

CHAPTER 6

SPHERE AND CYLINDER PACKINGS

In this chapter and the next we discuss periodic three-dimensional structures. This extends the discussion from finite polyhedra, circle packings, and two-dimensional nets, to infinite polyhedra, sphere and cylinder packings, and three-dimensional nets. Now we are approaching the real world of crystal structures and examples of them will be met more frequently.

In many crystal structures one or several kinds of atom are in positions corresponding to the centers of spheres in a sphere packing, and other atoms are in positions corresponding to interstices of that packing. It is common (especially for mathematicians) to refer to such interstices as "holes," but that word has been appropriated to have a special meaning (referring to an electronic defect) in solid state science, so we avoid it. We generally just refer to "sites." In the same vein, the word "vacancy" has the meaning of a site that *should* be occupied but at some particular point in a real crystal is not (i.e. a special kind of atomic defect). We recommend using "vacancy" *only* in the context of defect thermodynamics and kinetics (and then with great care), and at other times using a term such as "unoccupied site" instead.

It is essential at the outset to recognize that we are here only concerned with the geometry of certain patterns of points which are of common occurrence in crystal structures. It is convenient to consider such patterns as arising from packings of spheres, but as they can also arise in several other contexts, it is important not to get a mental image of crystals as assembled from a packing of hard sphere "atoms" as is sometimes seen illustrated (we do this ourselves in § 6.1 and 6.2, but nowhere else). We shall see, for example, that in several simple and familiar crystal structures of binary compounds *AB* the arrays of *both* the *A* and the *B* atoms are the same as the centers of spheres in closest packing. Unless the spheres representing *A* and those representing *B* interpenetrate substantially there cannot be simultaneous *A-A* and *B-B* contacts.

One reason for discussing sphere packings is that it is hard to read the literature of crystal chemistry without some knowledge of the subject and its associated terminology. The most compelling reason is, however, that the topic introduces patterns that are ubiquitous in crystal structures; indeed it is hard to invent a simple symmetrical sphere packing that does not occur in nature. Our organization is by coordination number, starting with the densest packing of spheres; however, this is for convenience only; we could equally have chosen one of a number of other schemes.

6.1 The densest packing of spheres

We consider first the classical problem of packing equal-sized spheres in space as densely as possible (closest packing). It should be apparent that this is the same problem as that of arranging points of an infinite array with given density (number per unit volume) so

that the shortest distance between them is a maximum; stated this way, the problem is an extension of Tammes' problem (§ 5.1.9) which referred to arranging points (with fixed number per unit area) on the surface of a sphere such that the minimum distance between them was a maximum. Another problem with the same solution is to ask for ways of arranging points in space so that every point has twelve equidistant nearest neighbors. Yet another problem, again with the same solution, is to ask for the arrangement of vertices in space-filling packings of regular octahedra and tetrahedra with equal edges.

Thus the same geometrical arrangement arises in very different contexts, only one of which involves spheres in contact. When we want to emphasize such considerations we use the term *eutaxy* to mean "an arrangement corresponding to the centers of spheres in closest packing" and describe such arrays as *eutactic*. Generally though, we follow established usage indicated by bold face abbreviations in the next paragraph.

If we restrict ourselves to arrangements in which the points (or the centers of the spheres) fall on a lattice, there is just one solution to the above problem. The arrangement is commonly referred to as cubic closest packing (**ccp**), but we also use the term *cubic eutaxy*.¹ If the restriction to points on a lattice is lifted, we find a second arrangement of equivalent (symmetry-related) points known as "hexagonal closest packing" (**hcp**) or *hexagonal eutaxy*. There is an infinity of other arrangements with the same density, but with more than one kind (in the crystallographic sense) of point as we will see. We refer to these generically as **cp** or as *eutactic*. We consider only periodic patterns and state results mostly without proof.² The construction of models with a dozen or so polystyrene balls and toothpicks to hold them together will be found invaluable.

6.1.1 Stacking of close-packed layers

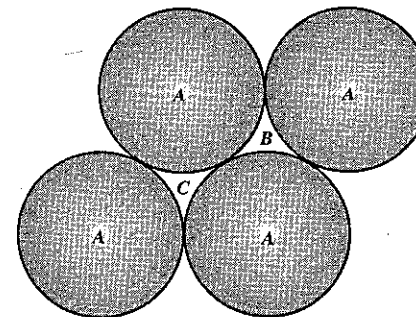


Fig. 6.1. Part of a layer of close-packed spheres. A marks the corners of a unit cell.

¹The term is used [as is "cubic closest packing" (**ccp**)] also for arrangements that only approximate the ideal arrangement.

²Some "obvious" results are remarkably difficult to prove in a way acceptable to mathematicians. For comments on the proof (by W. Hsiang) that "closest packing" is just that see N. Max, *Nature* **355**, 115 (1992).

Conceptually the simplest way to generate these patterns is to start with a layer of spheres lying on a flat surface in a closest-packed way.¹ Their centers will be on the vertices of a 3^6 net (a *cp* layer), just as in the densest circle packing. Fig. 6.1 shows four such spheres with centers at the corners of a hexagonal unit cell of 3^6 . In the figure the letters "A" are at these corners.

Now we add a second close-packed layer on top of the first. To have maximum density we want the spheres of the second layer to nestle in the depressions of the first, i.e. over the points marked "B" or "C." (It should be clear that B and C are too close for spheres of the second layer to be simultaneously over both of these positions). Accordingly there are two possibilities for the two-layer structure: AB or AC. These are of course identical arrangements (remember the layers are infinite in the plane). For the sake of subsequent discussion let the arrangement chosen be AB for the moment.

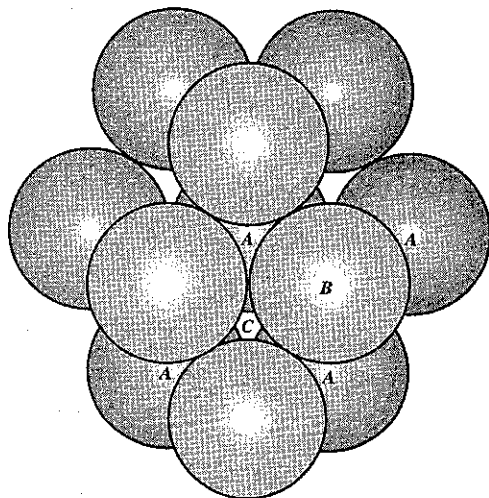


Fig. 6.2. Part of two layers of close-packed spheres. The letters are in the same place as in Fig. 6.1.

A small fragment of the two-layer packing is shown in Fig. 6.2. It should be clear from that figure that if we now add a third layer in a similar way, the centers of the spheres in the third layer must lie over either A or C so we have two *distinct* three-layer sequences: ABA and ABC. These differ in that in the first case the layers below and above the middle one are in same (A) positions, and in the second case the layers below and above the middle one are in different positions (A and C).

For unit diameter spheres in contact, the perpendicular distance between layers will be $\sqrt{2/3} = 0.8165$ (this is the height of a regular tetrahedron of unit edge, cf. p. 133).

¹This is why we pack spheres rather than, for example, polyhedra.

Fig. 6.3 shows parts of the two different three-layer sequences. At the top the spheres are packed ABC and at the bottom the sequence is ABA. The two simplest infinite packings would be obtained by repeating these sequences indefinitely: ABCABC... and ABAB....

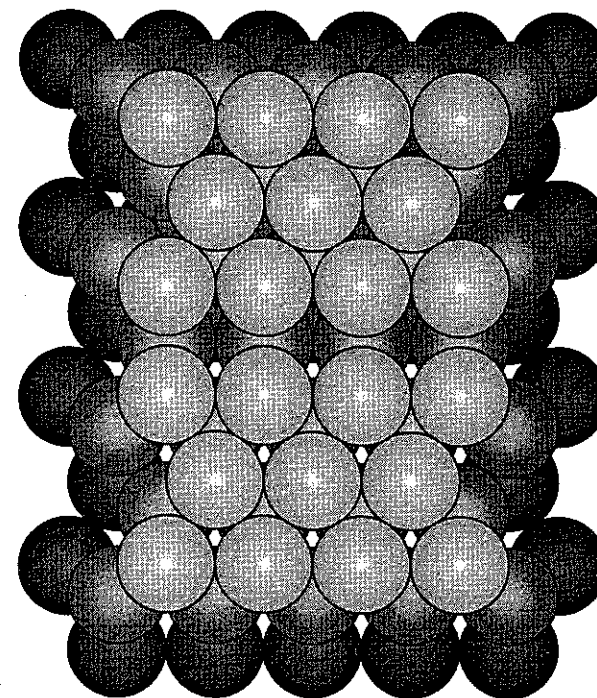


Fig. 6.3. Spheres packed in the sequence ABC (top half) and ABA (bottom half).

The centers of the spheres in a slab of two layers divide the slab into regular tetrahedra and octahedra. Fig. 6.4 shows how a tetrahedron and an octahedron are so defined by four and six sphere centers respectively. The eutactic arrangements of points thus also arise as the positions of the vertices when regular tetrahedra and octahedra are packed to fill space, and this is possibly the real reason for the common occurrence of eutaxy as the arrangement of cations and/or anions in so many compounds in which there is 4- and/or 6-fold coordination (see Notes § 6.8.3).

Figure 6.5 illustrates the arrangement of octahedra and tetrahedra in a two-layer slab. Each octahedron shares edges with six other octahedra. The tetrahedra can be divided into two groups (see Fig. 6.5): those "pointing down" and those "pointing up." Tetrahedra of each type share only vertices with each other, but each "up" tetrahedron shares three edges

with “down” tetrahedra in the same layer and *vice versa*. Altogether space is divided into equal numbers of octahedra, “up” tetrahedra and “down” tetrahedra.

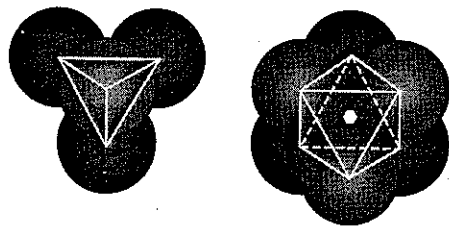


Fig. 6.4. A tetrahedron and an octahedron formed by spheres in contact.

