provided by the vertices of a regular icosahedron and for 24 points by the vertices of a snub cube ($3^4.4$). See also the Notes (§ 5.6.2) for a discussion of related problems.

5.1.10 Polyhedra with divalent vertices

In the polyhedra considered so far at least three edges meet at a vertex and each pair of contiguous edges (an *angle*) is part of only one face. However for some purposes it is convenient to generalize the concept of polyhedra to include those in which only two edges

¹From the Greek for "well-arranged". We thought that we had invented the word, or rather that it was coined for us by Marie Hyde who knows about such things, but subsequently we found that it had been used earlier by Schläfli in a mathematical context [see H. S. M. Coxeter *Regular Polytopes*, 3rd Edition, Dover, New York (1973) p. 251] and it is in the *Oxford English Dictionary*. As the term has now gained some currency in the sense we use it, it is retained.

²Recent papers with extensive results are B. W. Clare & D. L. Kepert, *Proc. Roy. Soc. (London)* A405, 329 (1986); D. A. Kottwitz, *Acta Crystallogr.* A47, 158 (1991).

³The distances between vertices expressed as multiple of r are: for the trigonal bipyramid, $\sqrt{2}$ ($6\times$) $\sqrt{3}$ ($3\times$) and 2; for the square pyramid, $\sqrt{2}$ ($8\times$) and 2 ($2\times$) and for the octahedron $\sqrt{2}$ ($12\times$) and 2 ($3\times$).

⁴Molecular chemists are used to considering non-bonding valence electrons as well as ligands when discussing coordination figures. Compare PF_5 (trigonal bipyramid, no non-bonding valence electrons) with ClF_5 (square pyramid with the non-bonding electron pair completing an octahedron around Cl). In crystalline PbO Pb has 4 O atoms in a square on one side of Pb with a lone pair completing a square pyramid.

meet at some vertices and the angles containing such vertices are part of two faces. We note two points about such polyhedra: (a) some of the faces are of necessity non-planar if angles of 180° are excluded, and (b) the number of vertices, edges and faces are still related by $V - E + F = 2$. We just give some simple examples here.

Polyhedra with divalent vertices can be derived in a formal way by inserting vertices in edges of conventional polyhedra. In Fig. 5.15 we show how polyhedra with six and eight vertices are derived in this way from a tetrahedron. The new polyhedra are facially-regular and, as there are four faces, they are also tetrahedra. The first (on the left in Fig. 5.15) is encountered as a building unit in the fibrous zeolites (§ 7.8.7); as it has four 4-cornered faces we call it a tetragonal tetrahedron. The second polyhedron (on the right in Fig. 5.15) has four 5-cornered faces so we call it a pentagonal tetrahedron. It occurs in the molecule As_4S_4 (realgar) with 3-coordinated As ($\{\text{As}\}\text{AsS}_2$) and 2-coordinated S ($\{\text{S}\}\text{As}_2$).

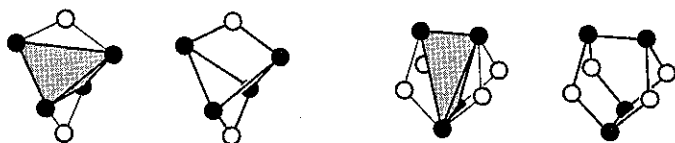


Fig. 5.15. On the left are two drawings of a tetragonal tetrahedron and on the right two drawings of a pentagonal tetrahedron. In each case the right-hand member of the pair shows only the polyhedron edges. Vertices shown as open circles are divalent.

The next polyhedron in the series is a hexagonal tetrahedron with ten vertices shown in Fig. 5.16. This is an important geometry in structural chemistry. If CH_2 units are at the six 2-coordinated vertices, and CH units at the four 3-coordinated vertices, the hydrocarbon *adamantane*, $\text{C}_{10}\text{H}_{16}$ results. If the CH groups are replaced by the isoelectronic N, hexamethylenetetramine, $\text{N}_4(\text{CH}_2)_6$ is produced. P_4O_6 has the same structure.

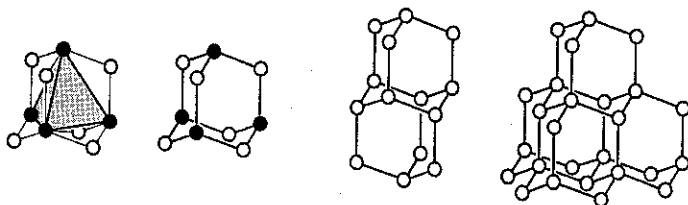


Fig. 5.16. From the left are: two drawings of a hexagonal tetrahedron, two such polyhedra sharing a face, a cluster of five hexagonal tetrahedra. Compare Fig. 5.15.

If a wire model of the hexagonal tetrahedron framework is dipped in a soap solution and withdrawn, the soap film will form a curved surface on the faces of the polyhedron.

Remarkably, such a polyhedron with curved faces is a space-filling solid.¹ In Fig. 5.16 two such tetrahedra are shown sharing a face and also a cluster of five tetrahedra sharing faces.² In fact the structure of vertices and edges obtained by filling space with hexagonal tetrahedra is just that of the atoms and bonds in the diamond form of carbon, and Fig. 5.16 should be compared with Fig. 7.10 illustrating the diamond structure. Much of the interest in polyhedra with divalent vertices is as building units of three-dimensional nets.

Another example of a tetragonal tetrahedron is shown in Fig. 5.17. Four 2-connected vertices are on a square of edge d , and the 4-connected vertices are a distance d apart so that the edge lengths are $\sqrt{2}d/2$. If all vertices were 4-connected the polyhedron would be a squashed octahedron. The figure shows curved surfaces such as might be made by a soap film on the framework. Such a polyhedron is also space-filling (the packing requires three different orientations of the tetrahedra). The vertices are on the points of a body-centered cubic lattice and, as discussed in § 6.2, the centers of the polyhedra are at the "octahedral" sites of a body-centered cubic sphere packing.

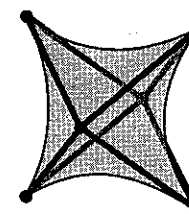


Fig. 5.17. A space-filling tetragonal tetrahedron with curved faces.

5.2 Polyhedral clusters

We are interested in polyhedra because their vertices often represent the positions of atoms coordinating a central one. In this way we can reduce a group, such as $\{M\}X_6$ to a single entity such as an octahedron or a trigonal prism. In many structures it is convenient

¹ Such polyhedra appear to have been first described by P. Pearce in Chapter 8 of *Symmetry in Nature is a Strategy for Design* [MIT Press (1978)]. A beautifully illustrated systematic account of them and their packings is given by S. T. Hyde & S. Andersson, *Zeits. Kristallogr.* **168**, 221 (1984).

² This topic provides an excuse for some free-association historical notes: Hexamethylenetetramine was the first organic compound to have its structure determined by X-ray diffraction [R. G. Dickenson & A. L. Raymond, *J. Amer. Chem. Soc.* **45**, 22 (1923)]. Dickenson was the first person to get a Ph.D. degree from the California Institute of Technology (in 1920); in 1922 he took on a graduate student named Linus Pauling who was to be a major force in structural chemistry for more than the next half century (Nobel prize in Chemistry, 1954). The hydrocarbon corresponding to the two face-sharing polyhedra ($\text{C}_{14}\text{H}_{20}$) is known as *congressane* as its structure served as the emblem of the XIX congress of the International Union of Pure and Applied Chemistry (1963). Its structure was solved "by inspection" from X-ray data by the famous team of I. L. Karle and J. Karle in 1965. J. Karle went on to share the Nobel prize in chemistry with H. Hauptman in 1985 (for the development of "direct methods" of X-ray diffraction analysis).

to continue the process and consider the structural units to be groups (clusters) of polyhedra (which may or may not be centered). This approach allows us to describe the structures of complex crystals in a hierarchical way: we first describe how atoms form coordination polyhedra, then we describe how the polyhedra are assembled into clusters, and finally we describe how the clusters are linked in the crystal. A similar procedure is familiar to molecular chemists who are long used to replacing functional groups (clusters!) such as, for example, $-C_6H_5$ by $-Ph$ and C_5H_5 by Cp .

In this section we describe some simple examples of clusters, that are often found in crystal structures and give some examples of their occurrence.

5.2.1 Clusters of tetrahedra

In § 5.1.2 (Fig. 5.3) we introduced the *stella quadrangula* which may be derived by fusing tetrahedra to the faces of a central tetrahedron, and the *stella octangula* which is similarly derived by capping the faces of a central octahedron with tetrahedra.

The composition of the stella octangula can be written A_6B_8 with the six vertices A forming an octahedron and the eight capping vertices B at the corners of a cube. This is a configuration frequently found in crystal structures. A notable example is as the Mo_6S_8 cluster in $PbMo_6S_8$ (one of the so-called Chevrel phases). The same cluster is often found in Nb and Mo halides; in Nb_6I_{11} , Nb_6I_8 clusters are linked by Nb-I-Nb bonds to produce overall stoichiometry $Nb_6I_8I_{6/2} = Nb_6I_{11}$.

If just four (non-adjacent) faces of an octahedron are capped with tetrahedra a "supertetrahedron" as shown in Fig. 5.18 is produced. If the small tetrahedra are centered by T and the octahedron vertices are X and the capping vertices Y , the stoichiometry is $T_4X_6Y_4$. A molecular example is provided by the molecule $Ge_4S_6Br_4$. These units are also familiar as P_4O_{10} and P_4S_{10} molecules, and as the complex anions $[P_4N_{10}]^{10-}$ in $Li_5P_2N_5$ and $[Si_4S_{10}]^{4-}$ in $Na_2Si_2S_5$.¹

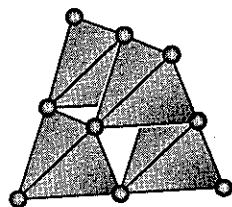


Fig. 5.18. A "supertetrahedron" cluster of four tetrahedra.

Joining supertetrahedra (with $Y = X$) into a three-dimensional network by sharing the four outer vertices results in stoichiometry $T_4X_6X_{4/2} = TX_2$. This is the situation in

¹Note that P_4O_{10} and $[P_4N_{10}]^{10-}$ are isoelectronic as are P_4S_{10} and $[Si_4S_{10}]^{4-}$. In every case there are 80 valence electrons.

compounds such as ZnI_2 and $Be(NH_2)_2$.

Clusters of condensed $\{T\}X_4$ tetrahedra sharing vertices are very common in crystal structures. A pair of such tetrahedra with one common vertex has stoichiometry T_2X_7 , and is found in oxide chemistry (especially, but by no means exclusively) with $T = Si, P$ and S (the compounds are often called pyrosilicates, pyrophosphates and pyrosulfates respectively). It is rare for the $T-X-T$ link to be linear, but an example occurs in the mineral thortveitite, $Sc_2Si_2O_7$. SiP_2O_7 is an elegant example of a structure made of linked $\{Si\}O_6$ octahedra and P_2O_7 double tetrahedra. Cl_2O_7 provides an example of a neutral cluster.

Larger clusters of tetrahedra are also common and we give some examples of their occurrence in silicate minerals. Rings of n tetrahedra sharing vertices (Fig. 5.19) have stoichiometry T_nX_{3n} ; for silicates the cluster has formal charge $[Si_nO_{3n}]^{2n-}$.

Common stoichiometries are $n = 3$ (as in benitoite, $BaTiSi_3O_9$), 4 (as in kinosite, $Ca_2Y_2[Si_4O_{12}](CO_3) \cdot H_2O$) and 6 (as in diopside, $CuSiO_3 \cdot H_2O = Cu_6Si_6O_{18} \cdot 6H_2O$).

Rings of corner-connected tetrahedra are "flexible" and the conformation found is determined in part by the $T-X-T$ angle which usually has a characteristic value for given T and X (about 145° for $Si-O-Si$ and 128° for $Ge-O-Ge$). Fig. 5.19 illustrates some extreme configurations of three-membered and four-membered rings and gives the $T-X-T$ angles for regular tetrahedra. Not surprisingly, three-membered rings are more common for germanates than for silicates. A special case is the linear chain ($n = \infty$) which occurs in many important minerals (such as enstatite, $MgSiO_3$).

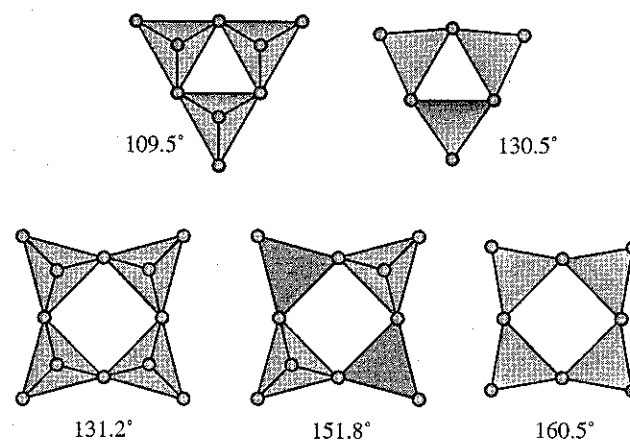


Fig. 5.19. Symmetrical configurations of rings of regular $\{T\}X_4$ tetrahedra. Numbers are $T-X-T$ angles.

Double rings of tetrahedra are also common in silicates. These are made by further corner sharing to produce stoichiometry $T_{2n}X_{5n}$. The $n = 4$ member of this family is obtained by fusing tetrahedra to the eight triangular faces of a cuboctahedron (Fig. 5.20,

middle) so that the T_8 array is a cube. For regular tetrahedra the maximum $T-X-T$ angle is 148.4° . A nice example of the occurrence of this cluster is as $[\text{Si}_8\text{O}_{20}]^{8-}$ units in steacyite, $\text{KNaCaThSi}_8\text{O}_{20}$.

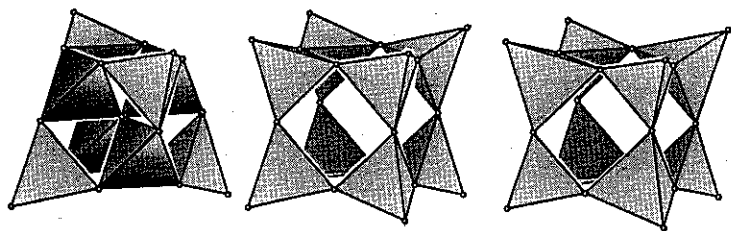


Fig. 5.20. Left: a $T_4T'_4X_{17}$ cluster. Middle: a T_8X_{20} cluster obtained by capping the triangular faces of a cuboctahedron with tetrahedra. Right: a similar cluster with alternating tetrahedra of two different sizes.

Many compounds with vertex-sharing tetrahedra have two (or more) kinds of tetrahedra of different sizes. For example, there known many analogs of silicates with a framework such as AlPO_4 with alternating $[\text{Al}]\text{O}_4$ and $[\text{P}]\text{O}_4$ tetrahedra. It is interesting that if the centers alternate in a $T_4T'_4X_{20}$ cluster as shown on the right in Fig. 5.20, the maximum $T-X-T$ angle is still 148.4° for regular tetrahedra.

A second kind of cluster ($T_4T'_4X_{17}$) of eight vertex-sharing tetrahedra occurs in $\text{Na}_{10}\text{Be}_4\text{Si}_4\text{O}_{17}$. This is shown on the left in Fig. 5.20; the $[\text{Be}]\text{O}_4$ tetrahedra are the inner ones (darker shaded). With regular tetrahedra (which must be congruent) the $T-X-T$ angles are all 109.5° .

With two six-membered rings of tetrahedra, the tetrahedron centers are on the vertices of a hexagonal prism, the corresponding silicate anion is $[\text{Si}_{12}\text{O}_{30}]^{12-}$ which also is found in complex minerals.

Clusters of tetrahedra commonly occur in condensed structures such as zeolite frameworks with overall stoichiometry TX_2 . When describing the topology of such structures, it is common to omit the anions and to represent clusters such as T_8X_{20} and $T_{12}X_{30}$ as cubes and hexagonal prisms respectively, and to describe the structure as a linkage of such units. Examples will be found in Chapter 7.

5.2.2 Clusters of octahedra

Discrete and linked clusters of octahedra are found in great variety in the chemistry of the oxides of the early transition elements (particularly Nb, Mo and W) and we give only a few simple examples of them here. The discrete clusters are usually anionic and referred to as *isopolyanions* if they contain just one kind of metal atom (i.e. one metallic element) and *heteropolyanions* otherwise.¹

¹For a review of such species see D. L. Kepert, Chapter 51 in *Comprehensive Inorganic Chemistry*, Vol. 4. [Pergamon Press, Oxford (1973)].

Face-sharing in extended clusters of centered polyhedra is rather rare, but pairs of octahedra sharing a common face are rather common as anions (e.g. $[\text{W}_2\text{Cl}_9]^{3-}$ with two $\{\text{W}\}\text{Cl}_6$ octahedra sharing a face) and such pairs linked by corners are a conspicuous feature of many structures. Usually in such a group M_2X_9 , the M atoms move "off center" to increase their mutual separation. Such displacements are only possible for pairs, so that longer chains of centered octahedra sharing faces are less common unless the cluster is stabilized by metal-metal bonding through the shared face. The "anti-structure" (with the roles of metal and nonmetal reversed) is found in Rb_9O_2 in which there are pairs of $\{\text{O}\}\text{Rb}_6$ octahedra with metal-metal bonding between the clusters.

The dihedral angle of a regular octahedron is $\cos^{-1}(-1/3) = 109.47^\circ$ so that if three meet at a common edge, there will be a small gap between some of the faces. However three can meet at a common edge with three pairs of adjacent faces shared if the octahedra are distorted to make the angle between shared faces 120° (Fig. 5.21). The stoichiometry is now M_3X_{11} . Such clusters (linked by sharing edges) may be identified in the structure of Nb_3Te_4 . The anti-structure cluster occurs in oxides such as Cs_{11}O_3 and $\text{Rb}_7\text{Cs}_{11}\text{O}_3$.

Edge-sharing pairs of $\{M\}X_6$ octahedra have stoichiometry M_2X_{10} and are rather common as discrete units (e.g. $\text{NbCl}_5 = \text{Nb}_2\text{Cl}_{10}$).

With more than two octahedra joined by edges, the number of distinct topologies rapidly becomes rather large, but generally it is the most condensed (minimum value of X/M) and symmetrical that are of greatest interest.¹

With three octahedra joined by edges there are three possibilities as shown in Fig. 5.21. The first two have stoichiometry M_3X_{14} and the third (on the right in the figure) has stoichiometry M_3X_{13} . This last occurs as, for example, $[\text{Te}_3\text{Cl}_{13}]^-$ and (condensed by further edge sharing) in Nb_3Cl_8 .

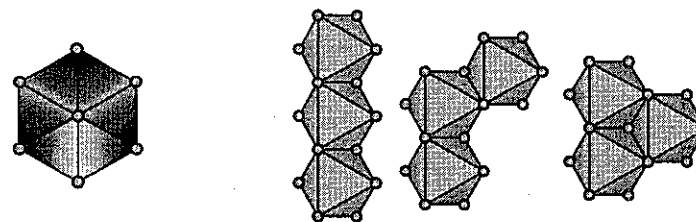


Fig. 5.21. Left: three distorted octahedra sharing faces and a common edge. Right: the three distinct ways of linking three octahedra by sharing edges only.

For four octahedra joined by edges, there are eight possibilities with stoichiometries ranging from M_4X_{18} (five cases), through M_4X_{17} (one case), to M_4X_{16} (two cases). Fig. 5.22 illustrates the two M_4X_{16} isomers. In the first the centers are coplanar, and fall on the vertices of a 60° rhombus, so we call it the rhombic isomer. In the second isomer the centers form a tetrahedron so we call it the tetrahedral isomer. The second cluster can also

¹For a discussion see P. B. Moore, *Amer. Mineral.* 55, 135 (1970).

be described as consisting of four octahedra sharing faces with a central tetrahedron. It is interesting that $\text{Te}_4\text{Cl}_{16}$ has the tetrahedral structure but Te_4I_{16} has the structure of the rhombic isomer [in these clusters Te is "off center" in the octahedron to give a 3 + 3 coordination often found for Te(IV) compounds]. The tetrahedral group is also found as the anion $[\text{W}_4\text{O}_{16}]^{8-}$.

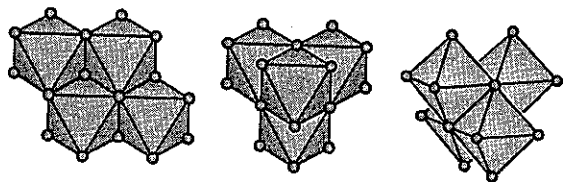


Fig. 5.22. The two T_4X_{16} clusters of four edge-sharing octahedra. Left the rhombic isomer. Center and right: two views of the tetrahedral isomer.

The M_4X_{16} unit may be linked by tetrahedra in three mutually perpendicular directions to give a cubic $M_4T_3X_{16}$ framework as shown in Fig. 5.23. Examples of compounds with structures based on this framework are $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{12}$ ($M = \text{Mo}$, $T = \text{P}$) and minerals of the pharmacosiderite family such as $\text{BaM}_4\text{As}_3\text{O}_{12}(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ ($M = \text{Al}$ or Fe , $T = \text{As}$), and $\text{K}_3\text{Ge}_7\text{O}_{15}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ (with $M = \text{viGe}$ and $T = \text{ivGe}$).

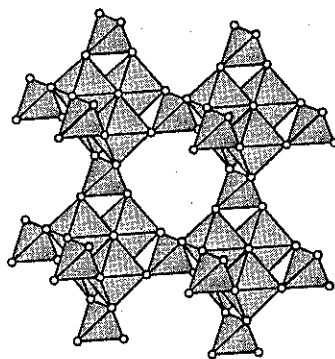


Fig. 5.23. A part of the M_7X_{16} framework of pharmacosiderite.

In Fig. 5.24 we illustrate the most symmetrical and condensed cluster of six edge-sharing octahedra with stoichiometry M_6X_{19} which we call, for reasons that should be obvious, a "superoctahedron." This is found as the anion $[\text{Mo}_6\text{O}_{19}]^{2-}$. Also shown in the figure is a five octahedron cluster M_5X_{18} which is also a common anion configuration. Two of the five-octahedron clusters can condense by sharing four vertices to produce the configuration found in the $[\text{W}_{10}\text{O}_{32}]^{4-}$ ion. Clearly the possibilities are endless.

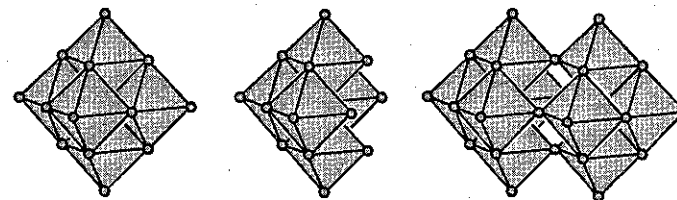


Fig. 5.24. Left: A "superoctahedron" M_6X_{19} . Center: a cluster M_5X_{18} . Right: a cluster $M_{10}X_{32}$.

The structure of Nb_2F_5 is a nice example of a three-dimensional structure built up from superoctahedra (for crystallographic data see Appendix 5). In this instance the central anion is missing so there are $\{\text{Nb}\}\text{F}_5$ square pyramids and we really have a cluster of six square pyramids (Fig. 5.25). The cluster composition is $\text{Nb}_6\text{F}_{12}\text{F}'_6$ where F' is on the outer vertices of the superoctahedron. Sharing these outer vertices produces an open three dimensional network of corner-connected clusters with composition $\text{Nb}_6\text{F}_{12}\text{F}'_{6/2} = \text{Nb}_6\text{F}_{15}$. The formula is usually given as Nb_6F_{15} (rather than Nb_2F_5) to emphasize the presence of Nb_6 groups in the structure.

To finish the description of this beautiful structure we note that the topology of the corner-connected network of (super) octahedra is that of ReO_3 (see p. 170) and in Nb_2F_5 , two such networks interpenetrate. Fig. 5.25 shows a fragment of one network.

Three points concerning this structure might be noted: (a) the Nb atoms form an empty Nb_6 octahedron, a very common feature of the chemistry of niobium in lower oxidation states, (b) we describe the Nb_6F_{12} part of the cluster as an edge-capped octahedron cluster in § 5.2.4, and (c) the F atoms and the sites (empty) at the center of the Nb_6 octahedra combine to form **cep** (§ 6.1.3).

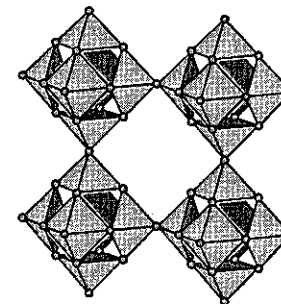


Fig. 5.25. Four of the corner-connected clusters of square pyramids in the Nb_6F_{15} structure.

Frameworks of vertex-sharing octahedra with stoichiometry $\text{MX}_{6/2} = \text{MX}_3$ are rather important, and some will be discussed in § 5.3.4 and in Chapter 6. Here we call attention

to a finite group, which may be considered as composed of four octahedra sharing non-contiguous faces of a central octahedron. In Chapter 6 we call this a "pyrochlore" unit; it is illustrated in Fig. 5.26. (Compare the supertetrahedron, Fig. 5.18.) As the dihedral angle of an octahedron is 109.48° , the angle between the unshared faces of the outer octahedra and the adjacent face of the empty octahedron is $360^\circ - 2 \times 109.48^\circ = 141.04^\circ$; which is close to the dihedral angle of a regular icosahedron (138.18°). This means that if the remaining four faces of the central octahedron of the pyrochlore unit are capped with icosahedra, the assembly will fit together rather snugly. Such units are an important feature of some intermetallic structure types (with the icosahedra and octahedra very slightly distorted so that they have common vertices).

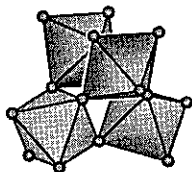


Fig. 5.26. The "pyrochlore unit" of four vertex-sharing octahedra.

Finally, if three regular octahedra share a common vertex, but without edge sharing, the shortest inter-octahedron distance between vertices is, of necessity, less than the octahedron edge length. Such configurations occur in the structure of compounds such as pyrite, FeS_2 . In this structure $\{\text{Fe}\}\text{S}_6$ octahedra have all their vertices shared in this way (so the stoichiometry is $\text{FeS}_{6/3}$) and the short distances correspond to S-S bonds. The octahedron edge lengths are $\text{S}\cdots\text{S} = 3.07$ and 3.32 \AA and the S-S bond length is 2.18 \AA . Fig. 5.27 illustrates a fragment of the structure (for crystallographic data see Appendix 5).

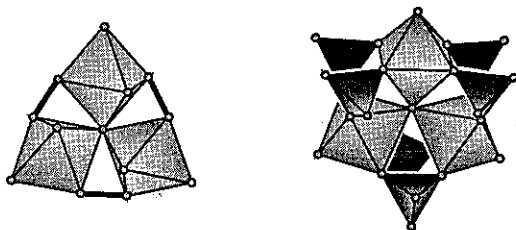


Fig. 5.27. Left: fragment of the pyrite, FeS_2 , structure showing three $\{\text{Fe}\}\text{S}_6$ octahedra with a common vertex. Heavy lines represent S-S bonds. Right: the anion in Maus's salt shown as $\{\text{Fe}\}\text{O}_6$ octahedra and $\{\text{S}\}\text{O}_4$ tetrahedra.

Another example of three octahedra sharing a common vertex is provided by the complex anion $\text{Fe}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3^{5-}$ (also shown in Fig. 5.27) which occurs in the mineral

metavoltine and in the compounds known as Maus's salts.¹ The $\{\text{Fe}\}\text{O}_6$ octahedra are fairly regular with edge lengths of 2.73 – 2.90 \AA . The edge lengths in the $\{\text{S}\}\text{O}_4$ tetrahedron range from 2.31 – 2.37 \AA .

5.2.3 Octahedra plus tetrahedra: Keggin and spinel units

There are very many niobates, molybdates and tungstates (and some other related oxides) of various dimensionalities that can be described as assemblies of $\{M\}\text{O}_4$ tetrahedra and $\{M\}\text{O}_6$ octahedra. An adequate description of all known structures would require a rather large book. Here we describe two particularly interesting clusters involving four groups each of three edge-sharing octahedra about a central tetrahedron.

First we examine the M_3X_{13} cluster of Fig. 5.21 a little more closely. The cluster has symmetry $3m$ which means that the two faces normal to the 3 axis are different, and have 3-fold symmetry as illustrated in Fig. 5.28.

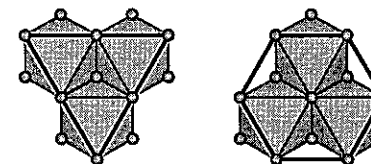


Fig. 5.28. Two views of the M_3X_{13} cluster in projection down the 3 axis.

Examination of the figure will show (on the right) that one face of the cluster consists of a centered hexagon of vertices, so that the cluster can cap hexagonal faces of a polyhedron, but as the symmetry is only 3-fold this can be done in two different ways. The clusters we now consider involve capping of the hexagonal faces of a truncated tetrahedron.

In the first case, the clusters of three octahedra share vertices with each other, to form stoichiometry $M_{12}X_{40}$. In this structure, shown in Fig. 5.29, four central X atoms form a tetrahedron which can be centered by a T atom to give stoichiometry $M_{12}TX_{40}$.

This unit is usually named after J. F. Keggin who first determined the structure of phosphotungstic acid which contains a $[\text{W}_{12}\text{PO}_{40}]^{3-}$ group.² The same grouping has been

¹These have the general formula $M_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot n\text{H}_2\text{O}$ with $M = \text{Li, Na, K, Rb, Cs, NH}_4$ and Ti . Those who object to trivial names might note that *Structure Reports* lists the anion under the heading "triaquo- μ_3 -oxo-hexa- μ -sulphato-triferrate(III) dihydrate."

²This was done by X-ray diffraction in 1934 and was a remarkable *tour de force* for the time; locating light atoms (O) in the presence of heavy atoms (W) is difficult even with the greatly improved equipment available today. The formula for phosphotungstic acid is $\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 6\text{H}_2\text{O}$ but it is perhaps better written $(\text{H}_5\text{O}_2)_3\text{W}_{12}\text{PO}_{40}$ as it contains H_5O_2^+ groups. These provide a rare example of a symmetrical (linear) hydrogen bond $\text{O}-\text{H}\cdots\text{O}$, linking two water molecules, with $d(\text{O}-\text{H}) = 1.21 \text{ \AA}$ [G. M. Brown *et al.* *Acta Crystallogr.* B33, 1038 (1977)]. The record in 1995 for cluster size appears to be a remarkable toroidal oxoanion with approximate 7-fold rotation symmetry and containing 154 Mo atoms [A. Müller *et al.*, *Angew. Chem. Int. Ed. Engl.* 34, 2122 (1995)].

identified in numerous anions, particularly with $M = \text{Mo}$ or W and with $T = \text{P}$, As or Si . The M atoms are at the vertices of a cuboctahedron. The complex mineral zunyite contains condensed $\text{Al}_{13}\text{O}_{40}$ units with the same structure, and the O_{40} arrangement also serves as structural units in some complex intermetallic structures.

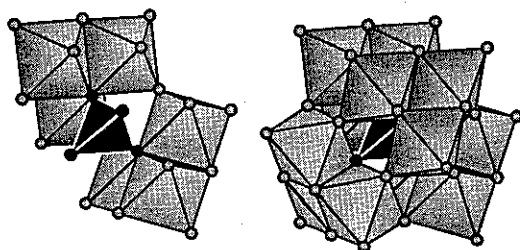


Fig. 5.29. The Keggin cluster, $M_{12}TX_{40}$. On the left only six of the twelve octahedra are shown. Compare Fig. 5.30.

If the three-octahedron units of the Keggin structure are rotated by 60° , they are then joined by edge sharing in the more compact cluster shown in Fig. 5.30. The M atoms are now at the vertices of a truncated tetrahedron. We call this structure, which has the same stoichiometry as the Keggin structure, a "spinel unit" because the important spinel (MgAl_2O_4) structure can be considered as made up of a condensation of such units. Partly hydrolyzed Al salts have been found to contain $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ units with this structure. It is of interest that dehydration of hydrous alumina at low temperatures produces so-called " γ -alumina" (used as a polishing powder) which has a spinel-related structure.

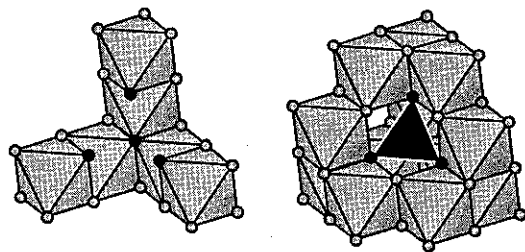


Fig. 5.30. The "spinel cluster." On the left only six of twelve octahedra are shown. Compare Fig. 5.29.

5.2.4 Edge-capped clusters

Capping the *edges* of polyhedra with additional vertices produces what can be considered as clusters made of polyhedra and *triangles*. We can generate many useful groupings in this way. Recall that in § 5.1.10 we derived polyhedra with divalent vertices

by edge-capping polyhedra (tetrahedra).

Capping the six edges of an A_4 tetrahedron with B produces a cluster A_4B_6 . This is shown in two ways in Fig. 5.31, first as an edge-capped tetrahedron, and second as a B_6 octahedron with A centering four of the faces. The latter emphasizes the triangular coordination of A by B . An example of its occurrence is as the Cu_4S_6 grouping in complex anions such as $[\text{Cu}_4(\text{SPh})_6]^{2-}$.

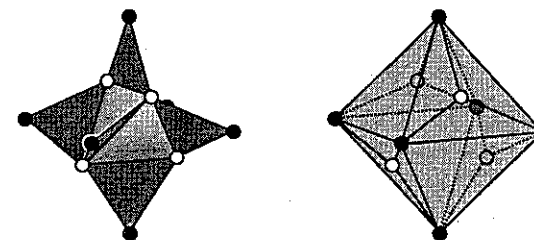


Fig. 5.31. Two views of an edge-capped tetrahedron.

Our second example is obtained by capping the edges of an M_6 octahedron with X atoms to produce stoichiometry M_6X_{12} as shown in Fig. 5.32. In the figure, the capping vertices have been placed so that M is in square planar coordination by X . This grouping is very common in the halides of early transition metals, both as neutral molecules (as in $\text{PtCl}_2 = \text{Pt}_6\text{Cl}_{12}$) and as complex cations (as in $[\text{Nb}_6\text{Cl}_{12}]^{n+}$, $n = 2, 3, 4$). A similar cluster, but with more nearly equilateral triangles, forms the basis of an elegant description of the Mn_5Si_3 structure in which Mn_6 octahedra share opposite faces to form columns and the non-shared edges (six per octahedron) are capped by further Mn.

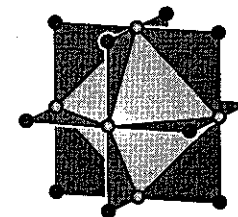


Fig. 5.32. An edge-capped octahedron.

As a final example of edge-capping we describe the build-up of the structural unit of γ -brass (Cu_5Zn_8). In Fig. 5.33 where we start (top left) with a Zn_4 tetrahedron and cap its faces with Cu (at the vertices of an "outer tetrahedron") to produce a Cu_4Zn_4 stella quadrangula. Next (top right) we cap the six edges of the Zn_4 tetrahedron with Cu (at the vertices of an octahedron) to produce the cluster $\text{Cu}_{10}\text{Zn}_4$. Finally (bottom left) we cap the

12 outer edges of the stella quadrangula with Zn arriving at a cluster $\text{Cu}_{10}\text{Zn}_{16}$. The crystal structure is made up of a body-centered cubic array of such discrete clusters. It might be noted that the 12 outer Zn atoms are at the vertices of a distorted cuboctahedron (bottom right in the figure) with four small and four large equilateral triangle faces; the remaining faces are rectangular instead of square. Such a distorted cuboctahedron (with tetrahedral = $43m$ symmetry) is met in other intermetallic structures (see e.g. Fig. 6.77, § 6.8.6).

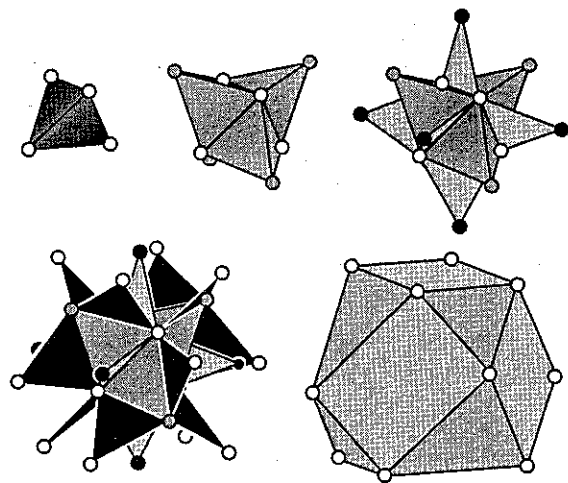


Fig. 5.33. Build-up of the gamma brass structure (see text).

5.2.5 Clusters of truncated tetrahedra and icosahedra

Some complex crystal structures (with over a thousand atoms per unit cell in some instances) can be decomposed into clusters of truncated tetrahedra and/or icosahedra.¹ We describe one relatively simple structure to illustrate the kind of groupings found.

The dihedral angle between the hexagonal faces of a truncated tetrahedron is the same as that of a regular tetrahedron [$\cos^{-1}(1/3) = 70.53^\circ$] so with just a minor distortion a group of five can share faces around a common edge (Fig. 5.34). We mentioned above that an icosahedron can be considered as made up of twenty tetrahedra with a common vertex (the center of the icosahedron). The tetrahedra have three edges of d (the edges of the

¹For beautifully illustrated descriptions of these structures in terms of clusters of truncated tetrahedra and icosahedra, see S. Samson in (a) *Developments in the Structural Chemistry of Alloy Phases*, B. C. Giessen, ed. Plenum Press, New York (1969); (b) *Structural Chemistry and Molecular Biology*, W. H. Freeman, San Francisco (1968). For alternative descriptions see also S. Andersson in *Structure and Bonding in Crystals*, M. O'Keeffe & A. Navrotsky, eds. Vol 2. Academic Press, New York (1981) and B. Chabot, K. Czuczal & E. Parthé, *Acta Crystallogr.* A37, 6 (1981).

icosahedron) and three of $0.95d$ (the distance from the center of the icosahedron to one of its vertices). Perhaps less obvious is the fact that twenty truncated tetrahedra will fit around a central icosahedron of edge d if nine of its eighteen edges are d and nine are $0.95d$. Fig. 5.35 shows an icosahedron sharing a triangular face with a truncated tetrahedron. The longer edges of the truncated tetrahedron are those of the shared face and the opposite hexagon.

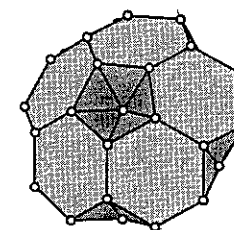


Fig. 5.34. A pentagonal cluster of five truncated tetrahedra

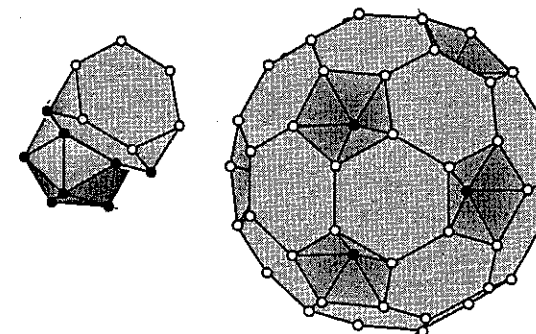


Fig. 5.35. Left: a truncated tetrahedron and an icosahedron sharing a face. Right: twenty truncated tetrahedra around a central icosahedron.

Figure 5.35 also shows the complete assembly of twenty truncated tetrahedra sharing faces with a central icosahedron. The twenty hexagonal faces form a regular truncated icosahedron. The pentagonal faces of the truncated icosahedron are capped on the inside producing depressions that are pentagonal pyramids. The cluster so far described contains 84 vertices (12 for the central icosahedron, 60 vertices of the truncated icosahedron and the 12 apices of the pentagonal pyramids).

This unit occurs in a number of intermetallic compounds (some approximate compositions are $\text{Li}_3\text{Al}_5\text{Cu}$, $\text{Na}_2\text{Au}_3\text{Sn}$ and $\text{Li}_2\text{Zn}_3\text{Ga}$) with the icosahedron and the 20 truncated tetrahedra centered, so the cluster now contains 105 atoms. To build up the

crystal structure, the truncated icosahedron unit is put inside a truncated octahedron so that eight of the hexagonal faces of the truncated icosahedron are coplanar with the (larger) hexagonal faces of the truncated octahedron as shown on the left in Fig. 5.36. The resulting unit (shown on the right in the figure) can now be packed to fill space with their centers on a body-centered cubic lattice (see § 7.3.10 for a discussion of space filling by truncated octahedra). To count atoms in the unit cell, note that there are two units per unit cell and that 48 atoms (those in the hexagonal faces of the truncated octahedron) of each 105 atom cluster are common to two units. Accordingly the number of atoms in the unit cell is $2 \times (105 - 48/2) = 162$.

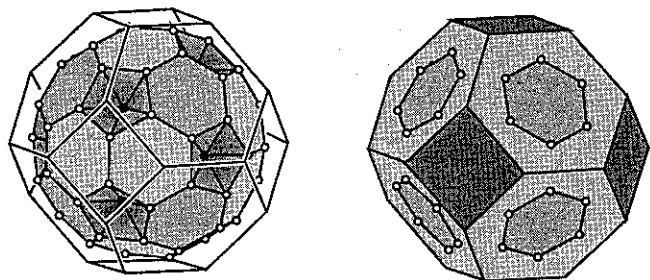


Fig. 5.36. Illustrating how a truncated icosahedron fits into a truncated octahedron with 48 of its vertices in the hexagonal faces of the truncated octahedron.