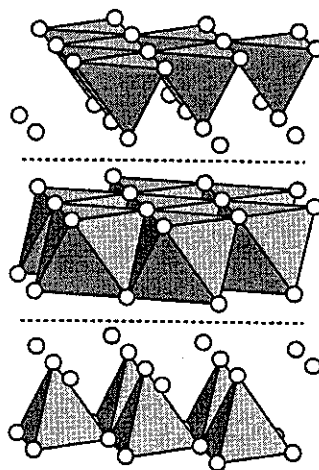


Fig. 6.5. Middle: the centers of 24 spheres (represented by circles) in a double layer of close packing showing the octahedral interstices. Top: the same points, but now showing the “down” tetrahedra. Bottom: the same points showing the “up” tetrahedra.

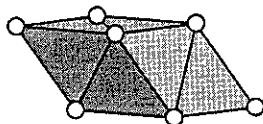


Fig. 6.6. A rhombohedron composed of an octahedron and two tetrahedra (compare Fig. 6.5).

The reader is urged to assemble such a layer with polyhedra. When that is done it will surely be noticed that two tetrahedra may be combined with an octahedron to form a 60° rhombohedron as shown in Fig. 6.6. Clearly this polyhedron fills space and contains one each of an “up” tetrahedron, a “down” tetrahedron and an octahedron. We will see that it is a unit cell of **ccp**. It should be clear that each two-layer slab can be divided into such rhombohedra, so all **cp** arrays are made up of octahedra, “up” tetrahedra, and “down” tetrahedra in equal amounts (one each per **cp** sphere).

6.1.2 Hexagonal eutaxy (**hcp**)

We discuss the case *AB...* first. We could equally label the sequence *AC..., BC..., etc.* which would describe exactly the same packing but with a different choice of origin. In fact if *A* is at the origin of a hexagonal cell, it is useful now to describe the two-layer repeat as *BC...* We can then get a convenient description in crystallographic terms of a hexagonal unit cell with sphere centers at $1/3, 2/3, 1/4$ and $2/3, 1/3, 3/4$. If the spheres are unit diameter, *a* will be 1.0 (see Fig. 6.1) and *c* will be $2\sqrt{2/3} = \sqrt{8/3} = 1.6330$. The *z* coordinates are chosen as $1/4$ and $3/4$ (rather than e.g. 0 and $1/2$) because we then have the origin of coordinates at a center of symmetry. The space group is $P6_3/mmc$. The arrangement of sphere center points is not a lattice, as a vector from the center of a sphere to the center of a contiguous sphere in an adjacent layer is not a lattice vector. The spheres are related by symmetry though; their centers are in the special positions $2c$ of $P6_3/mmc$.

In **hcp**, the planes normal to *c* and containing the centers of the spheres are mirror planes. It follows therefore, that the octahedra in successive layers share common faces and form face-sharing columns (parallel to *c*). The centers of the octahedra are at $0,0,0$ and $0,0,1/2$ in the unit cell ($2a$ of $P6_3/mmc$). On the other hand the tetrahedra will form pairs (one “up” and one “down”) with a common face. Recall that the “up” set of tetrahedra have only common vertices (are corner-sharing) as do the “down” set. The centers of the tetrahedra are in $4f$: $\pm(1/3, 2/3, z; 2/3, 1/3, 1/2+z)$ with $z = -1/8$.

6.1.3 Cubic eutaxy (**ccp**)

The rhombohedron of Fig. 6.6 with points at the vertices can be considered as the unit cell of a structure with the points coinciding with a lattice. The 60° rhombohedron is, in fact, a primitive cell of the face-centered cubic lattice (see § 4.4). Fig. 6.7 shows 14 spheres with their centers at the lattice points of a face-centered cubic cell. As can be seen from the figure the centers of the spheres lie in close-packed $\{111\}$ planes.

The structure we are describing is cubic eutaxy or “cubic close packing” (**ccp**). Discussed in terms of a stacking of close-packed layers the sequence is *ABC...* The simplest way to see this is to use the description of a rhombohedral lattice in terms of a centered hexagonal cell. Thus if the rhombohedral cell (Fig 6.7) has $a = 1$, $\alpha = 60^\circ$ then the hexagonal cell has $a = 1$, $c = 3\sqrt{2/3} = \sqrt{6} = 2.449...$ and the lattice points are at $0,0,0$ (*A*); $2/3, 1/3, 1/3$ (*B*); and $1/3, 2/3, 2/3$ (*C*).

The face-centered cubic cell contains four lattice points (at $0,0,0$; $1/2, 1/2, 0$; $1/2, 0, 1/2$

and $0, 1/2, 1/2$) and must therefore contain four octahedra. The octahedron centers are at $1/2, 1/2, 1/2$; $1/2, 0, 0$; $0, 1/2, 0$ and $0, 0, 1/2$ (i.e. at the body center and in the middle of each edge). These octahedral sites also fall on the points of a face-centered cubic lattice (displaced from the first by $1/2, 1/2, 1/2$).

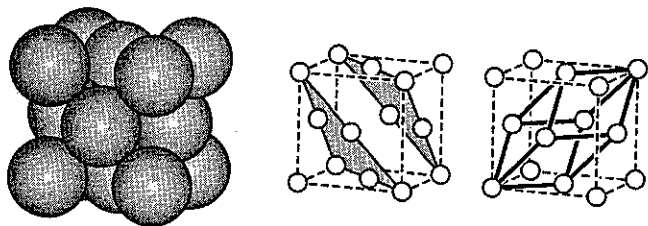


Fig. 6.7. Left: a face-centered unit cell with spheres centered at lattice points arranged in **ccp**. Center: the arrangement of the centers on (111) planes. Right: the primitive cell is heavily outlined.

The cubic unit cell also contains eight tetrahedral sites with centers at $\pm 1/4, \pm 1/4, \pm 1/4$.¹ Their centers are on a primitive cubic lattice with one-half the cell edge (see Fig. 6.11 below). The symmetry of **ccp** is $Fm\bar{3}m$ and the sphere centers are in $4a$. The octahedral sites are in $4b$ and the tetrahedral sites are $8c$.

The centers of the spheres in the {100} planes (i.e. parallel to the faces of the cubic unit cell) are on 4^4 nets so it can be seen that an alternative description of **ccp** is in terms of a stacking of such nets (see § 6.4.2). In close packing there is only one position for a second 4^4 layer on top of a first one, so **ccp** is the only close packing that admits this description.

In contrast to **hcp**, the octahedra in **ccp** share only edges (i.e. not faces), and as we have seen, their centers are also in **ccp**. The tetrahedra likewise share only edges. Viewed along one of the $\langle 111 \rangle$ directions the tetrahedra can be considered to fall into “up” and “down” sets in each of which, as for **hcp**, they share only vertices. We shall see that the centers of each of these sets are also **ccp**.

6.1.4 Other eutactic (cp) arrangements

The hexagonal and cubic arrangements **AB...** and **ABC...** are obviously just the simplest of an infinite number of possibilities of stacking close-packed layers. The next possibility is **ABAC...**

In all **cp** arrays each sphere is coordinated by 12 nearest neighbors and there are just two possibilities for the coordination figure. The first is the cuboctahedron, illustrated on the left in Fig. 6.8. The central sphere is in one of the positions *A*, *B* or *C* and the spheres in the layer above in one of the other two remaining positions and the spheres below in the third. To avoid the redundancy arising from the arbitrariness in the labels *A*, *B* or *C* it is often more convenient simply to label such a central layer *c*.

¹Recall that $-1/4$ is the same as $3/4$ in this context

The spheres in **hcp** have neighboring spheres at the vertices of a “twinned cuboctahedron” (also sometimes called an *anticuboctahedron*), shown on the right in Fig. 6.8. The spheres in the layers above and below the central sphere are now in the *same* positions. If the central sphere is in, for example, position *A*, those in the layers above or below are either both *B* or both *C*. Such a central layer is labeled *h*.

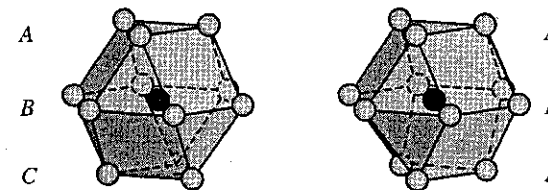


Fig. 6.8. The coordination of an atom (filled circle) by its neighbors in **ccp** (left) and **hcp** (right).

Any eutactic array can be described by a sequence of *c*'s and *h*'s as we now demonstrate. First write out the sequence in terms of *A*, *B* and *C* and then identify each layer as *h* or *c*. The layer will be *h* if the letters on either side are the same as each other, and will be *c* if the letters on the left and right are different from each other. Conversely a sequence of *c*'s and *h*'s can be converted to a sequence of *A*'s, *B*'s and *C*'s by starting arbitrarily with (e.g.) *AB*. A number of examples is given below (with on the right the conventional label).

<i>h h h h</i>	<i>h</i>
<i>A B A B A B</i>	<i>AB</i>
<i>c c c c</i>	<i>c</i>
<i>A B C A B C</i>	<i>ABC</i>
<i>h c h c h c</i>	<i>hc</i>
<i>A B A C A B A C</i>	<i>ABAC</i>
<i>h c c h c c h c c h c c</i>	<i>hcc</i>
<i>A B A C B C A B A C B C A</i>	<i>ABACBC</i>
<i>h h c h h c h h c h h c h h c</i>	<i>hhc</i>
<i>A B A B C B C A C A B A B C B C A</i>	<i>ABABCBCAC</i>

The symbolism in terms of *h* and *c* is more concise, but does not immediately reveal how many layers are in the repeat unit. Thus the repeat unit is six layers for *hcc* but nine layers for *hhc*. Many of the metallic elements crystallize as either *h* or *c* but more-complicated sequences are found. *Sm* for example occurs as both *hc* and *hhc* forms. We will meet **cp** arrays many times and in several different contexts later.

Another way of specifying stacking sequences is preferred by some authors. In this method, due originally to Zhdanov, a change from $A \rightarrow B$ or $B \rightarrow C$ or $C \rightarrow A$ is symbolized "+" and the reverse, i.e. $B \rightarrow A$ or $C \rightarrow B$ or $A \rightarrow C$ is symbolized "-". Thus **ccp** (c) is +++... (or ---...) and **hcp** (h) is +-+-... (or -+-+...). The packing is specified by a sequence of numbers, each of which represents the number of repetitions of a given sign. We have then that **ccp** is ∞ and **hcp** is 11. hc is $ABAC...$ i.e. +-+-... = 22. The reader should verify that hcc is 33 and that hhc is 21. The sequence $hhhc$ corresponds to +-+-+--- i.e. 211211. A commonly encountered modification of this notation is to omit the second half of the symbol when it is a repetition of the first and to enclose the symbol in angle brackets. Thus 22 becomes $\langle 2 \rangle$ and 211211 becomes $\langle 211 \rangle$ (but 21 is $\langle 21 \rangle$). The rule is that if the symbol in brackets contains an odd number of entries, the Zhdanov symbol is the bracketed symbol repeated twice.¹

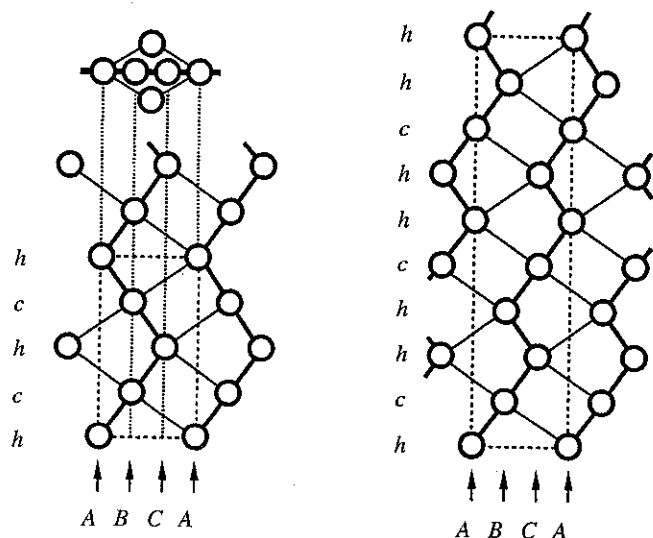


Fig. 6.9. $(11\bar{2}0)$ slices of hc (left) and hhc (right). c is vertical and a unit cell is shown with dashed lines. In the top left is shown a (0001) projection with the trace of a $(11\bar{2}0)$ plane as a heavy line.

A simple geometrical interpretation of the Zhdanov notation can be obtained from Fig. 6.9 which shows *slices* (not a projection) of two **cp** arrays. The slice is a $(11\bar{2}0)$ plane of a hexagonal cell (outlined) and heavy lines connect nearest neighbors in this plane. In $hc = 22$ (left) the line, as it ascends up in the c direction, goes two places right then two places left alternately. In $hhc = 21$, the line goes two places right then one left alternately. Notice

¹It should be clear that a Zhdanov symbol (other than that for **ccp**) always has an even number of terms.

that h layers are at positions of change of direction.¹

Fig. 6.9 also shows that a **cp** array can be described as a two-layer stacking of 4^4 nets made up of two kinds of tiles—rectangles and twinned rectangles ("kites") with edges in the ratio of $1:\sqrt{2}$. In **ccp** the tiles are all rectangles and in **hcp** they are all kites.

Sometimes a symbol nX is used to specify a packing. n is the number of layers in the repeat unit of the packing and X is H if the structure is hexagonal (*sensu stricto*), R if the structure is rhombohedral, and T if the structure is trigonal (but not rhombohedral). Thus h is $2H$, and hc is $4H$ and hhc is $9R$. Other examples are given in Exercise 2. Unfortunately as n gets large there is generally more than one packing with the same such symbol. For the use of Zhdanov symbols to determine the space group of the packing see the Notes (§ 6.8.1).

6.1.5 Patterns of filling interstitial sites in **cp** arrays

Reference to Fig. 6.4 (p. 212) shows that the center of an octahedron between two close-packed layers A and B is in the C position, and midway between the layers. It is a common practice to specify the positions of these interstitial sites by Greek letters: α , β and γ instead of A , B and C , so such an octahedral site position between A and B layers is labeled γ (Fig. 6.10). Fig. 6.4 also shows that the center of an "up" tetrahedron is underneath the top sphere, so the center of an "up" tetrahedron formed by layers AB with B on top is in a β position (Fig. 6.10); it is located $1/4$ of the way up between the two layers. Similarly the center of a "down" tetrahedron between the same layers AB is in the α position $3/4$ of the way up.

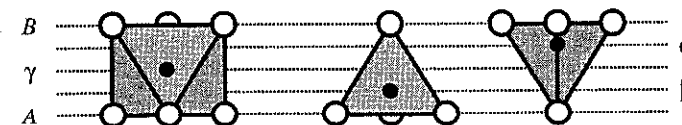


Fig. 6.10. Location of octahedral and tetrahedral sites in a **cp** layer AB . In the middle is an "up" tetrahedron; right is a "down" tetrahedron.

Suppose we fill only the "up" tetrahedral sites in **hcp**. The arrangement can be symbolized $A\beta\cdot B\alpha\cdot A\beta\cdot B\alpha\cdot$.² The pattern of tetrahedral sites is $\beta\cdot\alpha\cdot\beta\cdot\alpha\cdot$, i.e. also **hcp**. Filling only the "down" tetrahedral sites will produce $A\cdot\alpha B\cdot\beta A\cdot\alpha B\cdot\beta$. The pattern of these tetrahedral sites is $\alpha\cdot\beta\cdot\alpha\cdot\beta$, i.e. again **hcp**. The structure obtained by filling either the "up" set or the "down" set of tetrahedral sites of **hcp** is that of the **wurtzite** form of ZnS which may be described *either* as an **hcp** array of Zn with S in

¹Note also that the unit cell is chosen at an unconventional origin for clarity. Normally the origin would be taken on a c atom which is at a center of symmetry (see Exercises 1 and 2).

²We use dots " \cdot " as space markers for clarity, but they are not absolutely necessary and they are sometimes omitted later. Distinguish such dots from the ellipsis " \dots " at the end of a sequence indicating that the sequence continues indefinitely.

one-half of the tetrahedral sites (all "up" or all "down") or as an **hcp** array of S with Zn in one-half of the tetrahedral sites.

We repeat the exercise for **ccp**. Filling the "up" tetrahedral sites produces the sequence: $A\beta\cdot B\gamma\cdot C\alpha\cdot A\beta\cdot B\gamma\cdot C\alpha\cdot$ and filling the "down" sites only produces the sequence $A\cdot\alpha B\cdot\beta C\cdot\gamma A\cdot\alpha B\cdot\beta C\cdot\gamma\cdot$. The sequence of tetrahedral sites is $\beta\cdot\gamma\cdot\alpha\cdot\beta\cdot\gamma\cdot\alpha\cdot$ and $\alpha\cdot\beta\cdot\gamma\cdot\alpha\cdot\beta\cdot\gamma\cdot$ respectively; in both cases **ccp**. The structure obtained by filling either the "up" set or the "down" set of tetrahedral sites of **ccp** is that of the **sphalerite** form of ZnS which may be described either as a **ccp** array of Zn with S in one-half of the tetrahedral sites (either all "up" or all "down") or as a **ccp** array of S with Zn in one-half of the tetrahedral sites (again either all "up" or all "down"). (For the structures of ZnS see § 4.6.4, especially Fig. 4.11, for data for **wurtzite** ZnO see Appendix 5.)

Notice that both Zn and S are in 4-coordination in these structures, and we could consider the structure as a network of 4-connected atoms (a "4-connected net"). Such structures are one of the topics of the next chapter where we see (§ 7.3.1) that if all the atoms were the same (say C) then we would have the structures of the hexagonal **lonsdaleite** and cubic **diamond** forms of carbon.

Filling all the tetrahedral sites of **ccp** produces the **fluorite** structure of CaF_2 (with **ccp** Ca) which we can code as $A\beta\cdot\alpha B\gamma\beta C\alpha\cdot\gamma A\beta\cdot\alpha B\gamma\beta C\alpha\cdot$. Note that the sequence of tetrahedral sites is $\beta\cdot\alpha\cdot\gamma\beta\beta\alpha\cdot\gamma\beta\beta\alpha\cdot$ as in **ccp**; but because the spacing between layers is only one-half the distance between close-packed layers, the pattern is no longer **ccp** but is in fact primitive cubic—see Fig. 6.11. Accordingly care must be taken to ensure that the spacing between layers is appropriate before describing structures as **cp**. The spacing between each symbol (letter or ".") is (at least approximately) $1/4$ of the distance between the **cp** layers, i.e. $1/\sqrt{24}$ of the distance between atoms in the close-packed layers.

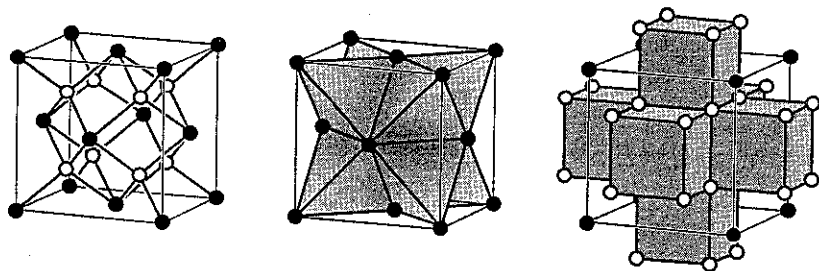


Fig. 6.11. Left: a unit cell of **ccp** (filled circles) with tetrahedral sites shown as open circles. If the open and filled circles are Ca and F respectively, we have a representation of the structure of CaF_2 . Center: the same structure shown as $\{\text{F}\}\text{Ca}_4$ tetrahedra (shaded). Right: the same structure but now some $\{\text{Ca}\}\text{F}_8$ cubes are outlined.