Note that in increasing distance from the atom at the center of the cluster: this central atom has 12 neighbors at the vertices of the central icosahedron, 20 at the vertices of a pentagonal dodecahedron (these correspond to the centers of the truncated tetrahedra), 12 more at the vertices of a larger icosahedron (the apices of the pentagonal pyramids), and 60 at the vertices of the truncated icosahedron: all fitted into a truncated octahedron which is a space filling solid.¹

Of course in analyzing this fascinating structure more completely we would have to inquire into the coordinations of all the atoms. It transpires that the near neighbors of each atom fall at the vertices of one of the Frank-Kasper polyhedra.

The icosahedron is also a conspicuous feature of the structures of elemental boron and boron-rich compounds. The most stable form of the element is the so called “ β -rhombohedral boron” which contains 105 atoms in the primitive cell. The truncated icosahedron appears in this structure also. Fig 5.37 shows a central B_{12} icosahedral unit joined to twelve B_6 pentagonal pyramids to give a B_{84} unit.

¹How Kepler would have loved this structure! His concept of nested polyhedra, which so deluded him about the sizes of planetary orbits, perhaps comes into its own here. We can't resist quoting [A. Koestler's translation in *The Sleep Walkers*, MacMillan, New York (1959)] from Kepler's *Mysterium Cosmographicum*: “I saw one symmetrical solid after another fit in so precisely between the appropriate orbits, that if a peasant were to ask you on what kind of hook the heavens are fastened so that they don't fall down, it will be easy for you to answer him.” Substitute “atoms” for “heavens.”

If an icosahedron is cut in half through a plane normal to a five-fold axis, the six vertices of each half will form a pentagonal pyramid. In this sense a pentagonal pyramid is half of an icosahedron. In β -rhombohedral boron each B_{84} cluster (one per primitive cell) is joined to six others by making additional icosahedra from a juxtaposition of pentagonal prisms of the neighboring B_{84} units. The other six pentagonal prisms (around a waist of the cluster) are united with B_{21} units (also one per primitive cell) constructed from two sets of three face-sharing pentagonal pyramids (B_{10} groups—see Fig. 5.37) and one additional atom. The central icosahedron is therefore surrounded by an icosahedron of icosahedra.

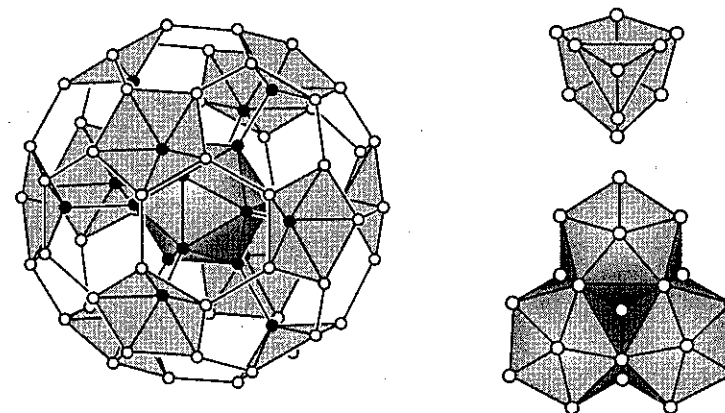


Fig. 5.37. Left: the B_{84} cluster in β -rhombohedral boron. Top right: a B_{10} group made from three face-sharing pentagonal pyramids. The B_{21} group in β rhombohedral boron is made from two B_{10} groups united by an atom at a center of symmetry. Bottom right: a B_{28} cluster of three face-sharing icosahedra formed when the B_{10} group is capped by pentagonal pyramids (one from each of three different B_{84} clusters).

Note that although the structure of β -rhombohedral boron is usually described in terms of linked and face-sharing icosahedra, the B_{84} cluster also contains 20 truncated tetrahedra as shown in Fig. 5.35.

It is remarkable that so stable an element (its heat of atomization is second only to that of carbon among non-metallic elements) should have so complex a structure—there are 15 crystallographically-distinct B atoms. Boron also has a simpler structure (known as α -rhombohedral boron) in which all the atoms are at vertices of icosahedra.

5.3 Circle packings and tilings of the plane

An extremum problem of interest in crystal chemistry is related to the problem of “points on a sphere” mentioned above (§ 5.1.9). It can be stated in the following way: What is the arrangement of non-overlapping equal circles on a plane such that the greatest possible

fraction of the area of the plane is covered; i.e. what is the closest circle packing?

The answer is familiar to anyone who has played with arranging coins on a table top. Each circle is in contact with six others and their centers are at the points of a hexagonal lattice. Equivalently we may say that the centers lie on a 3^6 net. If the circles have radius r , then their area is πr^2 per circle; the edge of the hexagonal cell is $2r$ and its area is $(\sqrt{3}/2)(2r)^2$. Thus the fraction of the plane covered is (area of circle/area of unit cell) = $\pi/\sqrt{12} = 0.907$.

In anticipation of similar questions in three dimensions we may also ask about circle packings in general. We define a *stable* circle packing to be one in which each circle has at least three neighbors, with the points of contact not all on the same semicircle. We direct attention first to arrangements of *equivalent* circles (i.e. related by a symmetry operation).

By a *tiling* of the plane we mean a covering of the plane, by (not necessarily convex) pieces or *tiles*. Our interest is mainly in periodic tilings by convex polygons (i.e. polygons with all interior angles $< 180^\circ$). In the context of crystal structures, the vertices of a tiling correspond to atoms and the edges (sometimes) correspond to bonds between atoms. The pattern of vertices and edges of a tiling is often called a *net*, especially when the emphasis is on the topology of the structure. We tend to use the term "net" and "tiling" (or "tessellation") interchangeably in referring to two-dimensional structures. We have earlier¹ given a comprehensive account of two-dimensional nets; in this chapter (only) we refer in several places to that work as *OKH* for brevity.

5.3.1 Regular tilings

The sequence 3^3 , 3^4 , 3^5 of regular polyhedra with equilateral triangles as faces leads to a consideration of the pattern 3^6 . Six such triangles meeting at a vertex will lie in a plane (the sum of the vertex angles is 360°) and in fact we arrive at the tiling of the plane with equilateral triangles discussed above. Thus a tiling of a plane can be considered a special case of a polyhedron in which the sum of the angles at each vertex is 360° .

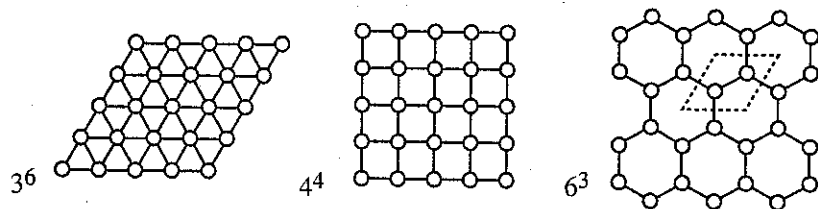


Fig. 5.38. The regular tilings 3^6 , 4^4 and 6^3 . Broken lines outline a unit cell of 6^3 .

It should be apparent from a consideration of the possibilities that the only regular tilings are 3^6 , 4^4 and 6^3 . These are illustrated in Fig. 5.38. Note that 3^6 corresponds to a

hexagonal lattice, and that 4^4 corresponds to a square lattice. The vertices of 6^3 , which we have called the honeycomb pattern, do not form a lattice as there are two points in a primitive cell (Fig. 5.38). The dual of 3^6 is 6^3 and *vice versa* and 4^4 is self dual.

5.3.2 Archimedean tilings

Tilings with one kind of vertex, but more than one kind of regular polygon as tile, are called Archimedean, or semi-regular, by analogy with the names used for finite polyhedra. The eight possibilities are listed in Table 5.4 and illustrated in Fig. 5.39. In the table v , e , and f are the number of vertices, edges and faces per unit cell (it is a good exercise to verify these numbers from the drawings). These quantities are related by $v - e + f = 0$. Also listed in the table is the density (fraction of the plane covered) of the circle packing obtained by placing equal circles in contact and with their centers at the vertices (another good exercise is to verify these also).

Table 5.4. The Archimedean tilings. v , e and f are the numbers of vertices, edges and faces (polygons) per unit cell.

symbol	symmetry	v	e	f	density
$3^4.6$	$p6$	6	15	9	0.7773
$3^3.4^2$	$c2mm$	4	10	6	0.8418
$3^2.4.3.4$	$p4gm$	4	10	6	0.8418
$3.4.6.4$	$p6mm$	6	12	6	0.7290
$3.6.3.6$	$p6mm$	3	6	3	0.6802
4.8^2	$p4mm$	4	6	2	0.5390
3.12^2	$p6mm$	6	9	3	0.3907
$4.6.12$	$p6mm$	12	18	6	0.4860

Some properties of these patterns that are of interest are mentioned here. $3^4.6$ exists in enantiomorphic forms (recall the polyhedra $3^4.4$ and $3^4.5$ with the same property). $3.6.3.6$ has all edges equivalent so it is quasiregular (recall the quasiregular polyhedra $3.4.3.4$ and $3.5.3.5$). The honeycomb, 6^3 , can be derived from 3^6 by removing $1/3$ of the vertices (centering the hexagons in 6^3 recovers 3^6). In a similar manner $3.6.3.6$ can be derived from 3^6 by removing $1/4$ of the vertices, and $3^4.6$ can be derived from 3^6 by omitting $1/7$ of the vertices.

The duals of the Archimedean tilings are tilings of the plane with one kind of (irregular) tile and more than one kind of vertex.

Tilings with one kind of vertex and composed of polygons with equal edges correspond to packings of equivalent (i.e. symmetry-related) circles. As the above list (combined with the regular tilings) is complete, we can immediately answer questions such as "Which is the least dense such circle packing?" Answer: 3.12^2 . Unfortunately Nature is not so kind in

¹M. O'Keeffe & B. G. Hyde, *Phil. Trans. Roy. Soc. (London)* A295, 553 (1980).

simply providing the answers to similar questions (now concerning *sphere* packings) in three dimensions.

We will find $3^2.4.3.4$, $3.6.3.6$, $3.4.6.4$, and 4.8^2 particularly useful in describing the patterns of layers of atoms in crystal structures and 4.8^2 and $4.6.12$ figure prominently in the derivation of three-dimensional nets in Chapter 7. We met $3.6.3.6$ in Chapter 1, where it was called the kagome pattern. $3.4.6.4$ is often called HTB as explained in § 5.3.4.

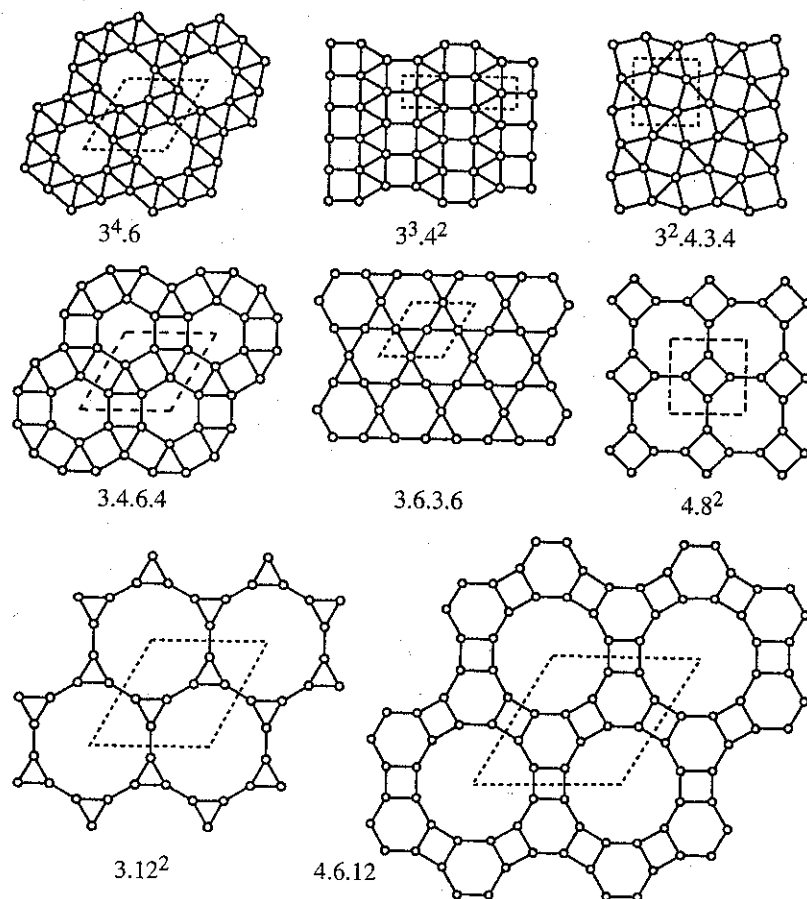


Fig. 5.39. The Archimedean tilings. Top row: $3^4.6$, $3^3.4^2$ and $3^2.4.3.4$. Middle row: $3.4.6.4$, $3.6.3.6$ and 4.8^2 . Bottom row: 3.12^2 and $4.6.12$. Unit cells are outlined with broken lines.

5.3.3 Relationships between tilings

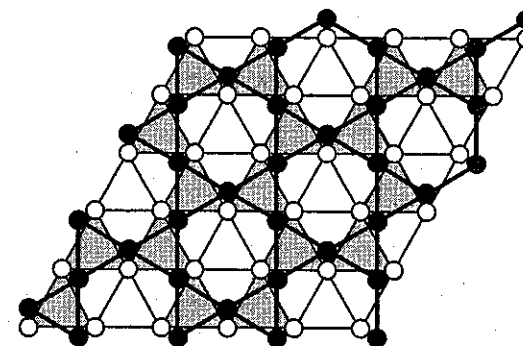


Fig. 5.40. Illustrating how $3.6.3.6$ (filled circles) can be transformed into 3^6 (open circles) and *vice versa*. Note how 3^6 is obtained by rotation (by 30°) and dilation (by 15%) of the sides of the triangles of $3.6.3.6$ (shown as lightly shaded in 3^6). The numbers of open and filled circles in the diagram are the same.

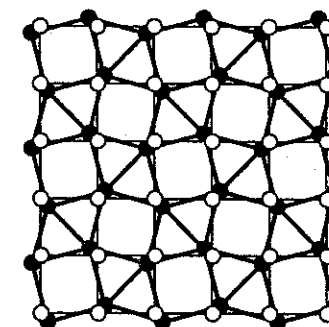


Fig. 5.41. Illustrating how $3^2.4.3.4$ (filled circles) can be transformed into 4^4 (open circles) and *vice versa*. 4^4 is obtained by rotating (by 15°) the squares of $3^2.4.3.4$, or alternatively by converting pairs of triangles (rhombuses) to squares. The numbers of open and filled circles in the diagram are the same.

It is of interest that the arrangement $3^3.4^2$ (to take an example) can be continuously deformed to an arrangement with density arbitrarily close to that of 3^6 (which has the highest possible density) while keeping five neighbors.¹ For this reason the interesting question is usually that of finding the *least* density for a given number of neighbors (coordination number). It is a common mistake when considering the analogous problem of

¹We will see other examples of these kinds of transformation later (Chapter 6). The present one is accomplished by shearing every second layer of $3^3.4^2$ so that the squares are transformed into rhombuses.

packing spheres in three dimensions to ask for the maximum density for a given number of neighbors, whereas, for similar reasons, it is the least-dense arrangement that is of interest.

Fig 5.40 shows, for example, how 3.6.3.6 (the least dense packing of equivalent circles with four neighbors, see Table 5.4, p. 165) which we met in Chapter 1, transforms to 3^6 (the densest packing of equivalent circles). This transformation, which can be effected by rotating triangular groups of vertices, will be found to occur in sequences of related crystal structures.

Another transformation of importance relates 4^4 and $3^2.4.3.4$. Now square groups of vertices are rotated as shown in Fig. 5.41.

We have seen (§ 2.5.7, p. 53) that converting a square to a pair of triangles transforms the polyhedron 3.4.4.4 (i.e. 3.4^3) to $3^4.4$, and transforms the polyhedron 3.4.5.4, to $3^4.5$. The same operation converts the plane tiling 3.4.6.4 to $3^4.6$. (see Fig. 5.72, p. 201). These three transformations can equally be described by rotations of a polygon (square, pentagon and hexagon respectively). We return to this topic in the Notes (§ 5.6.12).

5.3.4 Tilings including pentagons, and "bronzes"

The plane cannot be tiled with regular pentagons or with combinations of regular pentagons and other regular polygons. However it can *almost* be covered with regular pentagons, squares and triangles and this is good enough for nature, if not for mathematicians. Fig. 5.42 shows, at the top, two such packings that almost cover the plane (in the pattern on the left 96% of the plane is covered). At the bottom are tilings with irregular polygons derived in an obvious way from these arrangements. There are two kinds of vertex in each pattern. At the first, a 3-gon, a 4-gon and two 5-gons meet; if these were regular polygons the sum of the angles would be 366° , larger than 360° by six degrees. At the second kind of vertex, two 3-gons and two 5-gons meet and now the sum of angles for regular polygons is 336° , smaller than 360° by 24° . As the two kinds of vertex occur in the ratio 4:1, the sum of the excesses for the first vertices equals the sum of the deficits for the second vertices. This is a useful general rule that allows us to see what combination of vertices, and in what proportion, might occur in a tiling.

The tilings shown in Fig. 5.42 occur in a variety of contexts. The one on the left, which has symmetry $c2mm$, we call the $\beta\text{-U}_3\text{O}_8$ net because of its occurrence as an O net in that compound (it also occurs as atom layers in intermetallic compounds). This net can serve as the "parent" of a large number of derived triangle-quadrangle-pentagon nets (see OKH, § 10). The tiling on the right, which has symmetry $p4gm$, we call the Mn_2Hg_5 net as the Hg atoms in that compound fall on such a net.

These tilings have four edges meeting at each vertex; when we refer to them as nets we say that they are 4-connected. In a 4-connected net with, per unit cell, n_3 triangles, n_4 quadrangles and n_5 pentagons, it is easy to show (see Notes, § 5.6.11) that n_4 can have any value and $n_3 = n_5 = 4$ and $n_4 = 2$.

We digress for a moment on the structure of Mn_2Hg_5 (for crystallographic data see Appendix 5) which serves to illustrate some instructive points. Adding translations in the third direction and mirror planes (normal to this direction) to the two-dimensional space

group $p4gm$ generates the three-dimensional group $P4/mbm$. In Mn_2Hg_5 , which has this symmetry, the Hg atoms lie on the mirror plane at $z = 0$ on the Mn_2Hg_5 net; this is called the *primary* net of the structure. The Mn atoms are on the mirror plane at $z = 1/2$ and lie over the centers of the Hg pentagons. The net of the Mn atoms, is called the *secondary* net, and in this instance is $3^2.4.3.4$ (which also has symmetry $p4gm$). Thus the Mn_2Hg_5 structure, and indeed many others, are succinctly described in terms of a stacking of alternating primary and secondary nets. In many instances, the secondary net is one of the regular or simpler semiregular ones. Care should be taken to distinguish a *dual* net (in which the centers of *all* the polygons of the original net correspond to vertices of the derived net) from a *secondary* net (in which the centers of only the larger polygons of the original net correspond to vertices of the derived net).

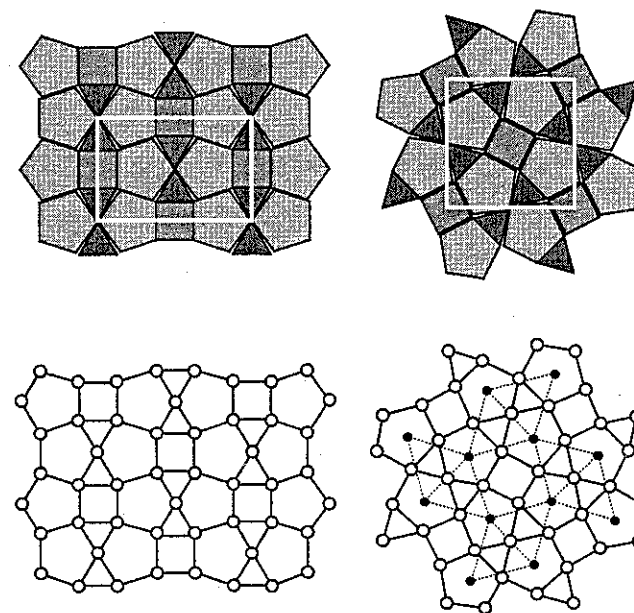


Fig. 5.42. Top: "almost" covering the plane with regular triangles, squares and pentagons of equal edge. Bottom: the derived tilings (nets). On the left is the $\beta\text{-U}_3\text{O}_8$ net and on the right the Mn_2Hg_5 net. The secondary net of the Mn_2Hg_5 net is indicated with filled circles.

A new 4-connected net can be derived from a given 4-connected net by placing vertices in the middle of each edge of the old net, and joining them by edges to make a quadrangle surrounding the old vertices, which are then deleted. The reader is invited to do this with the Mn_2Hg_5 net illustrated in Fig. 5.42. The new net we call the TTB net for a reason given below.

To most people, the term “bronze” refers to the beautiful copper-tin alloy, but solid state chemists also use the term to refer to compounds of variable composition involving (usually) alkali metal atoms combined with an early transition metal oxide. The tungsten bronzes, $M_x\text{WO}_3$ (here M is an alkali metal) have been known for nearly 200 years, and are so named for their striking colors and metallic luster. Their structures also illustrate a use of plane nets in crystal chemistry, so we digress a little on this topic.