Notice that because the F atoms are in 4-coordination, the Ca atoms must be in 8-coordination (there is only one Ca for two F atoms), and in light of the above discussion, it is not surprising to find that the coordination is $\{\text{Ca}\}\text{F}_8$ cubes.

If the roles of "cation" and "anion" are reversed in **fluorite** (as in, for example, Li_2O with **ccp** O) we get the **antistructure**, called in this instance **antifluorite**.

In the (idealized) structure of **NiAs**, Ni atoms occupy the octahedral sites of an **hcp** array of As. The sequence is $A\cdot\gamma B\cdot\gamma A\cdot\gamma B\cdot$. The pattern of octahedral sites is $\gamma\cdot\gamma\cdot\gamma\cdot$ corresponding to points of a primitive hexagonal lattice [ideally with $c/a = \sqrt{2/3}$]. Interchanging Ni and As will produce the antistructure (as in PtB with **hcp** Pt).

In the **NaCl** structure, the octahedral sites of **ccp** are filled. The structure is $A\cdot\gamma B\cdot\alpha\cdot C\cdot\beta\cdot A\cdot\gamma B\cdot\alpha\cdot C\cdot$. The octahedral sites alone are $\gamma\cdot\alpha\cdot\beta\cdot\gamma\cdot\alpha\cdot\beta\cdot$ i.e. again **ccp** (as observed in § 6.1.2). Interchanging Na and Cl produces the same structure (so it is its own antistructure).

One often sees structures such as **NaCl** and **NiAs** projected down an axis contained in the **cp** layers (normal to $[111]$ for **NaCl** and normal to **c** for **NiAs**)—see for example Fig. 4.9, parts of which are repeated for convenience here as Fig. 6.12. The nature of the packing can be recognized quickly if it is realized that in **ccp** all the octahedral sites are related by primitive lattice translation vectors so all the octahedra have the same orientation; but in **hcp**, octahedra in alternate layers are related by reflection and two different orientations occur.

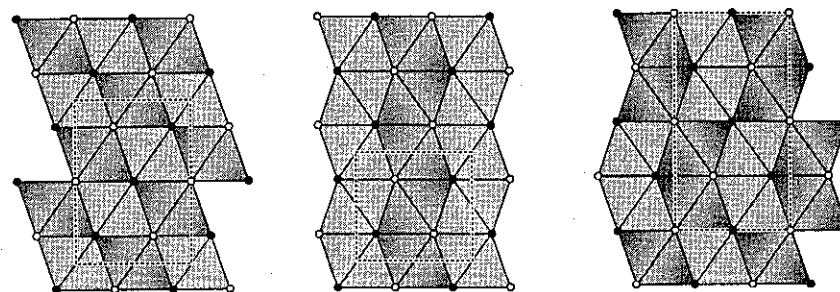


Fig. 6.12. From left to right **NaCl**, **NiAs** and **TiP** as cation-centered octahedra. Light and darker shaded polyhedra have elevations that differ by half the repeat distance in the direction out of the page.

In **TiP** there is **hc** packing of P and the $\{\text{Ti}\}\text{P}_6$ octahedra again occur in two orientations. As now only every second layer is **h**, double layers of octahedra in one orientation alternate with double layers in the other orientation (see Fig. 6.12 again).

NaCl is the only one of these octahedral structures that is its own antistructure. As noted above, in **NiAs** the Ni are at the points of a primitive hexagonal lattice and the As are in $\{\text{As}\}\text{Ni}_6$ trigonal prisms. In **TiP** the P are half in $\{\text{P}\}\text{Ti}_6$ octahedra and half in $\{\text{P}\}\text{Ti}_6$ trigonal prisms as illustrated in Fig. 6.13. Notice that crystallographically the structure is ternary, $\text{Ti}_2\text{P}(\text{1})\text{P}(\text{2})$, and that there are antistructure compounds such as RbScO_2 with $\{\text{Rb}\}\text{O}_6$ trigonal prisms and $\{\text{Sc}\}\text{O}_6$ octahedra. The anion packing (now not **cp**) in such structures is discussed in § 6.4.1.

There are many patterns of partly filling octahedral sites in **cp** structures and we mention

here just one or two of the simpler.

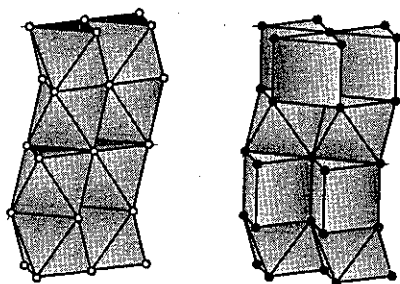


Fig. 6.13. Clinographic projections of **TiP** with **c** (normal to the **cp** layers of **P**) vertical. Left: as **(Ti)P₆** octahedra. Right: as **(P)Ti₆** octahedra and trigonal prisms.

Filling only alternate layers of octahedral sites in **hcp** gives the sequence **A·γB···A···**. The structure is generally known as **CdI₂**. There is a repeat every two **cp** layers and the symmetry is trigonal, **P3̄m1**, with *c/a* ideally = $\sqrt{8/3} = 1.633$. **Cd** is in 1 **a**: (0,0,0) and **I** is in 2 **d**: $\pm(1/3, 2/3, z)$ with *z* ideally = 1/4.

Filling only alternate layers of octahedral sites in **ccp** produces the sequence **A·γB···C·β·A···B·α·C···A···**. The structure is known as **CdCl₂** and it can be seen that now the repeat is every sixth **cp** layer. The symmetry is rhombohedral, **R3̄m**, with *c/a* ideally = $3\sqrt{8/3} = \sqrt{24} = 4.90$. **Cd** is in 3 **a**: **R** + (0,0,0) and **Cl** is in 6 **c**: **R** ± (0,0,*z*) with *z* ideally = 1/4. A related structure type is that usually called **α-NaFeO₂** in which **O** is **ccp** and alternate layers of octahedra sites are filled with **Na** and **Fe**. The crystallographic description is the same as for **CdCl₂** except there is also a cation in 3 **c**: **R** + (0,0,1/2).

There is a number of different structures known in which one half of the octahedral sites are filled in every **cp** layer. An example with (approximately) **hcp** anions is provided by **CaCl₂** and the closely-related **rutile** (**TiO₂**) structure (see Exercise 7).

In considering possible patterns of filling interstitial sites in **cp** arrays, perhaps the most important consideration is that in "ionic" crystals short distances between cations (or anions) are generally unfavorable. This means that face sharing between coordination polyhedra (especially tetrahedra) is avoided if possible. A good example of this principle at work is provided by structures in which there are slabs in which all octahedral sites are filled and slabs in which all tetrahedral sites are filled. To avoid face sharing between polyhedra the **cp** layers between like slabs must be **c**, and between unlike slabs they must be **h**.¹ Thus in **CaF₂** (all tetrahedral slabs) and **NaCl** (all octahedral slabs) every layer is **c**. In **La₂O₃** with **cp La**, slabs (**LaO₂**) with **O** in all the tetrahedral sites alternate with slabs (**LaO**) with **O** in all the octahedral sites and the **La** layers are all **h**. In **Th₃N₄** with **cp Th** (see Exercise 6) double slabs (2**ThN**) with **N** in all octahedral sites have **Th** in a **c** layer at the center and these double slabs are separated by **h** layers of **Th** from slabs with **N** in

tetrahedral sites (**ThN₂**). There are exceptions to these rules of course; in **NiAs** there is face sharing between octahedral slabs, and it is argued that, in some instances at least, this is due to metal-metal bonding (between **Ni** atoms across the shared face).

6.1.6 Stacking incomplete **cp** layers (honeycomb and kagome)

The notation of 6.1.4 for stacking complete **3⁶** layers of atoms is in wide-spread use. It is useful to extend it to more complicated packings of hexagonal layers derived from **3⁶**. There is no generally accepted notation—we use one that seems to us useful and is kept as simple as possible.¹

Consider first the honeycomb pattern **6³**. The unit cell for this is $\sqrt{3} \times \sqrt{3} = 3$ times as large as that for **3⁶**, as illustrated in Fig. 6.14. The position of a honeycomb layer (symbol **G** for graphite) is conveniently specified by the position of the center of a hexagon in the pattern. In stacking honeycomb layers, we recognize three *relative* positions (1, 2 and 3) indicated by small filled circles in the figure (upper left) at 0,0,*z*; 1/3,2/3,*z* and 2/3,1/3,*z* in the **3×** cell. This is particularly useful for describing partial filling of octahedral sites in **hcp** structures as illustrated next (note that it is less readily adaptable to **ccp**).

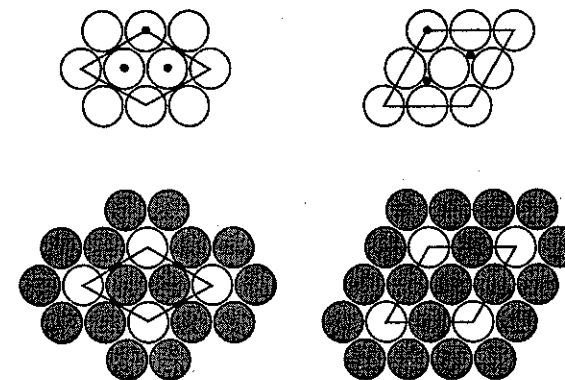


Fig. 6.14. Left: top a $\sqrt{3} \times \sqrt{3}$ cell of **3⁶** with below a **3⁶** net subdivided into a **G** (**6³**) layer (shaded circles) and a **g** layer (open circles). Right: top a **2 × 2** cell of **3⁶** with below a **3⁶** net subdivided into an **N** (**3.6.3.6**) layer (shaded circles) and an **n** layer (open circles). The small filled circles mark the three choices of origin (1, 2 and 3).

In the (idealized) **corundum** structure of **Al₂O₃**, **Al** atoms are located in 2/3 of the octahedral sites of an **hcp** array of **O**, each **Al** layer being a honeycomb. We can code this structure as follows: **A·G₁·B·G₂·A·G₃·B·G₁·A·G₂·B·G₃···**. By using dots as place markers we have automatically imparted the information that the **Al** atoms on the **G** layers are in

¹The reader will find that such statements are very readily verified if a few polyhedra are at hand.