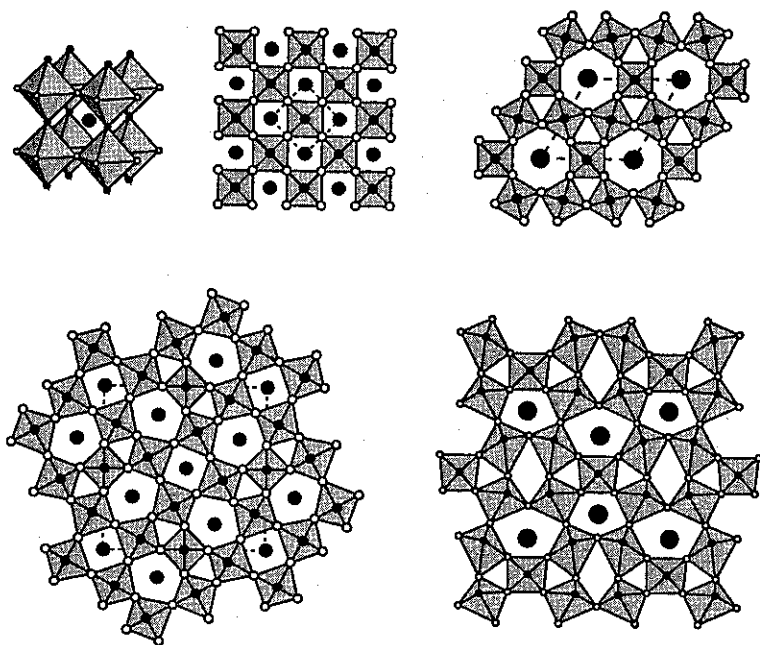


Fig. 5.43. Top left: a clinographic projection of a fragment of a cubic array of corner-connected octahedra. On the right of that the same structure (but with more octahedra) is shown in projection. Top right: the hexagonal tungsten bronze structure seen in projection. Bottom left: a similar view of the tetragonal tungsten bronze structure. Bottom right: The $\text{Ba}_4\text{MgTa}_{10}\text{O}_{30}$ structure (large circles Ba, Mg not shown).

The structure of WO_3 is based on a simple corner-connected array of $\{\text{W}\}\text{O}_6$ octahedra as shown schematically in Fig. 5.43 [this structure in its most symmetrical (cubic) form is usually called ReO_3]. When Na metal is added to WO_3 , the metal atoms enter the cavities (actually cuboctahedra) in the structure, in the position shown as a large filled circle in the figure. The structure, seen in projection down a cube axis, is illustrated in Fig. 5.43; the shaded squares are octahedra seen in projection. Open circles are O atoms around the octahedron “waist”; let’s imagine them to be in the plane of the paper. Small filled circles

then represent O atoms above and below the plane completing the octahedron about W (not shown). The Na atom positions, also above and below the plane, are shown by larger filled circles. The net of the O atoms in the plane is clearly 4^4 . If every Na site were occupied, the composition would be NaWO_3 and the structure is called **perovskite**.¹

If, instead of Na, Cs is used to form a tungsten bronze, a different structure is obtained (top right of Fig. 5.43). It is still based on an array of corner-connected $\{\text{W}\}\text{O}_6$ octahedra, but now the pattern of O atoms in the plane is $3.4.6.4$. The large cavities in the structure are over the hexagons of this net and if they are all filled, the composition is CsW_3O_9 . The structure is the hexagonal tungsten bronze (HTB) structure, and for this reason $3.4.6.4$ is often called the **HTB net**. Note that the W atoms fall on a $3.6.3.6$ net.

With K atoms another structure with composition $\text{K}_3\text{W}_5\text{O}_{15}$ is obtained.² Now the main oxygen atom net is made up of triangles, quadrangles and pentagons, and is in fact the net we derived from the Mn_2Hg_5 net earlier. The structure is that of tetragonal tungsten bronze (TTB), so we call the net the **TTB net** (see bottom left of Fig. 5.43). Recalling how we derived this net it should be clear that the W atoms (in the octahedra, hence centering the squares of the projection) are on the Mn_2Hg_5 net. Note that the tungsten compound with mixed valence $[\text{W}(\text{V}) \text{ and } \text{W}(\text{VI})]$ is a metallic conductor, but many insulating (and colorless) compounds have been made with the same structure and they are often also referred to as “bronzes.”

Another 4-connected net may be derived from the $\beta\text{-U}_3\text{O}_8$ net in the same way as the TTB net was derived from the Mn_2Hg_5 net (i.e. by putting new vertices in the middle of edges and removing the old vertices). This new net (Fig. 5.43, bottom right) is found as oxygen layers in, for example, the structure of $\text{Ba}_4\text{MgTa}_{10}\text{O}_{30}$ which is based on corner-sharing $\{\text{Ta}\}\text{O}_6$ octahedra. The Ta atoms are on the original $\beta\text{-U}_3\text{O}_8$ net, the Ba atoms are in the space over the pentagons and Mg atoms fill one-half of the space over the quadrilateral tunnels.

The structure of $\text{K}_3\text{V}_5\text{O}_{14}$ is based on corner sharing $\{\text{V}\}\text{O}_6$ octahedra and $\{\text{V}\}\text{O}_5$ trigonal bipyramids; it is illustrated in the same way as the tungsten bronzes in Fig. 5.44. As before, octahedra project as centered squares, and now trigonal bipyramids project as centered triangles. Again we have a 4-connected triangle-square-pentagon net, and K atoms lie over the pentagon centers above the plane of the paper. The overall stoichiometry of a corner-sharing trigonal bipyramid is $\text{VO}_{5/2}$ and that of a corner-sharing octahedron is $\text{VO}_{6/2}$. As there are two trigonal bipyramids and three octahedra in the unit cell (together with three K atoms), the cell content is $3\text{K} + 2 \times \text{VO}_{5/2} + 3 \times \text{VO}_{6/2} = \text{K}_3\text{V}_5\text{O}_{14}$.

The net of the V atoms in $\text{K}_3\text{V}_5\text{O}_{14}$ is also shown in the figure (note that not all vertices are 4-connected in this instance). This is also the Pd net in the structure of Th_3Pd_5 (for crystallographic data see Appendix 5). The Th atoms of Th_3Pd_5 are on the secondary net of this structure (over the centers of the pentagons) which may be seen to be (slightly distorted) 3^6 . Thus the K_3V_5 part of $\text{K}_3\text{V}_5\text{O}_{14}$ has the same structure as Th_3Pd_5 ; indeed it is commonly found that the cation array in oxides and related materials is that of an

¹The mineral perovskite is CaTiO_3 and its actual structure is a small distortion of the ideal cubic one.

²We have oversimplified the chemistry somewhat. Several structures occur for several different alkali atoms, and the observed structure depends on the stoichiometry as well as the size of the inserted atom.

intermetallic compound. The net of the V atoms in $K_3V_5O_{14}$ and of the Pd atoms in Th_3Pd_5 also occurs as the net of the O atoms in $\alpha-U_3O_8$ so we call it the $\alpha-U_3O_8$ net. Although it may not be obvious from a comparison of Figs 5.42 and 5.44, the $\alpha-U_3O_8$ net is closely related to the $\beta-U_3O_8$ net (see § 5.6.12).

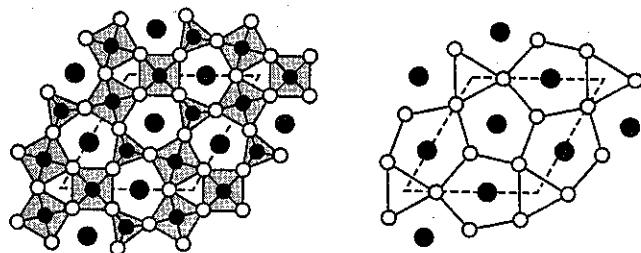


Fig. 5.44. Left: the structure of $K_3V_5O_{14}$ as corner-sharing octahedra and trigonal bipyramids. Larger circles are K atoms, and smaller circles are O atoms. V atoms (not shown) center the shaded octahedra and trigonal bipyramids. Right: the $\alpha-U_3O_8$ net of the V atoms (open circles) in $K_3V_5O_{14}$, with the K atoms (filled circles) on the secondary net.

Many other triangle-quadrangle-pentagon nets occur in crystal chemistry; for a review of some of them, and their interrelationships, see OKH.

5.3.5 Some 3-connected boron nets: AlB_2 , $YCrB_4$, $ThMoB_4$ and Y_2ReB_6

Examples of 3-connected nets already met are 6^3 , 3.12^2 , 4.8^2 and $4.6.12$. A unit cell of 4.8^2 contains one square and one octagon, so on average the polygons have six sides. The unit cell of 3.12^2 contains two triangles and one dodecagon, so again, the average number of sides per polygon is six. It is easy to show (see Notes § 5.6.11) that this must be the case in general for 3-connected nets. As each edge belongs to two polygons, the number of edges is $e = 3f$ where f is the number of polygons. In a 3-connected net $e = 3v/2$, where v is the number of vertices per cell, so $f = v/2$.

In many borides, the B atoms form 3-connected plane nets with metal atoms (M) in interleaved layers centering the polygons. It follows that the stoichiometry is MB_2 and the average polygon size in the B layer is 6. The simplest case is in the structure of AlB_2 in which the B atoms lie on 6^3 nets (as in the graphite form of carbon) with Al atoms over the centers of the hexagons forming larger-spacing 3^6 nets (see Fig. 5.46 on p. 174).

In some ternary borides the B atom layer contains pentagons and heptagons (which must occur in equal numbers) as well as hexagons. Three common structure types containing such layers are those of $YCrB_4$, $ThMoB_4$ and Y_2ReB_6 (for crystallographic data see Appendix 5). The B nets in these compounds are illustrated in Fig. 5.45. Those on the left and the right of the figure provide nice examples of patterns with symmetry $p2gg$. Adding translations and mirrors perpendicular to the translations of $p2gg$ produces the three-dimensional group $Pbam$ which is the symmetry of the corresponding compounds. The

pattern in the center has symmetry cm and the symmetry of the crystal structure is $Cmmm$.

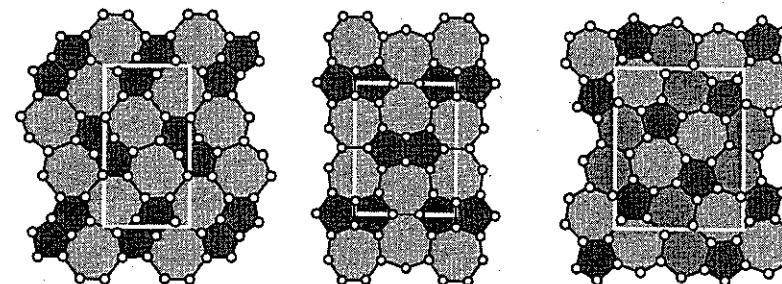


Fig. 5.45. The B nets in $YCrB_4$ (left), $ThMoB_4$ (left) and Y_2ReB_6 (right).

In each crystal structure the larger metal atoms lie over the heptagons (and the hexagons in Y_2ReB_6). The smaller metal atoms (Cr, Mo and Re respectively) lie over the pentagon centers and thus have pentagonal prismatic coordination by B. In $YCrB_4$ and $ThMoB_4$, the occurrence of adjacent pairs of pentagons in the net results in a very short metal-metal distances. Thus there is a Cr-Cr distance of 2.38 Å (compare the shortest distance of 2.50 Å in the metal) in $YCrB_4$; likewise there is an Mo-Mo distance of 2.56 Å (compare the shortest distance of 2.73 Å in the metal) in $ThMoB_4$.

5.3.6 Some boron-carbon nets

In the previous section we described some boron layers in borides; related nets are also to be found as boron-carbon layers. In these, it is often found that the C atoms are of lower connectivity than the B atoms. These nets again provide some nice exercises in recognizing symmetry.

Our first example, which occurs in the structure of LaB_2C_2 (for data see Appendix 5), is just a simple decoration of the 4.8^2 net as shown in Fig. 5.46. In the crystal structure, alternate layers of the net are rotated by 90° and La atoms center the octagonal prisms, so that the coordination of La is $\{La\}B_8C_8$. The La array is close to primitive cubic. Note that although the symmetry of one plane is rectangular (2-dimensional group $c2mm$), the three-dimensional symmetry has 4 axes and the crystal is tetragonal (space group $P4_2c$).

In the TbB_2C structure (for crystallographic data see Appendix 5) layers of B_2C alternate with Tb layers. The B_2C layer is shown in Fig. 5.47. It may be considered a 3-connected net of heptagons and quadrilaterals; but, as indicated in the figure, the quadrilaterals are better considered as two triangles, and some of the B atoms are then 4-connected. The secondary net of Tb (centering the heptagons) is $3^2.4.3.4$. In the crystal structure alternate B_2C layers are rotated by 90° ; thus although again the symmetry of one plane is rectangular ($p2gg$), the symmetry of the crystal is tetragonal ($P4_2/mbc$).

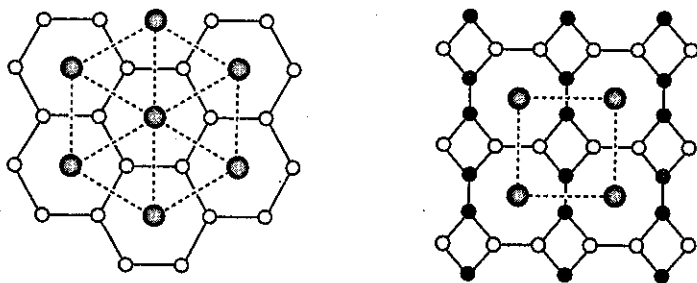


Fig. 5.46. Left: the AlB_2 structure. 6^3 layers of B (small open circles) alternate with 3^6 layers of Al (large shaded circles). Right: the LaB_2C_2 structure. A 4.8^2 net of B and C (filled circles) alternates with 4^4 nets of La (larger shaded circles).

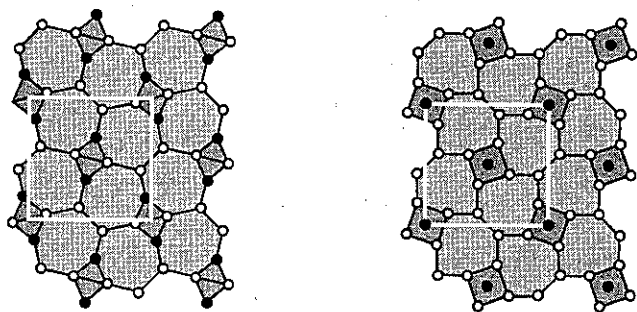


Fig. 5.47. Left the boron-carbon net in TbB_2C . Filled circles are C atoms. Right: the B net in ThB_4 (open circles). Now filled circles are B_2 groups above and below the plane of the net.

The crystal structure of ThB_4 (for data see Appendix 5) contains similar layers (Fig. 5.47) but now the quadrangles are squares; additional B atoms above and below the plane cap the squares to form octahedra, and strings of octahedra joined by additional edges run normal to the plane of the net. (Fig. 5.48). Thus the structure should really be considered a three-dimensional B net. We meet other example of B nets in Chapter 7.¹

In the structure of ThB_2C (also known as the UB_2C structure), there are B_2C layers with 3-coordinated B and 2-coordinated C as shown in Fig. 5.49. Crystallographic data are given in Appendix 5. Those who like to count electrons might care to speculate on why the

¹Note the influence of stoichiometry on coordination number. In compounds $M_n\text{B}$ ($n \geq 2$) there are usually B atoms that are not bonded to other B atoms. In compounds MB (such as CrB and FeB , § 6.4.2) B is 2-connected to other B atoms, in compounds MB_2 (discussed in the previous section) B is 3-connected, in ThB_4 , B is 3- and 5-connected (but 4-connected in CrB_4 , § 7.3.3), in CaB_6 and UB_{12} (§ 7.9) B is 5-connected, and in elemental B (§ 5.2.5) B is 6- and 7-connected.

TbB_2C structure is formed by Sc, Y and lanthanides (trivalent elements) but a different structure is formed by ThB_2C and UB_2C .

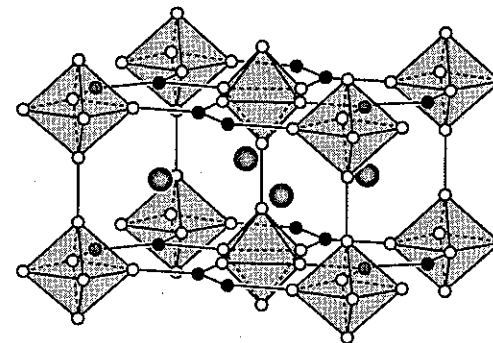


Fig. 5.48. The ThB_4 structure in clinographic projection. Small open circles are B atoms connected to five other B, small filled circles are B connected to three other B; larger circles are Th.

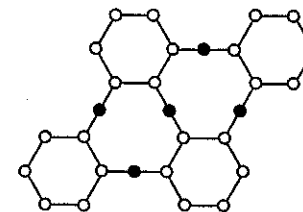


Fig. 5.49. The boron-carbon net in ThB_2C . Filled circles are carbon atoms.

5.3.7 Polyatomic tilings: self-dual nets

The tilings we have considered so far generally correspond to layers of one kind of atom (or two related atoms such as B and C) in crystal structures; in this section we describe some (chemically) ternary structures in which all three kinds of atom are in the same layer. As the different atoms may be of different "sizes," in general the tilings derived from these structures will be made up of polygons with unequal edges.

Very often in structures composed of layers, all the atoms lie on mirror planes and then there are just two layers in the structure (recall that mirror planes repeat with a translation equal to half the shortest lattice vector perpendicular to them). In some instances, the two mirror planes will be related by symmetry so that there is only one distinct kind of layer. This will occur when, for example, there are axes of the sort $2_1/m$, $4_2/m$, or $6_3/m$ normal to the mirror planes (say along c). In each of these cases the symmetry operation has a translation component of $c/2$ taking an atom on one mirror plane into an equivalent atom on

the other mirror plane. For example, in the commonly-occurring space group $Pnma$, there is a $2_1/m$ axis along $0,y,0$ and the mirror planes are at $y = 1/4$ and $y = 3/4$ (see Fig. 3.14, p. 72). The 2_1 axis operating on an atom at $x,1/4,z$ will take it into an equivalent atom located at $\bar{x},3/4,z$. In fact the whole layer at $y = 1/4$ (or $3/4$) is rotated by 180° about the y axis and translated to $y = 3/4$ (or $1/4$). The symmetry of the layer is $p1g1$. To take another example, it should be clear that in body-centered space groups, mirror planes normal to the axes of the conventional (centered) cell are related by the centering translation. For more on the symmetry of structures with a two-layer repeat of one kind of layer see § 5.6.14.

It is quite common for the vertices of one net to center (in projection) the polygons of the other net and *vice versa*, so that the net is self dual. For a self-dual net, the number of polygons with n edges must be equal to the number of vertices that are n -connected. The average polygon (ring) size must therefore be equal to the average connectivity of the vertices. It follows at once from Eq. 5.4 (§ 5.6.11, p. 198) that this average is 4. It follows further that either all the polygons are quadrangles (and all vertices 4-connected), i.e. the net is 4^4 , or that some of the polygons are triangles and correspondingly that some have more than four edges. A simple example of the latter case is provided by the structure of CrB (Fig. 5.50) in which there are equal numbers of pentagons and triangles. In this structure Cr atoms in one layer center (in projection) the pentagons of layers above and below and B atoms similarly center the triangles.

An atom centering (in projection) the triangles of identical nets above and below it is in (capped) triangular-prismatic coordination, so it is not surprising that such coordination is a feature of structures that can be described in terms of a stacking of self dual nets. In Fig. 5.50 the trigonal prisms (at two elevations) in CrB are shaded for emphasis.

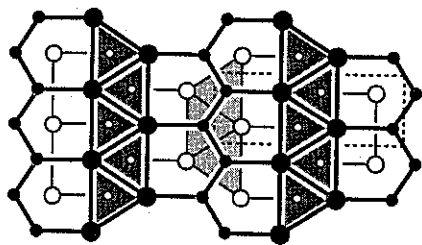


Fig. 5.50. The structure of CrB projected on (100). Larger circles are Cr.

As another example we illustrate (in Fig. 5.51), the structure of SrMgSi (which is one of the many compounds with the Co_2Si structure type) in which all atoms lie on the mirror planes of $Pnma$. In this structure Sr centers pentagons of adjacent nets, and Mg and Si similarly center quadrangles and triangles respectively. Accordingly the net (which has symmetry pg) has triangles, quadrangles and pentagons in equal numbers. For crystallographic data for SrMgSi see Appendix 5.

WCoB is isostructural with SrMgSi but NbCoB and TaCoB have a related structure (Fig. 5.51) with symmetry $Pmnn$ composed of self-dual nets of symmetry pm . Notice that

in a SrMgSi layer all the triangles are Sr_2Mg , but that in a NbCoB layer there are triangles Nb_3 , Nb_2Co and Co_3 .

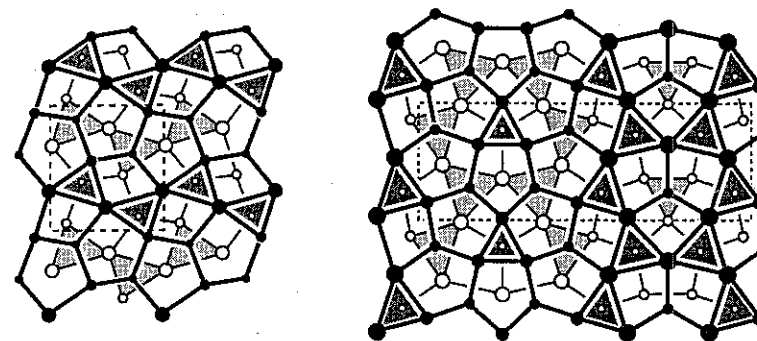


Fig. 5.51. Left: the structure of SrMgSi projected on (010), atoms at $y = 1/4$ and $3/4$. Large, medium and small circles are Sr, Mg and Si respectively. Right: the structure of NbCoB projected on (100), atoms at $x = 0$ and $1/2$. Large, medium and small circles are Nb, Co and B respectively. Trigonal prisms are shaded.

A second crystallographically ternary compound (the first was SrMgSi) with a structure based on self-dual nets is that Re_3B (Fig. 5.52). This is better written as $\text{Re}(1)\text{Re}(2)_2\text{B}$ to emphasize that there are two kinds of Re atom, and a more typical composition for this structure type is YAl_2Co . The symmetry is $Cmcm$ and the symmetry of the layers is pmg . Y centers pentagons, Al centers quadrangles and Co centers triangles. For crystallographic data for Re_3B see Appendix 5.

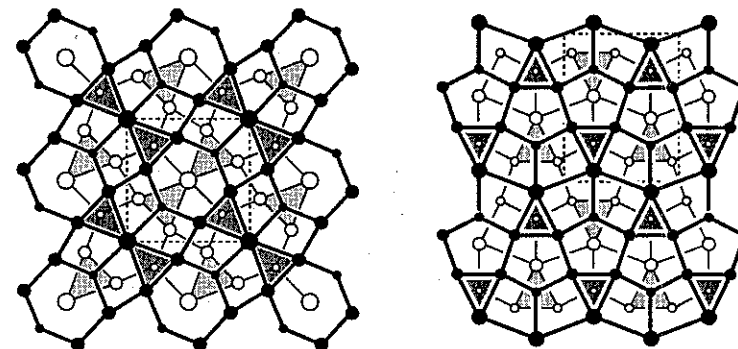


Fig. 5.52. Left: the structure of ZrFe_4Si_2 projected on (001), atoms at $z = 0$ and $1/2$. Large, medium and small circles are Zr, Fe and Si respectively. Right: the structure of YAl_2Co (Re_3B) projected on (100), atoms at $x = 0$ and $1/2$. Large, medium and small circles are Y, Al and Co respectively. Trigonal prisms are shaded.

Another ternary compound with a structure based on self-dual nets is that of ZrFe_4Si_2 (Fig. 5.52). Now there are hexagons, quadrangles and triangles (centered by Zr, Fe and Si respectively) in the ratio 1:4:2. The symmetry of the structure is $P4_2/mnm$ and that of the layers is $c2mm$ (for crystallographic data see Appendix 5).

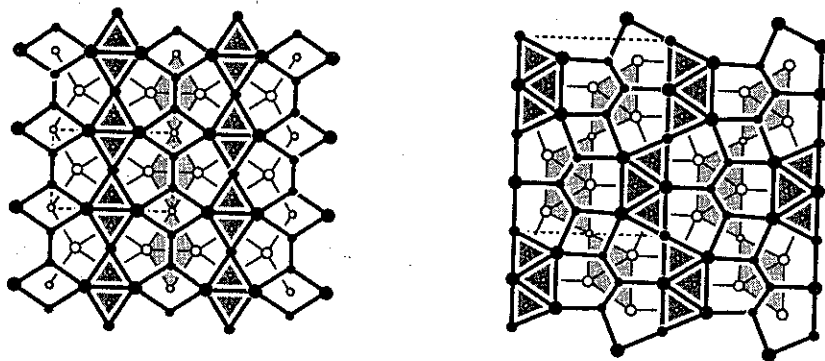


Fig. 5.53. The structures of W_2CoB_2 (left) projected on (001), atoms at $z = 0$ and $1/2$, and W_3CoB_3 (right) projected on (100), atoms at $x = 0$ and $1/2$. Large, medium and small circles are W, Co and B respectively. Trigonal prisms are shaded.

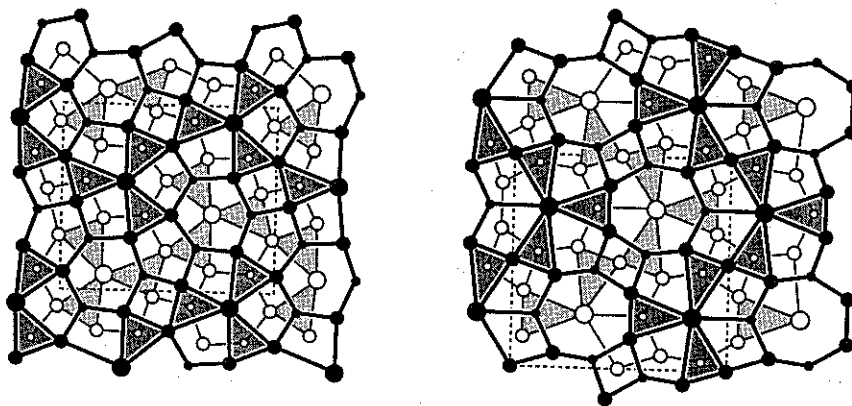


Fig. 5.54. Left: the structure of YCo_5P_3 projected on (010), atoms at $y = 1/4$ and $3/4$. Right: the structure of LaCo_5P_3 projected on (100), atoms at $x = 0$ and $1/2$. Large, medium and small circles are Y (La), Co and P respectively.

There is a series of compounds W_nCoB_n whose structures are composed of self-dual nets in which W centers pentagons, Co centers quadrangles and B centers triangles. The

case $n = \infty$ is WB which has the CrB structure (Fig. 5.50). $n = 1$ is WCoB which has the SrMgSi structure (Fig. 5.51). Fig. 5.53 illustrates the $n = 2$ and 3 cases. Note that in these structures there are groups of n trigonal prisms sharing rectangular faces so that there are B_n groups joined by bonds through these faces.

In LaCo_5P_3 (Fig. 5.54) with symmetry $Cmcm$, heptagons, quadrangles and triangles in the ratio of 1:5:3 form a self-dual net with symmetry $p2mg$. La centers the heptagons, Co the quadrangles and P the triangles. Note that the triangles are all LaCo_2 , but the quadrangles are LaCo_2P and Co_2P_2 . This structure type is sometimes named **LaNi₅P₃**.

In YCo_5P_3 (Fig. 5.54) with symmetry $Pnma$, the Y atoms center hexagons, and P atoms center triangles so hexagons and triangles occur in the ratio 1:3. As the average ring size must be four there is also one pentagon per hexagon, and Co centers pentagons as well as quadrangles. A third structure occurs for this stoichiometry in LaNi_5Si_3 (Fig. 5.55) this has the same symmetry and the net contains the same number of polygons as in YCo_5P_3 .

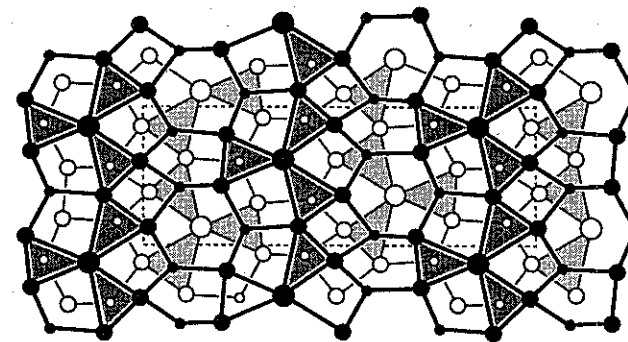


Fig. 5.55. The structure of LaNi_5Si_3 projected on (010). Large, medium and small circles are La, Ni and Si respectively at $y = 1/4$ and $3/4$.

To illustrate the variety and beauty of the structures that nature has devised we illustrate a number of other self-dual nets in Fig. 5.56. Properties of these and the other nets of this section are summarized in Table 5.5 (p. 181). The chemical formula of all the compounds discussed in this section is $A_aB_bC_c$ (CrB is considered to have $b = 0$). When this formula is written in the preferred way of most electropositive element first, it is observed that A centers the large polygons, B centers smaller polygons (usually quadrangles) and C invariably centers triangles (i.e. is in trigonal prismatic coordination). The table identifies the polygons so centered; as A centers the largest polygons and C the smallest, we refer to A, B and C as "large," "medium," and "small" respectively, referring, of course, to relative size. It may be verified that the average polygon (ring) size is four in every case. The structures illustrate the delicate balance between "size" and stoichiometry in determining coordination numbers although we should remark that the number of "caps" of the coordination prisms N_{42} is not always N . Also to be noted that as C is in trigonal prisms

of *A* and *B* the structures can always be represented in terms of trigonal prisms with centers at two heights (either 0 and 1/2 or 1/4 and 3/4). The number of structures that can be so described is considerably larger than those based on self-dual nets—see for example Fe_2P (§ 5.6.15).

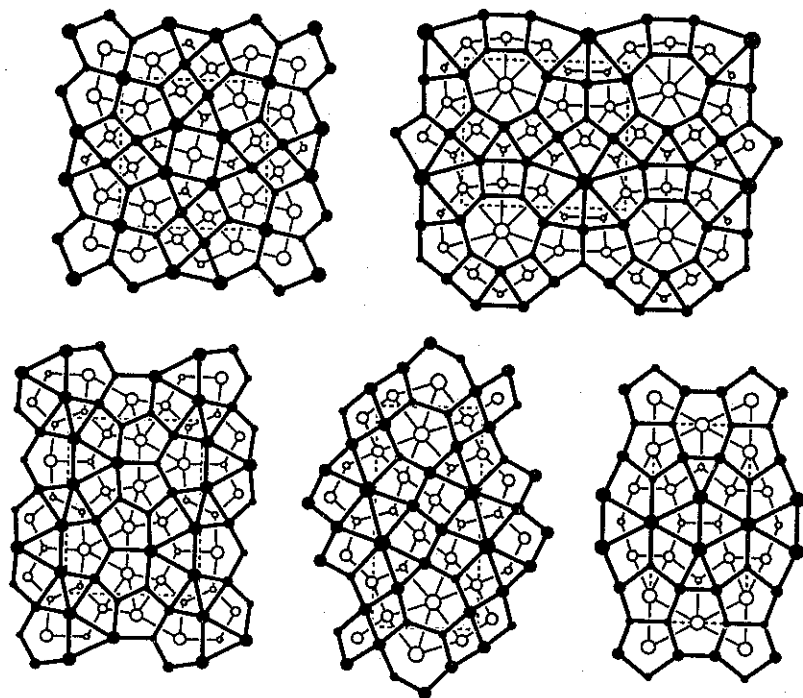


Fig. 5.56. Some structures based on self-dual nets. Top: left $\text{Nb}_5\text{Cu}_4\text{Si}_4$, right EuCo_8P_5 . Bottom, from the left: $\text{Hf}_3\text{Ni}_2\text{Si}_3$, NdRe_4Si_2 , $\text{Zr}_3\text{Cu}_4\text{Si}_4$. In all these structures of $A_nB_mC_p$ largest circles are *A* and smallest are *C* (the latter invariably centering triangles).

In the tetragonal structures listed in Table 5.5, atoms are on the mirror planes normal to the 4-fold axis. In some simple tetragonal structures (with small unit cell parameter *a*) the atoms are all on mirror planes parallel to the 4-fold axis (along *c*) and often the atoms on such layers form self-dual nets normal to *a*. There are of course equivalent layers normal to *b* and a description of such structures in terms of a stacking of nets is leaves something to be desired. Notable examples of such structures are ThCr_2Si_2 (also named BaAl_4) and BaMgSi (also named PbFCl), perhaps the two most populous structure types (for more on these structures see § 6.4.2).

Table 5.5. Some structures (with symmetries) based on self-dual nets. Numbers are *N*-gons per formula unit in the net

structure <i>N</i>	Fig.	crystal	layer	large atom				medium atom		small atom
				7	6	5	4	5	4	3
CrB	5.50	<i>Cmcm</i>	<i>p2mg</i>			1				1
SrMgSi	5.51	<i>Pnma</i>	<i>pg</i>			1		1		1
NbCoB	5.51	<i>Pmmn</i>	<i>pm</i>			1		1		1
YAl_2Co	5.52	<i>Cmcm</i>	<i>p2mg</i>			1		2		1
ZrFe_4Si_2	5.52	$P4_2/mnm$	<i>c2mm</i>	1				4		2
W_2CoB_2	5.53	<i>Immm</i>	<i>p2mm</i>		2			1		2
W_3CoB_3	5.53	<i>Cmcm</i>	<i>p2mg</i>			3		1		3
LaCo_5P_3	5.54	<i>Cmcm</i>	<i>p2mg</i>	1				5		3
YCo_5P_3	5.54	<i>Pnma</i>	<i>pg</i>		1			1	4	3
LaNi_5Si_3	5.55	<i>Pnma</i>	<i>pg</i>		1			1	4	3
$\text{Nb}_5\text{Cu}_4\text{Si}_4$	5.56	<i>I4/m</i>	<i>p4</i>			4	1		4	4
EuCo_8P_5	5.56	<i>Pmmn</i>	<i>pm</i>	1				2	6	5
$\text{Hf}_3\text{Ni}_2\text{Si}_3$	5.56	<i>Cmcm</i>	<i>p2mg</i>			3			2	3
NdRe_4Si_2	5.56	<i>Pnnm</i>	<i>c2</i>		1				4	2
$\text{Zr}_3\text{Cu}_4\text{Si}_4$	5.56	<i>Immm</i>	<i>p2mm</i>		1	2			4	4

5.4 Layers of tetrahedra and/or octahedra: sheet silicates

Many crystal structures are conveniently described as built up of slabs (multiple layers of atoms) rather than as a stacking of planes and we describe here some important layers of connected polyhedra. Specifically we describe layers of corner-connected tetrahedra and edge-connected octahedra.¹

5.4.1 Layers of tetrahedra and octahedra

Layers of corner-connected $\{T\}X_4$ tetrahedra can be constructed with each tetrahedron sharing three vertices with other tetrahedra so the stoichiometry is $TXX_{3/2} = T_2X_3$. The simplest, and most important way, of doing this is with the *T* atoms on the vertices of a 6^3 net as shown in Fig. 5.57.

As the figure illustrates, the layer of tetrahedra is flexible. In “expanded” form, the *T-X-T* angle is 141.1° and the base vertices are on a $3.6.3.6$ net. In “contracted” form (with the distance between vertices of neighboring tetrahedra equal to the tetrahedron edge) the *T-X-T* angle is 109.5° and the base vertices are on a 3^6 net (the two configurations are related exactly as shown in Fig. 5.40, p.167). In each case the *T* atoms and the vertices above them remain on a 6^3 net.

We note in passing that two such layers (one pointing “up,” and one pointing “down”) can be joined using the fourth vertex to produce stoichiometry TX_2 . Such layers are found in one polymorph of $\text{BaAl}_2\text{Si}_2\text{O}_8$ in “expanded” form, and in one polymorph of $\text{CaAl}_2\text{Si}_2\text{O}_8$ in “contracted” form (with the top layer “anti” to the bottom layer).

¹Slabs of edge-connected tetrahedra are discussed especially in § 6.4.2 (see Fig. 6.43, p. 249).

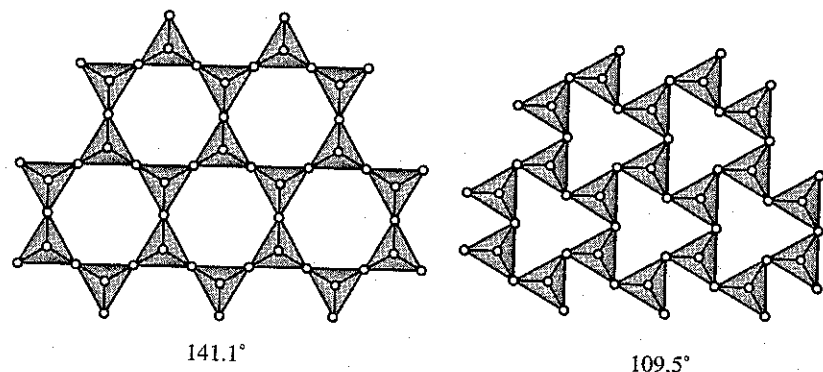


Fig. 5.57. Layers of corner-connected tetrahedra pointing "up." Left: in expanded form. Right: "contracted" to lower density. Numbers are the $T-X-T$ angles (in degrees) for regular tetrahedra.

The $T-X-T$ angle can be considerably larger (indeed up to 180°) if the tetrahedra alternate "up" and "down" as shown for two configurations in Fig. 5.58 and such alternating layers are common in silicates (in which the Si-O-Si angle is usually about 145° , or greater).

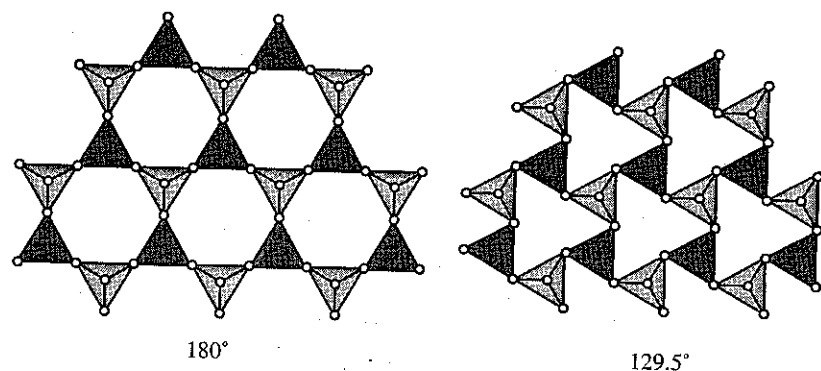


Fig. 5.58. Layers of corner-connected tetrahedra alternating up and down. Left: in expanded form. Right: "collapsed" to lower density. Numbers are the $T-X-T$ angles (in degrees) for regular tetrahedra.

Layers of $[\text{Si}_2\text{O}_5]^{2-}$ alternate with cations in compounds such as $\text{Na}_2\text{Si}_2\text{O}_5$ and BaSi_2O_5 . Because the apical O atoms are bonded also to cations, the layers can be considerably distorted from the high-symmetry configurations shown in Figs. 5.57 and 5.58. Fig. 5.59 illustrates the layers in $\text{Na}_2\text{Si}_2\text{O}_5$ and BaSi_2O_5 . In the former the tetrahedra alternate up and down; in the latter *pairs* of tetrahedra alternate up and down.

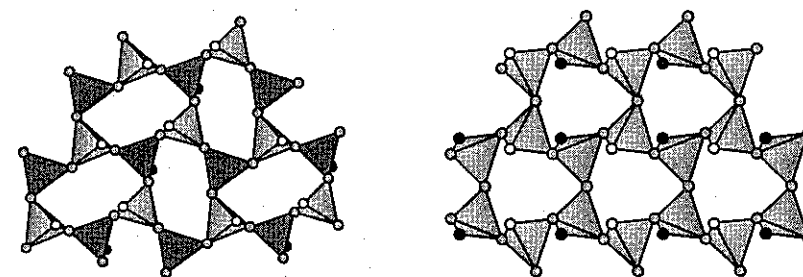


Fig. 5.59. The Si_2O_5 layers in $\text{Na}_2\text{Si}_2\text{O}_5$ (left) and BaSi_2O_5 (right). Filled circles are vertices pointing "down."

Layers of edge-sharing octahedra are also common in crystal structures. On the left in Fig. 5.60 we show a layer of $\{M\}Y_6$ octahedra sharing six edges with stoichiometry MY_2 . Such layers occur notably in CdCl_2 and CdI_2 (which differ only in the stacking of the layers—see § 6.1.5). The MgO_2 part of $\text{Mg}(\text{OH})_2$ (brucite) consists of similar layers. For a reason to become apparent below, mineralogists often refer to the MY_2 layer as a "trioctahedral layer."

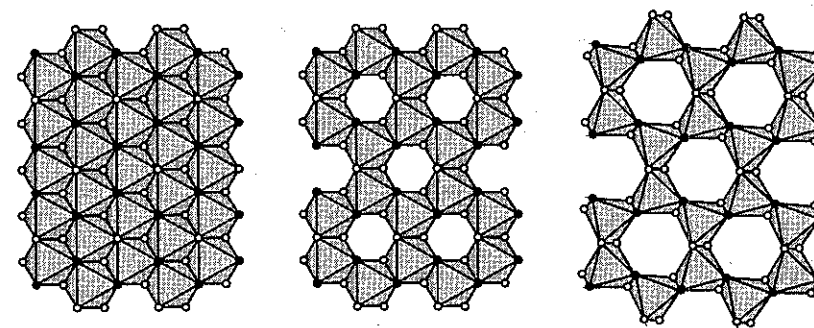


Fig. 5.60. Layers of edge-sharing octahedra. Left: an MY_2 layer. Center: an MY_3 layer of regular octahedra. Right: an MY_3 layer of metaprisms with shared edges shorter than unshared edges (see text). The filled circles are vertices that can be shared with a tetrahedral layer (see Fig. 5.57).