¹For another notation see particularly W. B. Pearson (Book List). Pearson describes over 100 structure types using a related system.

octahedral coordination. Note that the sequence requires six O layers to repeat. For ideal hcp of O atoms a distance d apart, the a axis would be $\sqrt{3}d$ (see Fig. 6.14) and the c axis would be $6\sqrt{(2/3)}d$ so that $c/a = \sqrt{8} = 2.83$; in the real structure $c/a = 2.73$.

Figure 6.15 shows the structure as $\{\text{Al}\}\text{O}_6$ octahedra. Notice that pairs of octahedra share faces; as also shown in the figure the Al atoms move away from the centers of the octahedra to avoid short Al...Al distances. Al_2O_3 with this structure is also known as $\alpha\text{-Al}_2\text{O}_3$. For crystallographic data see Appendix 5.

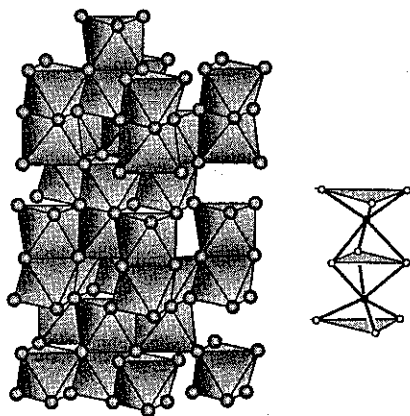


Fig. 6.15. The structure of $\alpha\text{-Al}_2\text{O}_3$ as articulated $\{\text{Al}\}\text{O}_6$ octahedra. c runs up the page. On the right the Al-O bonds are shown (on a larger scale) in a pair of face-sharing octahedra.

The centers of the hexagons of 6^3 fall on a 3^6 net with $\sqrt{3}$ times the spacing of a cp layer (see Fig. 6.14 again) and we label such nets g (note that combining g and G in one layer returns a cp layer). In the structure of PdF_3 , the Pd atoms fill one-third of the octahedral sites of an hcp F array. The structure is $A \cdot g_1 \cdot B \cdot g_2 \cdot A \cdot g_3 \cdot B \cdot g_1 \cdot A \cdot g_2 \cdot B \cdot g_3 \dots$ (see Fig. 6.28, p. 236). Note that the hexagonal cell is the same as for corundum; for PdF_3 , $c/a = 2.82$.

Often layers in structures are kagome ($3.6.3.6$) nets which are symbolized N (for net). The unit cell is now $2 \times 2 = 4$ times as large as that for 3^6 , as illustrated in Fig. 6.14, and again three relative positions (1, 2 and 3) of the net specified by the centers of the hexagons are recognized. These are now particularly useful for describing partial filling of octahedral sites in cp structures. The centers of the hexagons fall on a 3^6 net of twice the spacing of a cp layer and we label such 3^6 nets n (combining n with N produces a cp layer).

The three positions of the N and n nets are shown in Fig. 6.16. Some intermetallic compounds are variants of cp ordered in this way. In Cu_3Au the Cu atoms are on the kagome nets (N) and Au centers the hexagons of each layer (n). If atoms on the same layer are enclosed in parentheses, the code becomes: $(n_1N_1) \dots (n_2N_2) \dots (n_3N_3) \dots$ or (omitting place markers) $(n_1N_1) (n_2N_2) (n_3N_3)$, i.e. a superstructure of ABC . We meet the related structure $N_1N_2N_3$ below as an 8-coordinated sphere packing (lattice complex J , § 6.3.5).

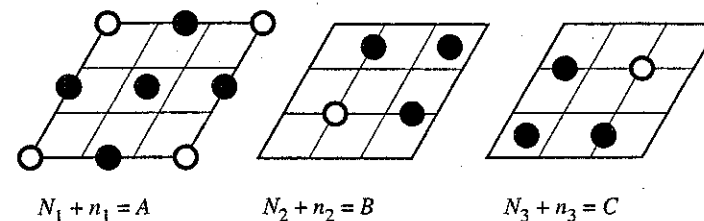


Fig. 6.16. The three positions of kagome (N) nets with respect to a 2×2 cell of 3^6 . We have (arbitrarily) labeled them so that N_1 combined with n_1 produce a cp layer with symbol A etc.

In the spinel structure typified by MgAl_2O_4 , O is on a ccp array with Mg in 1/8 of the tetrahedral sites and Al on 1/2 of the octahedral sites. The structure is cubic but for some purposes (such as describing related structures) is conveniently considered as stacking of layers normal to $[111]$: $N_1 \cdot Bn_1n_3n_2A \cdot N_2 \cdot Cn_2n_1n_3B \cdot N_3 \cdot An_3n_2n_1C \dots$. Another notation which has been used refers to the N layers as O ("octahedral") layers, and layers of the type $n_1n_3n_2$ (which contain one octahedral and two tetrahedral sites) as T_2 layers.

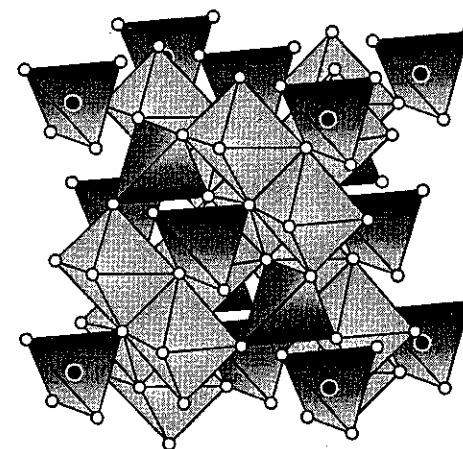


Fig. 6.17. MgAl_2O_4 as $\{\text{Mg}\}\text{O}_4$ tetrahedra and $\{\text{Al}\}\text{O}_6$ octahedra. Filled circles are Mg atoms at the corners of a cubic unit cell. For clarity some of the octahedra at the "back" of the unit cell have been omitted.

We cannot begin to do justice to spinel here.¹ Fig. 6.16 illustrates just one aspect of

¹In Volume II of this series we devote more than a dozen pages to describing spinel and its close relatives. We find a notation based on that given here to be invaluable.

the structure—as cation centered polyhedra. As an aid to deciphering the code, it is expanded below. The first row of numbers is the height along the *c* axis of the hexagonal cell in multiples of *c*/24. Recall that Al atoms are in octahedral sites and that Mg atoms are in tetrahedral sites. As we describe the packing in terms of a 2 × 2 supercell of a **cp** layer there are 4 O atoms per layer *A*, *B* or *C* and 3 Al atoms corresponding to the *N* layers. In the table we show these numbers as subscripts.

0	1	2	3	4	5	6	7	8	9	10	11	12
<i>N</i> ₁	·	<i>B</i>	<i>n</i> ₁	<i>n</i> ₃	<i>n</i> ₂	<i>A</i>	·	<i>N</i> ₂	·	<i>C</i>	<i>n</i> ₂	<i>n</i> ₁
Al ₃	·	O ₄	Mg	Al	Mg	O ₄	·	Al ₃	·	O ₄	Mg	Al

12	13	14	15	16	17	18	19	20	21	22	23	24
<i>n</i> ₁	<i>n</i> ₃	<i>B</i>	·	<i>N</i> ₃	·	<i>A</i>	<i>n</i> ₃	<i>n</i> ₂	<i>n</i> ₁	<i>C</i>	·	<i>N</i> ₁
Al	Mg	O ₄	·	Al ₃	·	O ₄	Mg	Al	Mg	O ₄	·	Al ₃

The Al array *N*₁...*n*₃...*N*₂...*n*₁...*N*₃...*n*₂... also will be met again as a 6-coordinated sphere packing (lattice complex *T*, § 6.3.9).

Very many other compounds can be described in terms of partial filling of octahedral and/or tetrahedral sites of **cp** (Exercises 6 and 13 give examples) and it is virtually impossible to master systematic crystal chemistry without some appreciation of the principles involved.

6.1.7 The “size” of interstitial sites.

For a regular tetrahedron of unit edge length the height (distance from a vertex to the center of an opposite face) is $\sqrt{2/3}$. The distance from a vertex to the center of the tetrahedron is 3/4 of the height (see Fig. 6.10) = $\sqrt{3/8}$ = 0.612. Conversely, the edge length of an {*A*}*B*₄ coordination tetrahedron with unit length *A*-*B* bonds is $\sqrt{8/3}$ = 1.633. The radius of a sphere that exactly fits inside a tetrahedron of touching spheres of radius 1/2 (unit diameter) is $\sqrt{3/8}$ - 1/2 = 0.1124. The ratio of the radius of the inner sphere to the radius of the outer spheres is $[\sqrt{3/8} - 1/2]/(1/2) = \sqrt{3/2} - 1 = 0.2247$.

It should be obvious that the perpendicular distance between opposite faces of an octahedron is the same as the height of a tetrahedron (see Fig. 6.10). For an octahedron of unit edge (formed by the centers of six spheres of unit diameter in contact) the distance to the center is $1/\sqrt{2}$. The ratio of the radius of the largest sphere that will fit inside an octahedral site to the radius of the close-packed spheres is $\sqrt{2} - 1 = 0.4142$.

It is sometimes stated that these “radius ratios” determine the coordination numbers of atoms in ionic crystals. The idea is that an atom (ion) that is too small for, say, an octahedral site (cation radius / anion radius less than 0.414) will instead go into a smaller (e.g. tetrahedral) site. Unfortunately to apply such considerations, radii must first be assigned to ions. Even when this is done, it will be found that the facts are not generally in accord with predictions even for the alkali halides (presumably the most “ionic” of crystals). Stated more bluntly the “rules” are generally not obeyed! The reader interested in this topic is referred also to § 6.8.3.

6.2 Body-centered cubic (bcc)

There are two interesting problems whose solutions are the same, and which lead to the body-centered cubic (**bcc**) array. The first problem is that of covering space completely with (partly overlapping) spheres of a given size such that their density is a minimum. The second concerns the filling of space with congruent tetrahedra. We have seen (Exercise 3, Chapter 5) that regular tetrahedra alone will not fill space, but a number of structures of metallic compounds are found in which space is divided into irregular tetrahedra.¹ The body-centered cubic array is the simplest such structure, and the only one in which all the tetrahedra have congruent faces and equivalent vertices. We refer to these tetrahedra as Sommerville tetrahedra.²

The Sommerville tetrahedron has faces that are isosceles triangles with one edge of length *a* and two edges of $\sqrt{3}a/2$, where *a* is the cubic unit cell edge for **bcc**. The angles of the triangles are $\cos^{-1}(1/3) = 70.53^\circ$ and $\cos^{-1}(1/\sqrt{3}) = 54.74^\circ$ (2×). The dihedral angles are 45° (4×) and 90° (2×). Fig. 6.18 shows how these tetrahedra are related to a body-centered cubic lattice. The figure also shows that four tetrahedra combine to form a space-filling octahedron with equivalent vertices and congruent faces so that the body-centered cubic array can be considered as arising from a packing of these (irregular) octahedra also. It is sometimes found stated (erroneously) that the body-centered cubic array divides space into tetrahedra and octahedra, but the octahedra are in fact clusters of four tetrahedra and the centers of the octahedra are the midpoints of the long edges of the tetrahedra so the term “octahedral site” is something of a misnomer (see below).³ Contrast eutactic (**cp**) arrays in which space is divided into separate regions which are regular tetrahedra and regular octahedra.

The figure also shows that six octahedra (= 24 tetrahedra) of the **bcc** packing combine to form a rhombic dodecahedron with lattice points at the vertices and at the center.

Some facts (that will be useful later) about the body-centered array are included here. The symmetry is *Im* $\bar{3}m$ and the lattice points are in 2 *a*: *I* + (0,0,0). The centers of the tetrahedra are in the faces of the cube at $12d: I + (\pm 1/4, 0, 1/2)\kappa$. The site symmetry at these points is $\bar{4}2m$ (tetragonal). Note that there are six tetrahedra for every lattice point. The tetrahedral sites in one unit cell are at the vertices of a truncated octahedron. We meet the pattern of tetrahedral sites as the “sodalite net” in the next chapter (§ 7.3.10). The tetrahedron around a tetrahedral site encloses all the space that is nearer to that tetrahedral site than to any other (it is the Voronoi polyhedron of the pattern of tetrahedral sites).

¹These are sometimes referred to as “topologically close packed.” The β -W (A15) structure (§ 6.6.4) is a well-known example.

²After D. M. Y. Sommerville who discussed this problem at length [*Proc. Edin. Math. Soc.* 41, 49 (1923)]. Sommerville also discusses three other space-filling tetrahedra derived by dissecting the basic tetrahedron, but these are of little interest in the present connection.

³To a mathematician a *hole* in a lattice is a site where the distance to the nearest lattice point is a local maximum. Points where the distance to the nearest lattice point is a global maximum are known as *deep* holes, other holes are *shallow* holes. In **ccp** the octahedral sites are deep holes and the tetrahedral sites are shallow holes. In **bcc** there is only one kind of hole (the tetrahedral sites). The positions of the “octahedral” sites correspond, not to local maxima in distance from the nearest lattice point, but to saddle points.

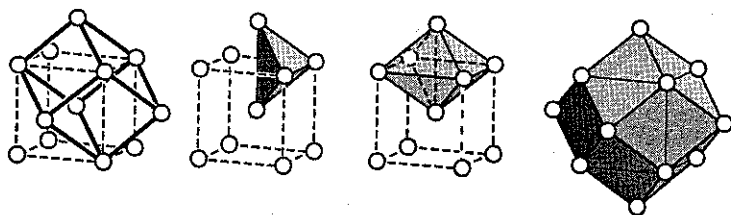


Fig. 6.18. Various aspects of the body-centered cubic lattice. At the left a cubic (centered) cell outlined with broken lines and a primitive rhombohedral cell ($\alpha = 109.47^\circ$) in full lines. Second from left: a Sommerville tetrahedron defined by four lattice points. Second from right: an octahedron composed of four Sommerville tetrahedra. Right: a rhombic dodecahedron composed of six octahedra = 24 tetrahedra.

The centers of the "octahedral sites" (better the midpoints of the long edges of the tetrahedra) are at $6b: 1 + (0, 1/2, 1/2)\kappa$. These correspond to the centers of the faces and edges of the unit cell. The site symmetry at $6b$ is again tetragonal: $4/mmm$. We meet the pattern of the octahedral sites as the NbO net in the next chapter.

There is an apparent paradox that has lead to confusion. There are six tetrahedral sites per bcc atom and three octahedral sites per bcc atom yet the octahedron is comprised of four tetrahedra. The resolution is to be found in the observation that the centers of long edges of a given octahedron are also octahedral sites. Thus if we placed (correctly oriented) octahedra with centers at every octahedral site we would cover space *twice*. In § 5.1.10 we called attention to a tetragonal tetrahedron with curved faces that filled space (Fig. 5.17). The six vertices of that polyhedron are arranged in space as the six vertices of the bcc octahedron, but because the surfaces are curved inward the volume of the tetragonal tetrahedron is only half as great as that of the bcc octahedron. In the space filling by these tetragonal tetrahedra, their centers are at the bcc octahedral sites.

The Voronoi polyhedron around an octahedral site is actually a polyhedron with 12 faces obtained by truncating four edges of the bcc octahedron. Three such polyhedra are shown in Fig. 6.19 in different orientations to suggest how they pack to fill space. The arrangement of the acute vertices in the packing is bcc.

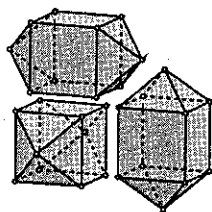


Fig. 6.19. The Voronoi polyhedron around "octahedral" sites in bcc shown in three different orientations to suggest how it fills space.

A nice example of filling all the tetrahedral sites in bcc is to be found in the structure of M_6C_{60} (M is an alkali atom such as K); in these compounds the centers of the approximately-spherical C_{60} molecules are bcc.

Structures based on bcc and on cp occur with comparable frequency in intermetallic compounds. On the other hand, although "ionic" crystal structures can be described in terms of cp arrays with partial or complete filling of interstitial sites, ionic structures similarly based on bcc arrays are rather rare.¹ In the cp case the coordination polyhedra around the interstitial sites are regular whereas in the bcc case they are not.²

Note that we use bcc to refer to a geometrical arrangement, not to a symmetry (which would be written *bcc*). In Cu_2O (Exercise 8, Chapter 3) the Cu atoms are ccp and the O atoms are bcc but the structure is primitive cubic (space group $Pn\bar{3}m$).

6.3 Sphere packings and relationships between them

Crystallographers have long been interested in the general problem of packings of spheres. *Stable* sphere packings are those in which each sphere is in contact with at least four others not all on the same hemisphere. *Equivalent* spheres are those related by symmetry operations (rotations, translations, etc.). We discuss here some interesting stable packings of equivalent spheres, referred to in this section just as "sphere packings" for brevity. Many packings with a given number of neighbors can be distorted smoothly to a higher density approaching arbitrarily close to that of closest packing so the interest is in finding low-density (rare) sphere packings which often correspond to a high-symmetry structures.³ Although the problem is interesting, it is one of mathematics rather than chemistry. Our *real* interest is in describing structures (and their inter-relationships) that are of importance in crystal chemistry.

The two arrangements (ccp and hcp) we have identified of densest packing of *equivalent* spheres are the only such arrangements in which each sphere has twelve neighbors and, as they both have the same density, they are both the densest and the rarest packings of spheres with twelve neighbors.

Sphere packings are often characterized by the fraction of space occupied by the spheres (or density ρ). This is determined as the ratio of the volume of spheres in a unit cell to the volume of the unit cell. To illustrate: the ccp arrangement of spheres of unit diameter has a unit cell containing four spheres and cell edge $a = \sqrt{2}$. The volume of the spheres is $4 \times 4\pi/3 = 2\pi/3$ and the cell volume is $a^3 = 2\sqrt{2}$. The ratio is $\rho = \pi/\sqrt{18} = 0.740\dots$ We generally give coordinates for packings of unit diameter spheres, the density is then given

¹If one considers *ordered* bcc arrays such as $CuZn$ (§ 6.6.2) then one finds that *perovskite* ABX_3 and many derived structures are based on a $CuZn$ array of cations AB with anions approximately in the center of some of the octahedral sites. What is rare is the case of ionic crystals in which just one kind of atom is bcc.

²One can extend this remark by observing that less dense arrays, such as primitive cubic and primitive hexagonal, that do provide regular coordination sites are indeed more common than bcc (see § 6.4).

³As we remarked in Chapter 5, the problem is often stated (incorrectly) as that of finding the *densest* sphere packing with a given number of neighbors, i.e. the opposite of what we have stated.

by $\rho = z\pi/(6V)$, where z is the number of spheres per cell and V is the cell volume.

A topic of interest in connection with the description of structural relationships and possible transformation mechanisms is the description of paths between packings. We will focus on paths that preserve as much symmetry as possible (the space group of the intermediate structure will either be the same as, or a subgroup of, those of the two end structures) and which are completely specified by one free parameter. Often this parameter will correspond to the angle of rotation of a group of points. We have met such transformations already for finite objects such as that of a cuboctahedron to an icosahedron (§ 2.5.7) and a trigonal bipyramid to a square prism (§ 5.6.1). For plane patterns, important transformations are from $3.6.3.6$ to 3^6 and from $3^2.4.3.4$ to 4^4 (§ 5.3.3).