A second layer of edge-sharing octahedra, now with each octahedron sharing only three edges, is obtained from the first by removing one third of the M atoms to produce stoichiometry MY_3 . In this layer the M atoms are at the vertices of a 6^3 net. A notable example of its occurrence is $\text{Al}(\text{OH})_3$. Such a layer is often referred to as "dioctahedral."

It is important to recognize that in real materials (such as oxides) the octahedra in layers are not regular. Because of metal-metal repulsions, the shared edges of octahedra are

shortened and the unshared edges are lengthened. This does not show up in a drawing of a projection of the MY_2 layer, but in the MY_3 layer it does; the octahedra become metaprisms, and the structure expands as illustrated on the right in Fig. 5.60. In $Mg(OH)_2$, the lengths of the shared and unshared edges are 2.78 and 3.15 Å respectively, and in $Al(OH)_3$ they are about 2.5 and 2.8 Å (the octahedra are rather irregular in this case).

5.4.2 Sheet silicates (phyllosilicates)

Many important minerals, known as “sheet” or “layer” silicates, are based on a combination of the above tetrahedral and octahedral layers. They have interesting and useful physical properties that are intimately connected to their structures. Here we outline some of the possibilities; in what follows it should be remembered that minerals typically have rather complicated compositions, and chemical formulas are often idealized.¹

Fig. 5.61 shows how two layers can be combined. Note that if the tetrahedral layer is contracted (or partly so) two distinct configurations (known as *O* and *H*) are possible.

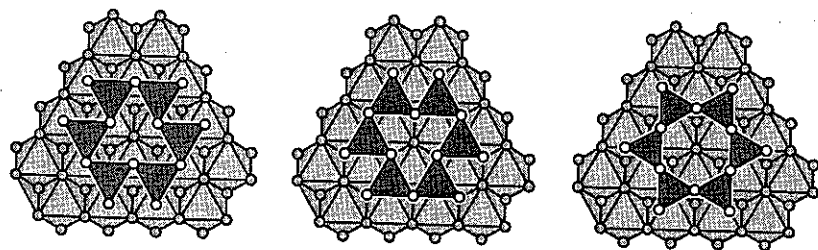


Fig. 5.61. Illustrating the positions of a tetrahedral layer (dark shading) with respect to an octahedral layer. Left: a contracted tetrahedral layer in the *O* orientation. Center: the same in *H* orientation. Right: an expanded tetrahedral layer.

Let's calculate the stoichiometry of a double layer formed from MY_2 and T_2X_5 layers. It should be clear from Fig. 5.61 that, per unit area, there are three *M* atoms for every two *T* atoms so we must combine 3 MY_2 (hence the term “trioctahedral”) with 1 T_2X_5 . The apices of the tetrahedra replace 2/3 of the *Y* atoms on one side of the MY_2 layer, i.e. 1/3 of the total *Y* atoms, so the double-layer stoichiometry is $M_3Y_4T_2X_5$. In layer silicates, *Y* is usually OH and *X* is O, so a typical composition for a neutral layer is $Mg_3(OH)_4Si_2O_5$. This is approximately the composition of antigorite and chrysotile asbestos. We return below to a further discussion of the structure of these materials.

In a double layer formed from MY_3 and T_2X_5 layers we must combine 2 MY_3 (hence the

¹We can only hint at the richness of this subject. A good account, with some of the history of the subject, is in Chapter 13 of Bragg & Claringbull (book list). Good recent references are: *Micas* (S. W. Bailey, ed.), *Reviews in Mineralogy* 13 (1984) and *Hydrous Phyllosilicates* (S. W. Bailey, ed.), *Reviews in Mineralogy* 19 (1988). The term *phyllosilicate* is generally considered to include all aluminosilicates with $(Si,Al)_2O_5$ layers of corner-connected $[Si]O_4$ and $[Al]O_4$ tetrahedra.

term “dioctahedral”) with 1 T_2X_5 and the stoichiometry is $M_2Y_4T_2X_5$; a typical composition for a neutral layer is $Al_2(OH)_4Si_2O_5$. This is approximately the composition of kaolinite (“china clay”).¹ Minerals with related structures are referred to as “clay minerals”; they are important components of soils.

In silicates, the Si-O-Si angles are about 145° so the tetrahedral layer is expanded (or very nearly so). The edge of a $[Si]O_4$ tetrahedron is about 2.62 Å, so for such a layer to be commensurate with an octahedral layer an octahedron edge (in the layer of the plane) of about $(2/\sqrt{3}) \times 2.62 = 3.03$ Å is needed. It transpires that the $[Al]O_6$ layers can adapt to this length, but the larger $[Mg]O_6$ cannot.

Accordingly in kaolinite there are flat sheets, but in chrysotile the sheets curve and form small cylinders of about $r = 100$ Å radius, with the octahedral layer on the outside and the tetrahedral layer inside. The separation between the octahedral and tetrahedral layers is about $\delta r = 2.7$ Å so the spacing in the octahedral layer is increased by $\delta r/r = 2.7\%$ compared to that in the tetrahedral layer. Thus the material really has translational symmetry in only one dimension (the cylinder axis).²

But nature shows great ingenuity in solving the mismatch problem in a number of different ways. In antigorite the tetrahedra in alternate laths of the tetrahedral layer are “up” and “down,” and the double layer is corrugated with a period of about 45 Å as shown schematically in Fig. 5.62; the radius of curvature of the sections is about 75 Å—approximately the same as in chrysotile. Still more complicated patterns are found in (for example) carlosturanite and manganpyrosmalite.³

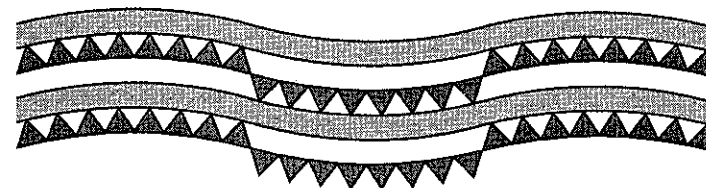


Fig. 5.62. A schematic illustration of the layers (seen end-on) in antigorite. Octahedral layers are lightly shaded.

Triple layers consisting of an octahedral layer joined on both sides to tetrahedral layers

¹Kaolinite was mined continuously from one location in Jiangxi province, China for about one thousand years and became known in England as “China clay”; ceramics made by firing it became known as *chinaware* or just *china*. *Kaolin* comes from the Chinese word *gaoling* (“high hill”) describing the location. Currently mining of kaolinite is a \$ billion industry; a major use is as a filler for paper.

²Actually, as well as cylinders one often finds a few turns of a cylindrical spiral (like a rolled-up carpet). The idea of cylindrical “crystals” seems to have originated with L. Pauling in 1930; subsequently electron microscopy provided dramatic direct evidence for such structures. See especially the now classic work of K. Yada, *Acta Crystallogr.* 23, 704 (1967) and A27, 659 (1971).

³For a good review see S. Guggenheim & R. A. Eggleton in *Hydrous Phyllosilicates* (S. W. Bailey, ed.) *Reviews in Mineralogy* 19 (1988), p. 675-725.

cab also be formed.¹ Combining an MY_2 (trioctahedral) layer with two tetrahedral layers produces composition $M_3Y_2T_4X_{10}$. A neutral composition is talc (also known as soapstone), $Mg_3(OH)_2Si_4O_{10}$. Note that layers that include two tetrahedral layers cannot bend (in contrast to chrysotile) and talc normally occurs as poorly-ordered microcrystals (talcum powder).

Minerals of the vermiculite group have alternating triple layers of the talc type and MY_2 layers. As, per unit area, 3 MX_2 are combined with 1 $M_3Y_2T_4X_{10}$, the ideal composition is now $M_6Y_8T_4X_{10}$.

Combining an MY_3 (dioctahedral) layer with two tetrahedral layers produces a triple layer with composition $M_2Y_2T_4X_{10}$. A neutral composition is that of pyrophyllite, $Al_2(OH)_2Si_4O_{10}$.

In the micas, part of the Si in the tetrahedral layer is replaced by Al and compensating cations are intercalated between the layers. Typical ideal compositions (with tetrahedral atoms in brackets) are:

- (a) using trioctahedral (MY_2) layers: muscovite, $KAl_2[AlSi_3]O_{10}(OH)_2$
- (b) using dioctahedral (MY_3) layers: phlogopite, $KMg_3[AlSi_3]O_{10}(OH)_2$

In constructing a three-dimensional crystal from the layers described here, attention must be paid to the way the layers stack.²

Clays³ also can have some cations between the layers. Montmorillonite is made up of triple layers consisting of two tetrahedral layers and a dioctahedral layer in which some of the Al is replaced with Mg. Typical compositions are $Na_xMg_xAl_{2-x}Si_4O_{10}(OH)_2$ (bentonite) and $Ca_{x/2}Mg_xAl_{2-x}Si_4O_{10}(OH)_2$ (Fuller's earth). The intercalated cations are readily exchanged for other cations at low temperatures in aqueous suspension (ion exchange). An interesting recent development has been the intercalation of large isopolycations such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (the "spinel cluster," see § 5.2.3, p. 157) which results in greatly increased interlayer spacing. Subsequent heat treatment removes much of the hydrogen (as water) leaving a "pillared" clay of high microporosity that has great potential for application as a catalyst.

Slurries of bentonite are thixotropic⁴ and find many applications (such as use as a drilling mud) exploiting this property.

¹Note that as the vertices on each side of an octahedral layer are not one above the other, there is an offset between the two tetrahedral layers, and the symmetry of the slab is at most rectangular.

²A good review and bibliography on this topic is given by J. B. Thompson in *Structure and Bonding in Crystals* Vol II [M. O'Keeffe & A. Navrotsky, eds., Academic Press, New York (1981)].

³The term *clay* is generally used loosely to mean any layer silicate that is (a) generally composed of very small crystallites and (b) can absorb water.

⁴A thixotropic material is a gel which becomes fluid when agitated. Platy microcrystals of bentonite have positive charges on their thin edges and negative charges on their faces and at rest orient themselves edge to face in the water producing a stiff gel. Agitation destroys this order resulting in a fluid of greatly reduced viscosity. "Non-drip" paints are thixotropic and usually contain bentonite.

5.5 Aperiodic tilings and quasicrystals

In recent years there has been considerable interest on the part of mathematicians and crystallographers in aperiodic tilings. These are tilings by basic tiles that cover the plane but in which there is no translational symmetry. The literature on this topic is now enormous and we can only attempt to provide some of the flavor of the subject.¹

The interest is in those sets of tiles for which every possible tiling is aperiodic. Many have been discovered in recent years. One of the simplest and most studied is the pair of Penrose tiles shown in Fig. 5.63. These have edge lengths of $\tau = (1 + \sqrt{5})/2 = 1.618...$ and 1 and the angle at the top is $2\pi/5 = 72^\circ$. If that were all, these tiles could cover the plane periodically as the two can fit together to form a rhombus. However the aperiodic property is forced by coloring the vertices of the tiles black and white as shown, and by requiring that only vertices of one color meet at a point.² A fragment of a tiling made from such tiles is also shown in the figure.

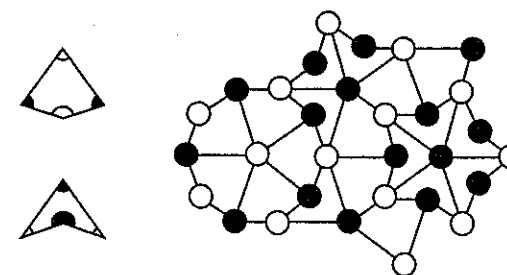


Fig. 5.63. On the left are shown the two Penrose tiles known as the kite (top) and dart (bottom) and on the right a fragment of an aperiodic tiling.

A closed fragment of a tiling (such as that shown in the figure) is known as a *patch*. A remarkable feature of a Penrose tiling is that it contains infinitely many patches congruent to any given patch. Even more remarkably, a local area with diameter d in any Penrose tiling has an identical area not more than $(1/2 + \tau)d$ away. In every such tiling the ratio of kites to darts (see figure legend) is τ .

Instead of darts and kites two different rhombuses (with acute angles of 36° and 72° respectively) can be used with aperiodicity forced by constraints on matching vertices and edges. A pair of such tiles and a tiling by them are shown in Fig. 5.64. Note that equivalent unmarked tiles with curved edges have the same property. The two rhombuses are often referred to as *skinny* and *fat* respectively.

In three dimensions there is an analogous pair of rhombohedral tiles which can be forced

¹A good introduction with references is in the book by Grünbaum & Shephard (Book List). A popular account is in M. Gardner *Penrose Tiles to Trapdoor Cyphers* [Freeman, New York (1989)].

²Aperiodicity can also be forced on monochrome tiles by curving the edges of the tiles shown.

to produce aperiodic tilings. These polyhedra¹ have faces that are fat rhombuses (angles of 72° and 108°). One rhombohedron is acute (three angles of 72° meet at a point) and the other is obtuse (three angles of 108° meet at a point). The faces have to be marked and appropriate matching rules applied to force aperiodicity.

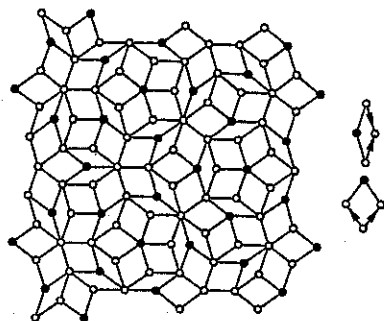


Fig. 5.64. A tiling (left) by rhombuses (right) with vertex colors and arrows on the edges matching.

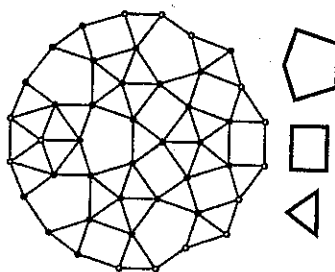


Fig. 5.65. The black circles are the black circles in Fig. 5.64, and open circles represent a continuation of the pattern using the tiles shown on the right and maintaining 5-coordination for each point.

The arrangement of black dots in Fig. 5.64 is suggestive. Fig. 5.65 shows that they form triangles, quadrangles and pentagons arranged to produce a five-connected net. The edge lengths of the polygons are 1 and $2\sin(\pi/10) = 1.176$. A conspicuous feature of the diagram is the groups of five triangles condensed to form regular pentagons. In three dimensions 20 tetrahedra (with edges in the ratio 1:1.05—see Exercise 3) can condense to form a regular icosahedron, and it is possible that (at least some) quasicrystal structures contain regular icosahedra and other polyhedra packed to fill space. Constraints analogous

¹Sometimes called *golden rhombohedra* or *Ammann rhombohedra*. They appear to have been first described by Ammann in 1976.

to those on matching edges and vertices of tiles in two dimensions may well arise in crystals. Such a constraint occurs for chemical compounds (black and white circles being different kinds of atom); another constraint is coordination number (cf. Fig. 5.65).

The Fourier transform of a periodic function is discrete; by this is meant that the Fourier integral is reduced to a sum. In particular the Fourier transform of a lattice is the reciprocal lattice. There are certain aperiodic functions (known as quasiperiodic) that also have discrete Fourier transforms.¹ Penrose tilings and the three-dimensional analogs (quasicrystals in the real world) are quasiperiodic and have discrete Fourier transforms and hence sharp diffraction patterns. One of the reasons for the excitement among crystallographers is that these diffraction patterns display symmetries not allowed for strictly periodic real-space patterns. The diffraction pattern of a two-dimensional crystal based on Penrose tiling has 5-fold symmetry—note that *local* regions of 5-fold symmetry are apparent in Figs. 5.63–65. Much larger patches with 5-fold symmetry can and do appear also. Quasicrystals have been found with diffraction patterns that have $m\bar{3}5$, $12/mmm$ and $10/mmm$ point symmetries (and also other non-crystallographic symmetries—see § 3.7.8).²

Readers who experiment with these tilings (as they are urged to) will find that as a tiling is being constructed, situations frequently arise where there is more than one way to proceed and that not all of these ways lead to acceptable tilings. One has therefore either to back-track frequently to eliminate “defects” in the tiling or to think ahead many moves (like a chess player). For this reason it has been argued that real quasicrystals cannot grow from such tiles, as atoms can neither think ahead nor readily undo their mistakes, although the difficulty can largely be avoided by recognizing additional rules for acceptable placing of tiles.³ The challenges to crystallographers and crystal chemists are to (a) identify the (three-dimensional) tiles that make up quasicrystals, (b) identify the rules for their assembly and (c) determine how atoms are situated on (or *decorate*) the tiles.⁴

A final note is in order. Mathematicians are mainly interested in tilings which are *forced* to be aperiodic. Solids often form aperiodic structures (such as glasses) not because they *have* to, but for kinetic reasons—silica is a notable example. The tiles in Fig. 5.65 do not *force* aperiodicity, but they can be put together in an aperiodic way that has a high concentration of patches with 5-fold symmetry.

¹Readers unfamiliar with Fourier transforms will have to skip this part. A simple example of a one-dimensional quasi-periodic function is $f(x) = \cos x + \cos \sqrt{2}x$.

²For a good introduction to quasicrystals see W. Steurer, *Zeits. Kristallogr.* **190**, 179 (1990) or *Lectures on Quasicrystals* (F. Hippert & D. Gratias, eds.) Les Edition de Physique (1994). Typical compositions are $\text{Al}_{73}\text{Mn}_{21}\text{Si}_6$, $\text{Al}_{70.3}\text{Pd}_{21.4}\text{Mn}_{8.3}$ and $\text{Li}_{30}\text{Al}_{60}\text{Cu}_{10}$ —notice that Al is the main component. Many materials studied to date are rapidly cooled from the melt, but there is now some evidence that the quasicrystal state is the most stable for compositions such as $\text{Al}_{62}\text{Fe}_{12.5}\text{Cu}_{23.5}$.

³These rules place additional constraints on the vertex figures that are allowed, and are thus “local” see G. Y. Onoda *et al.*, *Phys. Rev. Letts.* **62**, 1210 (1990).

⁴ MnAl_3 has a crystal structure believed to be closely related to that of a decagonal quasicrystal and relevant tiles for the quasicrystal have been described by K. Hiraga *et al.*, *Phil. Mag.* **B67**, 193 (1993). The structure of MnAl_4 is also believed to be relevant to quasicrystal structures; it is rather complex (574 atoms in the unit cell!)—C. B. Shoemaker *et al.*, *Acta Crystallogr.* **B45**, 13 (1989).

5.6 Notes

5.6.1 Relationships between polyhedra, and "pseudorotations"

The transformation from a trigonal bipyramid to a square pyramid involves just small displacements of the vertices. Figure 5.66 shows how a trigonal bipyramid can be transformed to a square pyramid, and thence to a trigonal bipyramid in a different orientation and with interchange of apical and equatorial atoms. Such a transformation path is known as a *Berry pseudorotation*. A bipyramidal molecule such as PF_5 appears to have five equivalent F atoms in ^{19}F NMR due to rapid changes of this sort.

Another example of a pseudorotation was given in § 5.1.8 where we showed how a square antiprism could be related to a bisdiphenoid. The different ways of converting the squares of the square antiprism into pairs of triangles will result in different orientations of the 4 axes of the bisdiphenoid which likewise can be converted back into antiprisms with different orientations. Analogously, small displacements can result in pseudorotations of extended structures such as layers (§ 5.6.13) or sphere packings (see e.g. § 6.3.1).

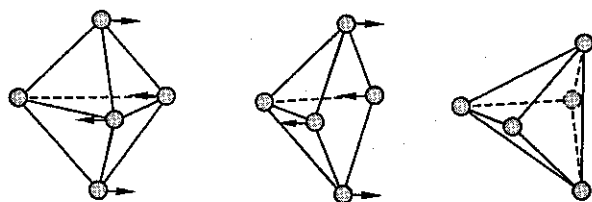


Fig 5.66. Transformation of a trigonal bipyramid into a square pyramid and then back to a bipyramid with the three-fold axis rotated by 90° .