6.3.1 11- coordination

11-coordinated sphere packings are rather rare. Here we describe a simple and well known 11-coordinated structure that is important in crystal chemistry. A formal description for spheres of unit diameter is:

$$P4_2/mnm, a = 1 + 1/\sqrt{2} = 1.707, c = 1, \rho = 0.7187$$

$$\text{Centers in } 4f: \pm(x, x, 0; 1/2 + x, 1/2 - x, 1/2), x = 1/(2 + \sqrt{2}) = 0.292$$

The arrangement can be seen from Fig. 6.20 in which sphere centers are taken as defining the vertices of regular octahedra, and which also illustrates the relationship of the structure to **hcp**. In fact the structure is a special (minimum density) arrangement of an orthorhombic structure with space group $Pnmm$ and centers of spheres in $4g: \pm(x, y, 0; 1/2 + x, 1/2 - y, 1/2)$ with:

$$a = \sqrt{3} \cos \phi, b = \sqrt{(8/3)} \cos \phi + \sqrt{(1/3)} \sin \phi, c = 1, \rho = 2\pi/(3ab)$$

$$x = (\sqrt{2} - \tan \phi)/\sqrt{18}, y = (1 + \sqrt{2} \tan \phi)/(4 + \sqrt{2} \tan \phi)$$

Eleven spheres are in contact for $0 < \phi < \sin^{-1}(1/3)$; the minimum density occurs at $\phi = (1/2)\sin^{-1}(1/3) = 9.74^\circ$ at which point the structure is the tetragonal one given above. When $\phi = 0^\circ$ or $\sin^{-1}(1/3) = 19.47^\circ$ the structure is that of hexagonal eutaxy (**hcp**) with symmetry $P6_3/mmc$ (and 12-coordination). The tetragonal structure is close to the anion arrangement in the rutile form of TiO_2 (see Exercise 7) so we call it the **rutile** packing. The density is $4\pi(9 + \sqrt{72}) = 0.7187$; no rarer 11-coordinated sphere packing seems to be known (for a second 11-coordinated sphere packing of the same density see § 6.4.1).

The transformation from **hcp** to the **rutile** packing and *vice versa* is accomplished by concerted rotations (by ϕ) of columns of octahedra of atoms as suggested by Fig. 6.20 in which the rotation axis is normal to the plane of the figure. It is interesting that rotation of the columns of octahedra by 19.47° has the same effect as rotation of the whole pattern by 90° . (i.e. is a pseudorotation). It may be seen that *in projection* the transformation corresponds (approximately—not all edges are equal) to a transformation between 3^6 and $3^2.4.3.4$.

We will encounter other such transformations involving concerted rotations of

polyhedral groups subsequently (in particular the **rutile** packing can be transformed to a low-density 6-coordinated sphere packing by rotation of tetrahedral groups).

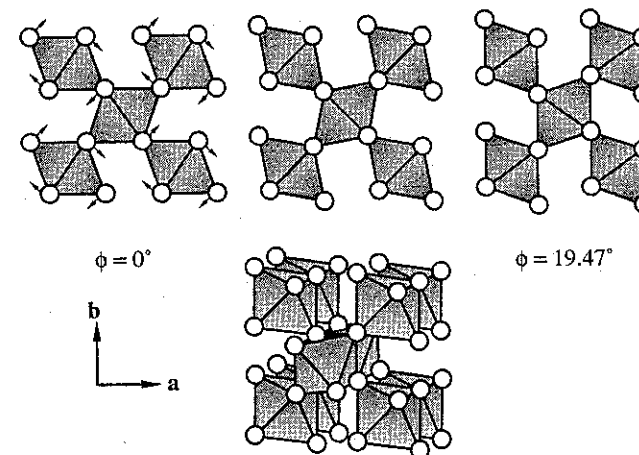


Fig. 6.20. Top: The transformation from **hcp** (left) to the minimum density tetragonal 11-coordinated sphere packing (center) and then to **hcp** rotated by 90° (right). The projection is along $\{001\}$ of the orthorhombic cell. Bottom: A clinographic projection of the tetragonal structure.

6.3.2 10-coordination (bct) and a relationship between **ccp** and **bcc**

A well-known 10-coordinated sphere packing is a lattice packing:

$$\text{bct} \quad I4/mmm, a = \sqrt{(3/2)} = 1.225, c = 1, \rho = 2\pi/9 = 0.698. \text{Centers in } 2a: 1 + (0,0,0)$$

We refer to this structure as **bct** (short for body-centered tetragonal). Fig. 6.21 illustrates the 10-fold coordination. The primitive cell has $a' = b' = c' = 1$, $\alpha' = \beta' = \cos^{-1}(-1/4) = 104.48^\circ$, $\gamma' = \cos^{-1}(-1/2) = 120^\circ$.

The reader may wish to verify that the points on (110) planes form regular 3^6 nets as illustrated on the right in Fig. 6.21. A description of this structure as a non-close-packed stacking of 3^6 nets is given in § 6.4.1 below.

Other special cases of the body-centered tetragonal lattice are of interest. If $a = c = 2/\sqrt{3} = 1.155$, the structure is the body-centered cubic (**bcc**) arrangement of unit spheres (symmetry $Im\bar{3}m$); and if $a = 1$, $c = \sqrt{2} = 1.414$, it is the face-centered cubic (**ccp**) arrangement (with symmetry $Fm\bar{3}m$) described in terms of a body-centered cell. It may be seen then that **bcc** and **ccp** are simply related to each other by a tetragonal compression or extension (Fig. 6.22). This relationship is known to metallurgists as the Bain relationship (or correspondence) and is of interest in connection with the transformation of iron from the γ form (**ccp**) to the α form (**bcc**) on cooling. The high-temperature form of iron

containing carbon is called austenite, on cooling it transforms rapidly with change of shape to a body-centered tetragonal (nearly cubic) form called martensite. Transformations of this type, which do not require diffusion of atoms, are called *martensitic* and have been extensively studied by metallurgists. [A. Martens (1850-1914) was a German metallurgist.]

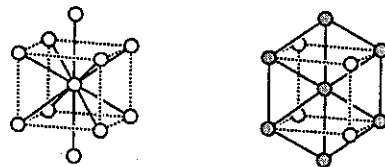


Fig. 6.21. Left: a fragment of the **bct** lattice showing 10-fold coordination of a central atom. Right: atoms on a 3^6 net on a (110) plane shown shaded and connected by full lines.

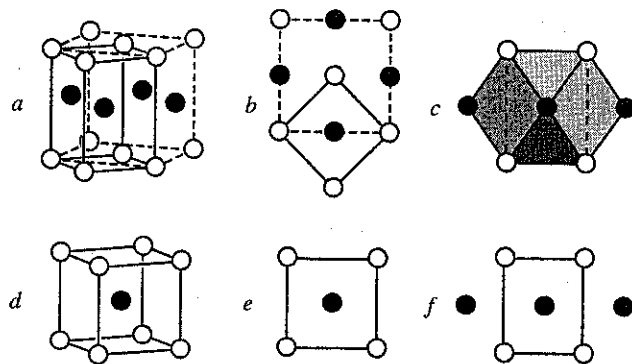


Fig. 6.22. (a) Face-centered cubic with the cubic cell outlined with broken lines and a body-centered tetragonal cell outlined with full lines. (b) *a* projected down the vertical axis. (c) *a* projected with the long axis of the tetragonal cell vertical on the paper. A cuboctahedron of atoms seen along a two-fold axis is depicted. (d) A body-centered cubic cell. Nearest neighbors are the same distance apart as they are in *a*. (e) *d* in projection. (f) The 10-coordinated tetragonal packing with its *c* axis horizontal on the paper. Its relationship to body-centered cubic can be seen by comparison with *e* and to face-centered cubic by comparison with *c*.

It should be obvious that the **bcc** structure can be tetragonally deformed until it is arbitrarily close to **ccp**, all the time keeping each sphere in contact with eight neighbors. The **bcc** structure is thus one at a local minimum (in coordinate space) of density.¹ It is less obvious that the 10-coordinate structure (**bct**) can be deformed to the **ccp** structure keeping

¹We don't preclude the possibility of some of these structures being at global density minima for a given coordination number. The question has not been much discussed except for the case of four coordination which gives the rarest (?) stable sphere packing (§ 7.5.2).

each sphere in contact with ten neighbors and that it is at a local density minimum. However, this is simply demonstrated analytically and is similar to the 11- to 12-coordinate transformation discussed earlier (§ 6.3.1, p. 228) in that again we need a lower symmetry cell for the general case. The symmetry is orthorhombic:

$$Immm, a^2 + b^2 = 3, 1 \leq a, b \leq \sqrt{2}, c = 1. \text{ Centers at } 2a: I + (0,0,0)$$

The special case $a = 1, b = \sqrt{2}$ (or $a = \sqrt{2}, b = 1$) corresponds to **ccp**. The case $a = b = \sqrt{3/2}$ corresponds to the tetragonal minimum density (**bct**).

The body-centered tetragonal arrangement is not common in elemental structures—examples are β -Hg ($c/a = 0.707$)¹ and Pa ($c/a = 0.825$)—but it is very often encountered in the structures of intermetallic compounds [e.g. **CuAu** and **MoSi₂** (§ 6.6.2)].

6.3.3 Another 10-coordination: C-centered orthorhombic (**cco**) and further relationships between **bcc**, **ccp** and **hcp**

Another 10-coordinated sphere packing with the same density as **bct** is derived by periodic twinning of **bct** on (101) planes. Fig. 6.23 shows, on the left, one such twin plane in **bct**. On the right in the figure is the new structure with the positions of twin planes indicated by arrows.

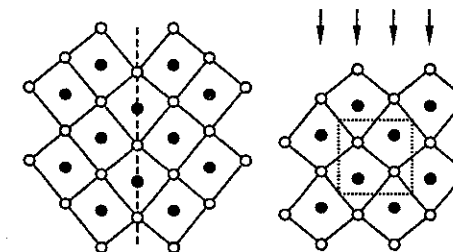


Fig. 6.23. Twinning of body-centered tetragonal (see text), on the right the broken lines indicate a unit cell (*b* vertical and *c* horizontal).