5.6.2 Polyhedra, points on a sphere, and related topics

The solution to Tammes' problem is appropriate for atoms in a coordination figure when there is a short range repulsion between neighboring atoms (fairly "hard" spheres). At the other extreme is the case of the long-range repulsion (Coulomb interaction) when the energy of interaction of the atoms is proportional to $1/\text{distance}$. It is convenient in this case to measure the repulsion energy, E , in units of $q^2/4\pi\epsilon_0 r$ where r is the bond distance and q the charge.¹

For 5-coordination the repulsive energy is (note that the second value is for the most favorable type of square pyramid which has equal edges):

¹This problem has been called the electron problem as it was the basis for early (ca 100 years ago) models of electronic configurations in atoms. It was first treated by L. Föppl. For recent results see J. R. Edmundson, *Acta Crystallogr.* A48, 60 (1992). If $q = ze$, where e is the electronic charge, and r is in Å, $q^2/4\pi\epsilon_0 r = 14.4z^2/r$ eV.

bipyramid:	$E = 6.475$
pyramid:	$E = 6.657$

Turning to 6-coordination we might compare the octahedron with the trigonal prism. On a sphere of unit radius the shortest distance between points arranged as the vertices of a regular octahedron is $\sqrt{2} = 1.414$; for a regular trigonal prism it is $\sqrt{12/7} = 1.309$. In the case of the trigonal prism, in calculating the electrostatic repulsion, we now allow a degree of freedom which is the ratio of the height (h) to the length (b) of the triangular face; the minimum energy is for $h/b = 0.917$. In the same units as before:

octahedron	$E = 9.985$
prism $h/b = 1$	$E = 10.114$
prism $h/b = 0.917$	$E = 10.096$

In the case of the tricapped trigonal prism (9-coordination), the solution to Tammes' problem has the distances from the "capping" atoms to their four nearest neighbors equal to the length of the base. The ratio of the height to base is now $h/b = \sqrt{5/3} = 1.291$. Alternatively if we again minimize the electrostatic energy, $h/b = 1.143$ for the minimum electrostatic energy, but the energy is only 1.5% lower in this second configuration. In either case we have $h/b > 1$. In general when capped trigonal prismatic coordination occurs in crystals it is observed (see Hyde & Andersson, p. 213) that as the number of capping atoms increases, the prism becomes more elongated (h/b increases) as the above considerations suggest it should.

Many fascinating results, conjectures, and unsolved problems relating to polyhedra are to be found in *Unsolved Problems in Geometry* by H. T. Croft, K. J. Falconer and R. K. Guy [Springer-Verlag, Berlin (1991)].

5.6.3 Constructing polyhedra

The easiest, and possibly the best, way of constructing polyhedra is to assemble them from individual polygons cut *accurately* from stiff cardboard. They can be assembled into polyhedra using masking tape, and the joints filled with white glue (such as Elmer's glue in the U.S.). Convex polyhedra are always rigid, so that when the glue has set, the masking tape can be removed and a very sturdy model will be obtained. Pictures of many remarkable models made in a similar way are to be found in A. Holden, *Space, Shapes and Symmetry* [Columbia University Press, New York (1971) also Dover reprint]. Many of the models depicted in that book are pertinent to crystal chemistry.

5.6.4 Schlegel diagrams and adjacency matrices

The topology of a polyhedron (the connection of vertices by edges) is conveniently expressed in a *Schlegel diagram* which is a planar graph in which there is a one to one correspondence between edges and vertices of the polyhedron and of the graph. The graph

is *planar* because it can be realized on a plane without any crossing of edges. A way to imagine such a graph is that it represents the view of the inside of the polyhedron one would have if one of its faces were transparent and the polyhedron were viewed from a point just outside that face. The Schlegel diagram of a cuboctahedron is shown in Fig. 5.67 in what appears to be two quite different graphs. (The first is a view through a square face, and the second is a view through a triangular face). They can be shown to be topologically identical by writing out the *adjacency matrix* which contains 1 as element ij if vertex i is connected to j and 0 otherwise. The matrix below uses the vertex numberings of the figure.

$i \backslash j$	1	2	3	4	5	6	7	8	9	10	11	12
1	0	1	0	1	1	0	0	0	0	1	0	0
2	1	0	1	0	0	1	0	0	0	1	0	0
3	0	1	0	1	0	1	0	0	1	0	0	0
4	1	0	1	0	1	0	0	0	1	0	0	0
5	1	0	0	1	0	0	0	0	0	0	1	1
6	0	1	1	0	0	0	1	1	0	0	0	0
7	0	0	0	0	0	1	0	1	0	1	0	1
8	0	0	0	0	0	1	1	0	1	0	1	0
9	0	0	1	1	0	0	0	1	0	0	1	0
10	1	1	0	0	0	0	1	0	0	0	0	1
11	0	0	0	0	1	0	0	1	1	0	0	1
12	0	0	0	0	1	0	1	0	0	1	1	0

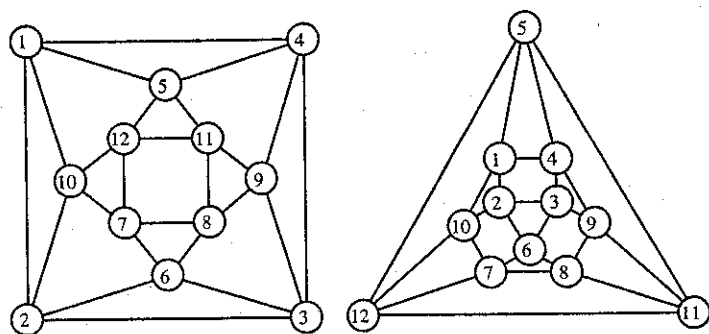


Fig. 5.67. Two representations of a cuboctahedron 3.4.3.4 by Schlegel diagrams. The numbering is the same as used for the adjacency matrix above.

A warning on terminology: Mathematicians refer to the graph of a polyhedron as 3-connected because *at least* three edges have to be cut to separate the graph into disjoint pieces. However, it is common usage in chemistry to call a net in which n edges meet at every vertex as n -connected. Mathematicians refer to such vertices as n -valent. Schlegel diagrams are sometimes used to describe the topology of coordination figures in solids.

The problem of enumerating polyhedra with a given number of vertices is the same as that of enumerating distinct 3-connected (in the mathematical sense) planar graphs.

Adjacency matrices are utilized extensively in molecular chemistry. Thus one way to recognize molecules with identical topologies in a computer is to compare their adjacency matrices. It might be mentioned that for large molecules, this is a far from trivial task as to get identical adjacency matrices the vertices must be numbered the same in each molecule.

5.6.5 Coordinates for drawing polyhedra and nets

Some important polyhedra are conveniently drawn on the framework of a cube. Let the origin be at 0,0,0 and the cube vertices $\pm 1, \pm 1, \pm 1$. The vertices of some other polyhedra are given below [remember κ stands for cyclic permutation and $\tau = (1 + \sqrt{5})/2$]. To get coordinates for a clinographic projection, use the method outlined in § 4.6.1.

tetrahedron	$1, 1, 1; (-1, -1, 1)\kappa$ or $-1, -1, -1; (1, 1, -1)\kappa$
octahedron	$(\pm 1, 0, 0)\kappa$
cuboctahedron	$(0, \pm 1, \pm 1)\kappa$
truncated octahedron	$(0, \pm 1/2, \pm 1; \pm 1/2, 0, \pm 1)\kappa$
rhombic dodecahedron	$\pm 1, \pm 1, \pm 1; (\pm 2, 0, 0)\kappa$
icosahedron	$(0, \pm \tau, \pm 1)\kappa$

For other cubic polyhedra the matrices for the symmetry operations of the appropriate symmetry group (see Exercises 7, 9 & 10 of Chapter 2) can be used to generate coordinates of the N vertices from those of the one given below (appropriate for unit edge). To generate coordinates for polyhedra with icosahedral symmetry, it is best to first generate the matrices for the symmetry operations of I and I_h as described in Exercises 7 and 16 of Chapter 2. These can be then applied to the coordinates of a typical vertex (given below). In the table, N is the number of vertices and the coordinates are appropriate for cartesian axes oriented as described in Exercise 16 of Chapter 2 and for unit edge length.

polyhedron	N	symmetry	coordinates
3.6^2	12	$\bar{4}3m$	$1/\sqrt{8}, 1/\sqrt{8}, 3/\sqrt{8}$
$3.4.3.4$	12	$m\bar{3}m$	$0, 1/\sqrt{2}, 1/\sqrt{2}$
4.6^2	24	$m\bar{3}m$	$0, 1/\sqrt{2}, \sqrt{2}$
3.8^2	24	$m\bar{3}m$	$1/2, y, y; y = (1+\sqrt{2})/2$
$3^4.4$	24	432	$0.3378, 0.6212, 1.1426$
3.4^3	24	$m\bar{3}m$	$1/2, 1/2, (1+\sqrt{2})/2$
$4.6.8$	48	$m\bar{3}m$	$1/2, 1/2+1/\sqrt{2}, 1/2+\sqrt{2}$
3^5	12	I_h	$0, 1/2, \pi/2$
5^3	20	I_h	$\pi/2, \pi/2, \pi/2$
$3.5.3.5$	30	I_h	$0, 0, \tau$
3.10^2	60	I_h	$0, (3\tau+1)/2, 1/2$
5.6^2	60	I_h	$0, 1/2, 3\pi/2$
$3.4.5.4$	60	I_h	$0, 1+\pi/2, (1+\pi)/2$
$3^4.5$	60	I	$0.3309, 0.3748, 2.0970$
$4.6.10$	120	I_h	$1/2, 1/2, 2\tau+1/2$

Coordinates of the vertices in Archimedean tilings with unit edge are also given below. For some other two-dimensional patterns see *OKH*. Recourse to the *International Tables* will be necessary to generate equivalent positions from the ones given.

tiling	symmetry	cell	x, y
$3^4.6$	$p6$	$a = \sqrt{7}$	$3/7, 1/7$ (or $1/7, 3/7$)
$3^3.4^2$	$c2mm$	$a = 1, b = 2 + \sqrt{3}$	$0, (1 + \sqrt{3})/(4 + \sqrt{12})$
$3^2.4.3.4$	$p4gm$	$a = \sqrt{2 + \sqrt{3}}$	$x, 1/2 + x; x = 1/\sqrt{16 + \sqrt{192}}$
$3.6.3.6$	$p6mm$	$a = 2$	$0, 1/2$
$3.4.6.4$	$p6mm$	$a = 1 + \sqrt{3}$	$x, \bar{x}; x = 1/(3 + \sqrt{3})$
4.8^2	$p4mm$	$a = 1 + \sqrt{2}$	$x, 1/2; x = 1/(2 + \sqrt{8})$
3.12^2	$p6mm$	$a = 2 + \sqrt{3}$	$x, \bar{x}; x = 1 - 1/\sqrt{3}$
$4.6.12$	$p6mm$	$a = 3 + \sqrt{3}$	$x, y; x = 1/(3 + \sqrt{27}), y = 1/3 + x$

5.6.6 Names of polygons and polyhedra

The names of polygons specify the number of angles they have, -gon comes from the Greek word for angle (a goniometer is an angle-measuring device). The names of polyhedra often specify the number of faces they have; -hedron likewise coming from the Greek for face. The prefixes come from Greek words for numbers. Some of the more commonly used are given below.

1	mono-	8	octa-	16	hexakaideca-
2	di-	9	ennea-	20	icosa-
3	tri-	10	deca-	30	triaconta-
4	tetra-	11	hendeca-	32	icosidodeca-
5	penta-	12	dodeca-	60	hexaconta-
6	hexa-	13	triskaideca-	many	poly-
7	hepta-	14	tetrakaideca-		

A polygon is called *skew* if all the vertices are not all in one plane.

The words "tetrahedra," "octahedra," etc. are plural. The singulars are "tetrahedron," "octahedron," etc. The usage "tetrahedrons," "octahedrons," etc. for the plural is also considered acceptable. The term "polyhedron" applies *only* to three-dimensional figures. For higher dimensional analogs use "polytope" (as in Appendix 2).

5.6.7 The shapes of crystals

It is worth recalling that the sciences of crystallography and solid state chemistry have their roots in mineralogy. Some symmetrical minerals crystallize in beautiful polyhedra. If a cubic crystal has a $\{100\}$ habit then with planes equally spaced from a center the crystal will be a cube (look at table salt under a magnifying glass). Similarly $\{111\}$ results in an octahedron in a centrosymmetric crystal and $\{110\}$ results in a rhombic dodecahedron. Cuprite (Cu_2O) occurs with all these habits and garnets sometimes form spectacular dodecahedra. Other common shapes include cuboctahedra and truncated octahedra in which the faces are $\{100\}$ (squares) and $\{111\}$ (triangles). Hexagonal crystals such as beryl often

occur as hexagonal prisms; the $\{11\bar{2}0\}$ faces are termed the prism faces and the top and bottom (0001) planes are referred to as pinacoid.

In class $m\bar{3}$ a form $\{hk0\}$ consists of the 12 cyclic permutations of $(\pm h \pm k 0)$. ($hk0$) and ($kh0$), for example, are related by a 4-fold rotation (about the z axis) which is not an operation in $m\bar{3}$ [so ($hk0$) and ($kh0$) are not part of the same form]. Pyrites (FeS_2), which has symmetry $Pa\bar{3}$, commonly crystallizes with a $\{210\}$ habit producing beautiful dodecahedra with pentagonal faces known as *pyritohedra*. Fig. 5.68 illustrates such a polyhedron which appears to be a regular pentagonal dodecahedron, but the eye is being deceived. There are two kinds of vertex: eight (X) at $\pm x, \pm x, \pm x$ (at the corners of a cube) shown as filled circles in the figure and twelve (Y) at $(\pm 3x/4, \pm 3x/2, 0)$ shown as open circles. The edge lengths are $Y-Y = 3x/2$ and $X-Y = \sqrt{2}x/4$ and the face angles are $XYX = 102.6^\circ$, $YXY = 106.6^\circ$ and $YXY = 121.6^\circ$ (contrast all are 108° for a regular pentagon).

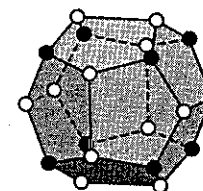


Fig. 5.68. The pyritohedron described in the text.

Some terms commonly used by mineralogists to describe the external form of crystals are:

<i>euhedral</i>	refers to crystal completely bounded by well-formed faces
<i>anhedral</i>	is the opposite of euhedral
<i>acicular</i>	needle shaped (long thin crystals)
<i>tabular</i>	having two prominent parallel faces (like a tablet)
<i>micaceous</i>	an extreme case of tabular (occurring as thin sheets as in mica)
<i>hemimorphic</i>	refers to crystals with different forms at each end
<i>lamellar</i>	occurring as a sheaf of thin sheets like pages in a book

5.6.8 $\text{Na}_3\text{Pt}_4\text{Ge}_4$: a structure with stellae quadrangulae

Stellae quadrangulae (§ 5.1.2, p. 135) are important in intermetallic structures. A nice example of their occurrence is in the structure of $\text{Na}_3\text{Pt}_4\text{Ge}_4$ ($\text{Eu}_3\text{Ni}_4\text{Ga}_4$ is isostructural). In this structure, a Pt tetrahedron has each face capped to make a Pt_4Ge_4 stella quadrangula. Each Ge atom is then linked to a fourth Pt on a neighboring stella quadrangula to make an open body-centered cubic array (Fig. 5.69). The open space in the structure is filled by a 4-connected net of Na atoms (in § 7.3.11 we refer to this as the NbO net). We note in passing that Na_3SbS_4 has a closely-related structure (sometimes called Ti_3VS_4) with $\{\text{Sb}\}\text{S}_4$ tetrahedra replacing the stellae quadrangulae (see Fig. 5.69).

Na is also in a distorted $\{\text{Na}\}\text{S}_4$ tetrahedron. Crystallographic data are in Appendix 5.

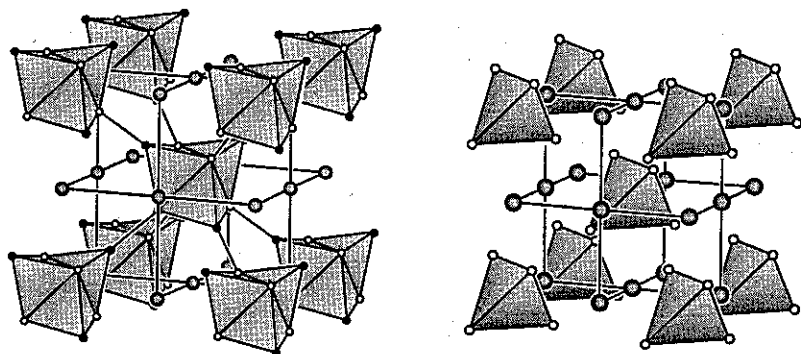


Fig. 5.69. Left: the structure of $\text{Na}_3\text{Pt}_4\text{Ge}_4$. Small open circles are Pt, small filled circles are Ge, and larger circles are Na. Right: the structure of Na_3SbS_4 showing $\{\text{Sb}\}\text{S}_4$ tetrahedra. Large circles are Na.

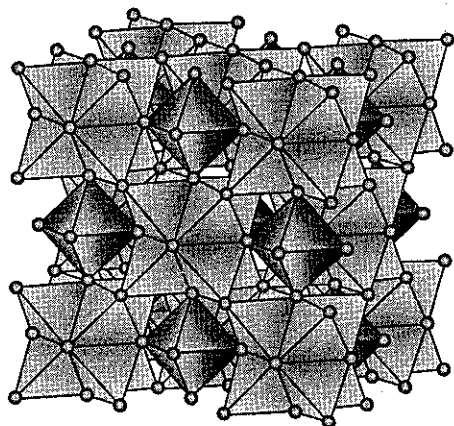


Fig. 5.70. The structure of Co_9S_8 shown as a packing of stellae octangulae and octahedra. Co atoms (not shown) are in $\{\text{Co}\}\text{S}_4$ tetrahedra and $\{\text{Co}\}\text{S}_6$ octahedra.

5.6.9 Co_9S_8 : a structure with stellae octangulae

The structure of Co_9S_8 [the mineral pentlandite = $(\text{Fe},\text{Ni})_9\text{S}_8$ is isostructural] is a nice example of a structure in which stellae octangulae are a conspicuous feature. A stella octangula (Fig. 5.3, p. 135) has 6 inner vertices and eight outer ones. In the Co_9S_8 structure (Fig. 5.70) Co centers the tetrahedra of a S_6S_8 stella quadrangula to produce a

$\text{Co}_8\text{S}_6\text{S}_8$ unit. These units are joined together as shown in the figure; each outer vertex is shared between four units, so the stoichiometry is now $\text{Co}_8\text{S}_6\text{S}_{8/4} = \text{Co}_8\text{S}_8$. There are empty S_6 octahedra inside the stella quadrangulae; in the packing, new S_6 octahedra are generated (one per Co_8S_8 unit), and these are also filled with Co to make the overall stoichiometry Co_9S_8 . The S atom arrangement is cubic closest packing (ccp, § 6.1.3).

Crystallographic data for Co_9S_8 are given in Appendix 5.

5.6.10 Enumeration of Archimedean polyhedra and tilings

We remarked (§ 5.3.1) that the regular tilings were limiting cases of regular polyhedra (the idea appears to have originated with Kepler) as in the sequence: 3^3 , 3^4 , 3^5 (polyhedra) and 3^6 (plane tiling). In Table 5.6 below, the archimedean polyhedra and tilings are listed in families according to the number of polygons meeting at a vertex.

Table 5.6. Archimedean polyhedra and tilings

polyhedra				tilings	
	3.6^2	3.8^2	3.10^2	3.12^2	
	4.6^2			4.8^2	
	5.6^2				
$N.4^2$	(prisms)				
		$4.6.8$	$4.6.10$	$4.6.12$	
$3^3.N$	(antiprisms)				
$3.4.3.4$	$3.5.3.5$			$3.6.3.6$	
$3.4.5.4$				$3.4.6.4$	
3.4^3					
$3^4.4$	$3^4.5$			$3^4.6$	
				$3^3.4^2$	$3^2.4.3.4$

How can we be sure that the list is complete? We need first to require the sum of the angles at the vertices is $\leq 360^\circ$ (with equality applying for plane tilings). The vertex angle of a regular plane n -gon is $180^\circ - 360^\circ/n$ so we must have for the sum over the i vertices:

$$\sum_i (1 - 2/n_i) \leq 2 \quad (5.1)$$

However this equation admits many more solutions than appear in the table. What about the polyhedron $3.4.6$ which is missing? Let's calculate the number of vertices, V , such a polyhedron should have. The number of edges, E , is $3V/2$ (as three edges meet at each vertex and each edge belongs to two vertices). An n -gon at a vertex is shared by n vertices and contributes $1/n$ of a face per vertex, so the number of faces is $F = V(1/3 + 1/4 + 1/6)$. Now solving Euler's equation $F - E + V = 2$, we find $V = 8$. Hence $F = 6$. So far, so good. But using our argument that there are $V/3$ triangular faces, $V/4$ square faces and $V/6$ hexagonal faces, we find that our polyhedron has to consist of $8/3$ triangular faces, 2 square faces and $8/6 = 4/3$ hexagonal faces; clearly impossible.

Actually in this case, simple topological considerations show that 3.4.6 is impossible. To see this, draw a triangle and the third edge meeting at each of the triangle vertices. The polygons must alternately be 4-gons and 6-gons on each side of these edges; this is impossible as the number of such edges is an odd number (3).

In general, the possible polyhedra or tilings are those that satisfy Eq. 5.1 and are of the sort:

$p.q.r$	with p, q, r all even
$p.q.q$	with q even
$p.p.p$	
4^4 and $3.p.q.r$	when $q \neq 3$, p and $r \neq 3$
$p.q.r.s.t$ and 3^6	

It is interesting that all the topological possibilities involving one kind of vertex can be realized with regular polygons. In general this is not the case when there is more than one kind of vertex. The general problem of deciding whether a given set of polygons (regular or not) can be combined into a polyhedron is of interest in chemistry (see Appendix 4 for more on this topic), but unfortunately it is also difficult and unsolved.

5.6.11 Euler's equation applied to plane nets

The celebrated Euler equation relating the numbers of faces, F , edges, E and vertices V for a finite polyhedron is

$$V + F = E + 2 \quad (5.2)$$

For a plane tiling

$$V + F = E \quad (5.3)$$

As V , F and E are all infinite, Eq. 5.3 is conveniently divided through by V . This equation also applies to a tiling on the surface of a torus ("doughnut").¹

Let ϕ_n be the fraction of the polygons in a tiling (or net) that are n -gons, then $\langle n \rangle = \sum n \phi_n$ is the average size of the polygons of the pattern. Likewise let f_i be the fraction of vertices at which i vertices meet, then $\langle i \rangle = \sum i f_i$ is the average connectivity of the net. Using the facts that each edge is common to two polygons and joins two vertices, it may be derived, using arguments similar to those used in the previous section, from Eq. 5.3:

$$1/\langle n \rangle + 1/\langle i \rangle = 1/2 \quad (5.4)$$

¹There are certain pathological kinds of tiling for which this equation does not hold: "Euler's Theorem for Tilings is of fundamental importance, but is a strong contender for one of the most frequently misquoted results in mathematics!"—B. Grünbaum & G. C. Shephard, *Tilings and Patterns* (Book List). The Swiss mathematician L. Euler (1707-83) was perhaps the most prolific in history—his bibliography requires a substantial shelf of volumes. He made significant contributions to virtually all parts of mathematics but geometry was his favorite.

An example of the application of this formula is to tilings of the plane by (not necessarily regular) triangles ($\phi_3 = 1$, $\langle n \rangle = 3$) to give $\langle i \rangle = 6$. This shows that the average number of triangles meeting at a point must be six. As $\langle n \rangle$ cannot be less than 3, $\langle i \rangle$ cannot be greater than 6.

For a pattern with three polygons meeting at a point (a 3-connected net, $\langle i \rangle = 3$) Eq. 5.4 shows that the average polygon size (ring¹ size) $\langle n \rangle = 6$. This means that there is no constraint on the number of six-rings. For the pentagon-hexagon-heptagon nets of § 5.3.5, let there be ϕ_5 pentagons, ϕ_7 heptagons and $1 - \phi_5 - \phi_7$ hexagons. Equation 5.4 becomes:

$$5\phi_5 + 6(1 - \phi_5 - \phi_7) + 7\phi_7 = 6, \text{ i.e. } \phi_5 = \phi_7.$$

In general for any infinite plane net in which all vertices have the same connectivity i (the vertices need not otherwise be the same) one has ("rings per vertex" refers to the average over all the vertices):²

Connectivity, i	rings per vertex	average ring size
6	2	3
5	3/2	10/3
4	1	4
3	1/2	6

5.6.12 Transformations between patterns: common unit cells

It should be clear that two patterns with the same densities of points can be converted from one to the other by shuffles of the points that involve just finite displacements.

A special kind of structural relationship is one in which there is no change in shape of the unit cell. A simple example is the relationship between the kagome (3.6.3.6) and 3^6 patterns (Fig. 5.40, p. 167). The common hexagonal cell is given in Exercise 11.

First a common cell that may be a supercell of one or both structures must be found. This supercell will, of course contain the same number of points for each of the patterns. The transformation can then be effected just by moving the points in the cell.

Consider square (two-dimensional) cells first. A primitive cell for the square lattice has sides a . A non-primitive cell can be chosen with translation vectors $ua + vb$ and $-va + ub$ with area $u^2 + v^2$ and containing $u^2 + v^2$ lattice points.

The number of atoms in a unit cell can be expressed uniquely as Ap , where p can be represented as the sum of two squares ($u^2 + v^2$, including zero as a square) and A is either 1 or a number that cannot be expressed as $u^2 + v^2$. Only if patterns have the same A , will they have a common square supercell.

Patterns with common A are described as *compatible*. Sorted by value of A , we have for $Ap \leq 21$:

¹In discussing chemical compounds it is more usual to talk about "rings" (as in "benzene ring") rather than "polygons." In the present context the terms are synonymous.

²As the average ring size is 3 for 6-connected nets, it follows that in the absence of 2-rings (loops) all the rings in a 6-connected net are 3-rings and 3^6 is the *only* 6-connected net.

$A = 1$	$Ap = 1, 2, 4, 5, 8, 9, 10, 13, 16, 17, 18, 20, \dots$
$A = 3$	$Ap = 3, 6, 12, 15, \dots$
$A = 7$	$Ap = 7, 14, \dots$
$A = 11$	$Ap = 11, 21, \dots$
$A = 19$	$Ap = 19, \dots$

The square lattice (the regular tiling 4^4) has one point per cell and so belongs in the class with $A = 1$. The important tiling $3^2.4.3.4$ (Fig. 5.39) has four vertices per unit cell (§ 5.6.5) and so is compatible with 4^4 . Fig. 5.41 (p. 167) illustrated that the transformation from one structure to the other can be effected by concerted rotations of squares. This relationship is valuable in relating layers of crystal structures.

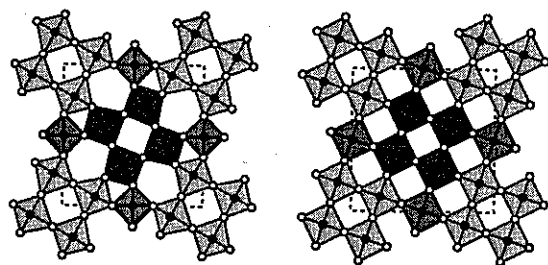


Fig. 5.71. The relationship between TTB (left) and 4^4 (right). Corresponding parts of each diagram are equally shaded for ease of comparison.

As a second example we illustrate (Fig. 5.71) the relationship between 4^4 and the tetragonal tungsten bronze (TTB) net (Fig. 5.43, p. 170) with 20 points in the unit cell (i.e. $A = 1$ again). Again the transformation between the two structures is effected by rotations of groups of vertices. For other examples see *OKH*.

In both these examples the common supercell is the larger of the two. If we wanted to inter-relate patterns with (say) 4 and 5 points per cell respectively, we would have to use a supercell with 20 points per cell to describe the transformation.

Similar considerations apply to two-dimensional hexagonal patterns. A non-primitive hexagonal cell with translation vectors $ua + vb$ and $-va + (u-v)b$ (derived from a primitive cell defined by a and b) will have area $u^2 - uv + v^2$ containing $u^2 - uv + v^2$ lattice points. Let the number of points in a hexagonal cell be Bq , where q can be expressed as $u^2 - uv + v^2$ and B is either 1 or cannot be so expressed. Hexagonal patterns with a common B will have a common super-cell and thus will be compatible.

Sorted by value of B we have for $Bq \leq 20$:

$B = 1$	$Bq = 1, 3, 4, 7, 9, 12, 13, 16, 19, \dots$
$B = 2$	$Bq = 2, 6, 8, 14, 18, \dots$
$B = 5$	$Bq = 5, 15, 20, \dots$
$B = 10$	$Bq = 10, \dots$
$B = 11$	$Bq = 11, \dots$

In Fig. 5.40 we demonstrated that 3^6 (one vertex per cell, $B = 1$) and $3.6.3.6$ (three vertices per cell, $B = 1$) were indeed compatible and illustrated their relationship.

6^3 (2 vertices per cell) belongs to the $B = 2$ family, so it cannot be transformed to 3^6 (for example) without a change of shape of cell. But 6^3 is compatible with $3^4.6$ and $3.4.6.4$ (both six vertices per cell, $B = 2$). Fig. 5.72 illustrates that the relationship between them is very simple and can be effected by rotating the shaded hexagonal groups of vertices.

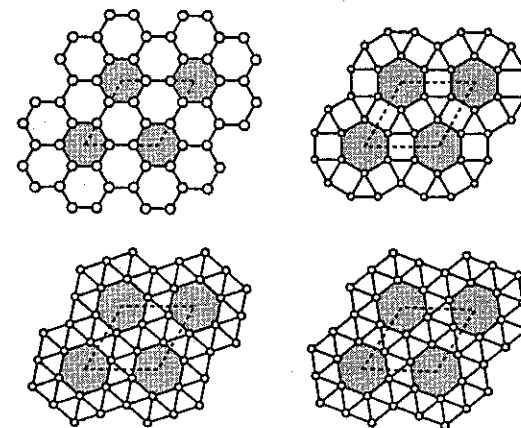


Fig. 5.72. Relationships between 6^3 (top left), $3.4.6.4$ (top right) and enantiomorphs of $3^4.6$ (bottom).

A slightly more subtle example involves the relationship between the $\alpha\text{-U}_3\text{O}_8$ and $\beta\text{-U}_3\text{O}_8$ nets (see § 5.3.4). $\alpha\text{-U}_3\text{O}_8$ is hexagonal with five vertices per cell ($B = 5$ family). $\beta\text{-U}_3\text{O}_8$ is centered rectangular with ten vertices per cell, but the primitive cell is *almost* metrically hexagonal (there are no 3- or 6-fold symmetry axes of course) and also has five vertices per cell. Fig. 5.73 shows that these two nets are simply related by rotation of pentagonal groups of vertices (shown shaded in the figure). In this example, because $\beta\text{-U}_3\text{O}_8$ is not strictly hexagonal, we do have a *small* change of unit cell shape.

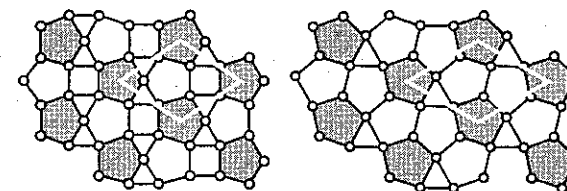


Fig. 5.73. Relationship between the $\alpha\text{-U}_3\text{O}_8$ (right) and $\beta\text{-U}_3\text{O}_8$ (left) nets. A primitive cell (with an unconventional origin) is shown as white lines.

this corresponds to the operation of c glide normal to a as indicated in the space group symbol). In $P6_3/mmc$ adjacent layers of symmetry $p3m1$ are related to each other by reflection in mirrors parallel to a (operation of c glide plane containing a as indicated in the space group symbol). Layers with symmetry $p6$ can be also be stacked with alternate layers related by c glide but now one set of glide planes automatically generates a second set and there is again only one possibility: symmetry $P6/mcc$.

A square layer has 4-fold axes at the center of the cell as well as at the corners (see Fig. 1.13, p. 16) so square layers can be stacked with alternate layers displaced by $1/2, 1/2, 1/2$. This is the only possibility for layers with symmetry $p4mm$ and $p4gm$.

Finally, note that a two-layer stacking of layers of symmetry $p6mm$ is not possible. This is because there is no three-dimensional crystallographic operation relating the layers that will not leave them unchanged, so the only possible stacking of such layers is that in which they are directly one above the other and then there is a single layer structure with symmetry $P6/mmm$. It follows at once that there cannot be a self-dual net with symmetry $p6mm$. On a little reflection (!) this result should become "obvious."

5.6.15 More structures with dual nets: Fe_2P

In § 5.3.7 we gave some examples of structures that were simply described as stackings of self-dual nets. The description is particularly attractive as once the 2-dimensional net and the spacing between layers are specified, the structure is completely determined; although to fully appreciate the structure, it should be illustrated in more than way (for example by also emphasizing the pattern of trigonal prisms).

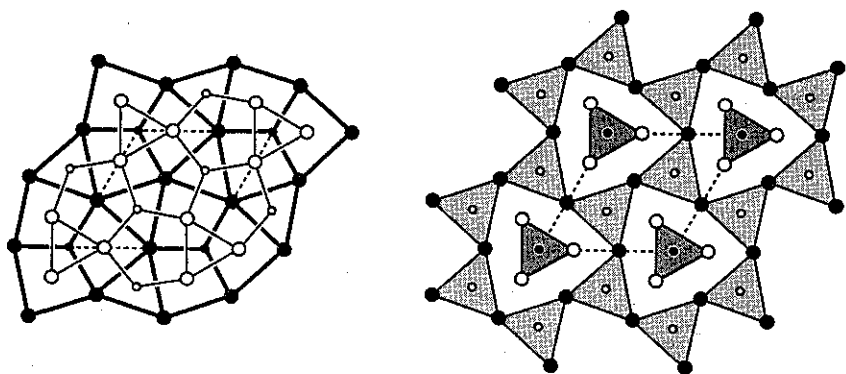


Fig. 5.75. The structure of Fe_2P projected on (0001). Larger circles are Fe. Filled (open) circles are at $z = 1/2$ (0). Left: showing the nets at $z = 1/2$ (heavy lines) and at $z = 0$ (lighter lines). Right: as $(P)Fe_6$ trigonal prisms centered at $z = 0$ (lighter shaded) and at $z = 1/2$.

A related group of structures can be described in terms of stackings of dual (but not self-dual) nets. These structures are generally more complicated, in the sense that there are more

crystallographic kinds of atom, because atoms on the two layers are not related by symmetry. The simplest structure of this sort is $Fe_2P = Fe(1)_3Fe(2)_3P(1)P(2)_2$ (for crystallographic data see Appendix 5).

Figure 5.75 shows a projection of the hexagonal ($P\bar{6}2m$) structure on (0001). It may be seen that the layers at $z = 0$ and $z = 1/2$ are different, but the nets are indeed the duals of each other.¹ Such an illustration allows a ready determination of the coordination of all the atoms, but it is hard to see the larger-scale organization of the structure. On the right in the figure $(P)Fe_6$ trigonal prisms centered at $z = 0$ and $z = 1/2$ are emphasized; now the linkage of these polyhedra is more apparent.

5.7 Exercises

1. The dual of the bisdisphenoid is an octahedron which also has $\bar{4}2m$ symmetry (of course!), and has four faces that are pentagons and four that are quadrilaterals. Can this polyhedron be made with faces that are regular polygons? (No.)

There is an octahedron with three pentagonal and five triangular faces that can be made with regular polygons. [Hint remove three vertices from a regular icosahedron.]

2. If polyhedra are to fill space, the solid angles at the vertices that meet at a point must sum up to 4π (720°) and the dihedral angles at a common edge must sum up to 360° . Verify that the solid angle at the vertex of a truncated octahedron is 180° (a useful formula is Eq. 4.15) and that the dihedral angles are 120° . Truncated octahedra indeed do fill space with three polyhedra meeting at an edge, and four meeting at a vertex (see § 7.3.10).

3. Regular tetrahedra alone cannot fill space. The solid angle at the vertex of a regular tetrahedron is $3\cos^{-1}(1/3) - \pi = 31.59^\circ$ so at most 22 regular tetrahedra can have a common vertex. But at most five regular tetrahedra can have a common edge (the dihedral angle of a regular tetrahedron is $\cos^{-1}(1/3) = 70.52^\circ$) so in fact only 20 regular tetrahedra can have a common vertex. (Do the experiment with 21 regular tetrahedra!). A regular icosahedron can be considered as made up of 20 tetrahedra with three edges equal to unity and three edges (meeting at the center) equal to $5^{1/4}\sqrt{[(1 + \sqrt{5})/8]} = 0.9511$. [These considerations are relevant to the shapes of small clusters of metal atoms].

4. A linear rod can be made of regular tetrahedra sharing faces (so that the tetrahedron centers fall on a straight line). The vertices fall on an aperiodic helix.² Are the positions of the vertices described by a quasiperiodic function? (Yes.)

¹The net at $z = 0$ (open circles in the figure) should be recognized as the $\alpha-U_3O_8$ net (see Fig. 5.44, p. 172).

²A nice, but challenging, problem. See H. Nyman *et al.*, *Zeits. Kristallogr.* **196**, 39 (1991) for some help. Such a rod is known as a "Bernal Spiral". For more on this beautiful structure see also C. Zheng *et al.*, *J. Amer. Chem. Soc.* **112**, 3784 (1990).

5. It is simple to demonstrate that the volumes of regular tetrahedra, octahedra and truncated tetrahedra with the same edge length are in the ratio 1 : 4 : 23. (Hint: combine each of the larger polyhedra in turn with four tetrahedra to make larger tetrahedra.)

6. The reader might enjoy deriving results similar to Eq. 5.4 from Eq. 5.2 for finite polyhedra. For example it is not difficult to show that if a closed shell (polyhedron) of "graphite" (three-connected C atoms) is made, in addition to hexagonal rings (as in graphite), there must be 12 pentagonal rings. C_{60} and C_{70} are well known examples.

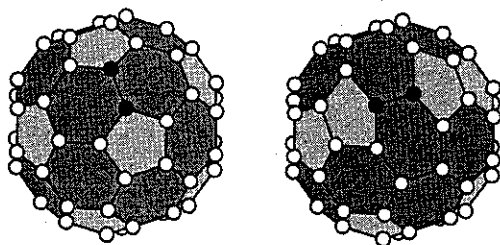


Fig. 5.76. The polyhedron shown on the left is the truncated icosahedron (5.6²). On the right is a topological isomer.

Hint: if three polygons meet at each vertex, $E = 3V/2$ [incidentally showing that the number of vertices must be even] and Eq. 5.2 becomes $2F = V + 4$. Let there be F_5 pentagonal faces and F_6 hexagonal faces so that $F = F_5 + F_6$. As each vertex belongs to three polygons there are $6/3$ vertices per hexagon and $5/3$ vertices per pentagon

Figure 5.76 shows, on the left, the truncated icosahedron (5.6²) which has 60 vertices, 20 hexagonal faces and 12 pentagonal faces. On the right of the figure is shown a topological isomer with the same number of faces but some vertices are 5².6 and 6³; it is derived from 5.6² by rotating the two vertices shown as filled circles.¹

7. The combination of two regular pentagons and a regular decagon meeting at a point have the sum of their angles equal to 360° but there is no tiling 5².10.² Show that nevertheless the combination of two pentagons and a decagon per vertex satisfies Eq. 5.3.

8. Verify for the Archimedean tilings (Table 5.4, § 5.3.2) that the average ring sizes and numbers of rings per vertex have the values given in § 5.6.11.

¹See A. J. Stone & D. J. Wales, *Chem. Phys. Letts.* **128**, 501 (1986).

²This problem fascinated Kepler, who produced some beautiful tilings consisting largely (but of course not entirely) of regular pentagons and decagons [see Grünbaum & Shephard (Book List)].

9. There is a simple tiling of the plane by congruent pentagons.¹ The symmetry is $p4gm$ with $a = \sqrt{(4 + \sqrt{7})}$. There are two kinds of vertex: one at $2a$: 0,0 ; 1/2,1/2 and the second at $4c$: $\pm(x, 1/2+x ; 1/2-x, x)$ with $x = 0.363$. Four pentagons meet at one vertex and three at the other (Fig. 5.77). The pattern is known as *Cairo tiling* or *MacMahon's net*.²

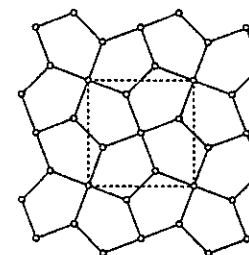


Fig. 5.77. MacMahon's net (Cairo tiling).

10. Show that the transformation $3.6.3.6 \rightarrow 3^6$ illustrated in Fig. 5.40 can be described analytically as follows: We take a cell containing three points at positions $3c$ of $p31m$ ($x,0; 0,x; \bar{x},\bar{x}$) with $x = (3 - 2\sin\phi)/6$ and unit cell edge $a = d/\sqrt{(3x^2 - 3x + 1)}$ where d is the shortest distance between points (the edges of the net). ϕ is the angle of rotation of the triangles of 3.6.3.6 so that $\phi = 0^\circ$ corresponds to 3.6.3.6 and $\phi = 30^\circ$ corresponds to 3^6 . The endpoints have symmetry $p6m$ and the true unit cell for 3^6 is $1/3$ the area of this cell. What happens when $\phi > 30^\circ$?

11. Describe the transformation $3^2.4.3.4 \rightarrow 4^4$ in a similar way to that in Exercise 10. (See Fig. 5.41; the symmetry in the general case in $p4gm$)

12. Consider tilings by the polygons shown in Fig. 5.65 such that every vertex is 5-connected. Show that Eq. 5.4 requires that $2/3 \leq \phi_3 \leq 5/6$, $0 \leq \phi_4 \leq 1/3$ and $0 \leq \phi_5 \leq 1/6$. Can you make a tiling with a 5-fold rotation point with these tiles? Can you make a periodic tiling using all three tiles and with all vertices 5-connected?

¹Enumerating the tilings of the plane with congruent pentagons is a famous problem and attempts at its solution have resulted in amateurs handily beating professional mathematicians. See M. Gardner in *Time Travel and Other Mathematical Bewilderments* [Freeman, New York (1988)].

²In Cairo (Egypt) the tiling is common for paved sidewalks. The net is featured in P. A. MacMahon's *New Mathematical Pastimes* [Cambridge, (1921)].