The crystallographic description of the new structure, which we call **cco** (for C-centered orthorhombic) is:

$$\text{cco} \quad Cmcm, a = \sqrt{3/2} = 1.225, b = \sqrt{5/2} = 1.581, c = \sqrt{12/5} = 1.549, \rho = 0.698 \\ \text{Centers in } 4c: C \pm (0, y, 1/4), y = 3/10$$

The structure is a maximum volume form of a 10-coordinated sphere packing with the same symmetry and atoms in the same positions and with parameters given by:

¹For mercury c/a is sufficiently small that Hg atoms have only two nearest neighbors so that strings of Hg atoms run parallel to *c* (compare Fig. 6.16 *f*).

$$a = \sqrt{[(3-8y)/(1-2y)]}, b = \sqrt{[1/(1-2y)]}, c = \sqrt{(8y)}, 1/4 < y < 1/3$$

When $y = 1/4$, the structure is **ccp**, with $a = b = c = \sqrt{2}$; when $y = 1/3$, the structure is **hcp**, with $a = 1$, $b = \sqrt{3}$, $c = \sqrt{(8/3)}$. For intermediate values of y each sphere has 10 neighbors at a unit distance away. The position of maximum volume is for $y = 3/10$, when the unit cell volume is 3 (compare $\sqrt{8} = 2.828$ for **cp**). This is the same volume per sphere as in the 10-coordinated body-centered tetragonal lattice packing (**bct**) described in § 6.3.2.

Fig. 6.24 shows the structure again projected on (100), but now with **b** horizontal and **c** vertical. In going from **ccp** (on the left) to **hcp** (on the right), a is decreased by $\sqrt{2}$, b is increased by $\sqrt{(3/2)}$ and c is increased by $\sqrt{(4/3)}$.

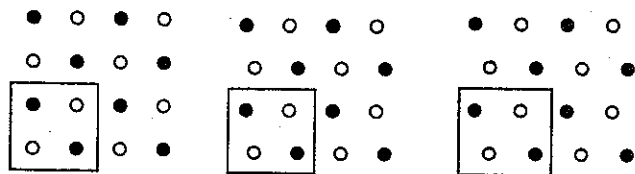


Fig. 6.24. Illustrating the relationship between **ccp** (left), $y = 1/4$; 10-coordinated packing (center) with $y = 3/10$; and **hcp** (right), $y = 1/3$.

If $a/b = a/c$ for **ccp** were reduced from 1 to $1/\sqrt{2} = 0.707$ the structure would be **bcc** (the Bain relationship again), so the figure would also represent the transformation from **bcc** to **hcp**. (So be careful in “reading” projections—check axial ratios.)

In general, periodic reflection twinning of body-centered orthorhombic cells (with parameters a_o , b_o and c_o) on (011) in the manner indicated will produce the **Cmcm** structure with:

$$a = a_o, b = \sqrt{(b_o^2 + c_o^2)}, c = 2b_o c_o / b, y = 1/2 - c_o^2 / 2b^2$$

For **bct**, $a_o = b_o = \sqrt{(3/2)}$, $c_o = 1$. Twinning this cell produces **cco** sphere packing.

For **ccp**, the “orthorhombic” (now actually tetragonal) cell with two lattice points has $a_o = c_o = 1$, $b_o = \sqrt{2}$. Twinning this cell produces **hcp** (the {101} planes of the tetragonal cell are {111} planes of the conventional cubic cell).

For **bcc**, $a_o = b_o = c_o = \sqrt{(4/3)}$. Twinning this cell produces **bcc** again which is not surprising as {101} planes of **bcc** are already mirror planes.

To summarize, here are the parameters for important sphere packings in terms of **Cmcm** with points in 4 c : $C \pm (0, y, 1/4)$:

structure	a	b	c	y
ccp	$\sqrt{2} = 1.414$	$\sqrt{2} = 1.414$	$\sqrt{2} = 1.414$	$1/4$
cco	$\sqrt{(3/2)} = 1.225$	$\sqrt{(5/2)} = 1.581$	$\sqrt{(12/5)} = 1.549$	$3/10$
hcp	1	$\sqrt{3} = 1.732$	$\sqrt{(8/3)} = 1.633$	$1/3$
bcc	$2/\sqrt{3} = 1.155$	$\sqrt{(8/3)} = 1.633$	$\sqrt{(8/3)} = 1.633$	$1/4$

6.3.4 8-coordination: packing of trigonal prisms

By now the **bcc** arrangement should be familiar as an example of an 8-coordinated sphere packing.

Another simple arrangement is provided by the points of a primitive hexagonal lattice with $a = 1$, $c = 1$. This arrangement occurs as one of the high-pressure polymorphs of elemental Si ($a = 2.53$, $c = 2.37$ Å at 20 GPa). It also occurs in several compound structure types in which there is trigonal prismatic coordination of atoms. The vertices are those of a space filling by trigonal prisms of which there are two per lattice point. (Two prisms sharing a square face form a unit cell.) The density is $\rho = \pi/\sqrt{27} = 0.604$.

The relationship between these two packings (**cl** and **hP**) is very simple, and interesting in several contexts, although the general intermediate structure contains two kinds of sphere so it is not a packing of *equivalent* spheres. Fig. 6.25 compares a primitive hexagonal lattice, described using a super-cell with three points per cell, with **bcc** described using a similar cell.

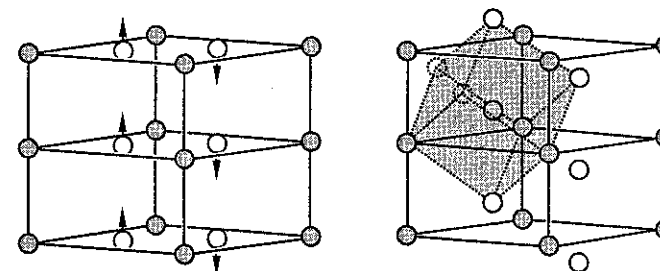


Fig. 6.25. The relationship between primitive hexagonal (= **hP**, left) and **bcc** (described using a hexagonal cell, right). The distance between neighboring lattice points is the same in each case. The conventional cubic cell for **bcc** is lightly shaded.

The intermediate structure is trigonal:

$$P\bar{3}m1, a = \sqrt{[3(1-z^2)]}, c = 1$$

$$\text{One sphere at } 1 \ a: 0,0,0; \text{ two spheres at } 2 \ d: \pm(1/3, 2/3, z)$$

When $z = 0$ we have the primitive hexagonal structure (symmetry $P6/mmm$) and when $z = 1/3$ we have the **bcc** structure described with the hexagonal cell. Note that c/a changes by only about 6% in the transformation. It should be noted also that in **bcc** we have 3^6 layers in *A*, *B* and *C* positions separated by $c/3$. The primitive hexagonal structure has these three layers collapsed to one layer of three times the density.

Note that combining any two of *A*, *B* or *C* will give a honeycomb (6^3) layer. This occurs if $z = 1/2$; at which point the structure is formally that of AlB_2 (§ 5.3.5) with symmetry again $P6/mmm$ (the honeycomb layers are *B*). The symmetry-breaking transition

from $z = 1/3$ (bcc) towards $z = 1/2$ is important in metallurgy and is known as the *bcc* $\rightarrow \omega$ transition.

There is a second way of filling space with trigonal prisms such that all vertices are equivalent (Fig. 6.26). Make a slab of face-sharing prisms with prism 3-fold axes all collinear. Now put such slabs together with the prism axes alternating. The prism vertices correspond to the centers of an 8-coordinated sphere packing:

$$14_1/amd, a = 1, c = \sqrt{12}, \rho = 0.6046. \text{ Centers in } 4a: 1 \pm (0, 3/4, 1/8)$$

This is the Th arrangement of ThSi_2 (Si centers the trigonal prisms). It is also the structure of a high-pressure polymorph of Cs.

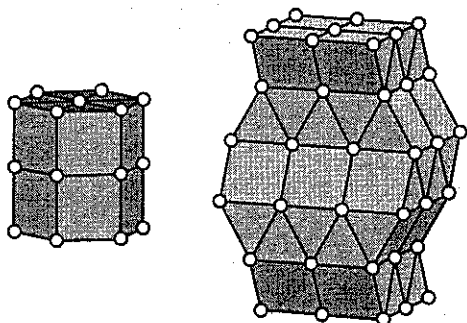


Fig. 6.26. Space fillings by trigonal prisms that correspond to 8-coordinated sphere packings. Left: primitive hexagonal. Right: a tetragonal sphere packing.

6.3.5 Another 8-coordination: the *J* lattice complex

Another 8-coordinated sphere packing is of very frequent occurrence in crystal structures. The arrangement is an example of an *invariant lattice complex*—an array of symmetry-related points on fixed positions. The more-common of these are sometimes described by symbols (see § 6.8.7) and the symbol for this one is *J*.¹

$$J \quad Pm\bar{3}m, a = \sqrt{2}, \rho = \pi\sqrt{32} = 0.5554. \text{ Centers in } 3c: (0, 1/2, 1/2)\kappa$$

It can be seen that this structure may be considered as derived from cubic eutaxy (*ccp*)

¹The reason for this particular symbol is apparently an association with the “jack” of the common game of that name [W. Fischer *et al.*, *Space Groups and Lattice Complexes*, National Bureau of Standards Monograph 134 (1973)]. However the jacks familiar to us have six points and $m\bar{3}m$ symmetry whereas the points in the *J* complex have $4/m\bar{3}m$ symmetry and eight neighbors. Nevertheless we like the name because of the association with K. H. Jack who appears to have been the first to point out the important relationship of this array to *hcp* [K. H. Jack & V. Guttman, *Acta Crystallogr.* 4, 246 (1951)].

by removal of 1/4 of the spheres (those at 0,0,0) and thus it has 3/4 of the density of eutactic arrangements.

The *J* complex occurs notably as the anion array in the cubic perovskite (ABX_3) structure (met earlier in § 5.3.4) which can be thought of as a three-dimensional array of corner-connected octahedra of anions *X* centered by cations *B*. The BX_3 arrangement alone is known as ReO_3 . The faces of the octahedra divide space into an equal number of regular octahedra and cuboctahedra (centered by *A* in *perovskite*). The packing could therefore also be considered as arising from a space-filling packing of regular octahedra and cuboctahedra (Fig. 6.27). The *A* atoms center the cuboctahedra, and we note, in passing, that the combination of *A* and *X* (AX_3) is *ccp* (see § 6.6.1).

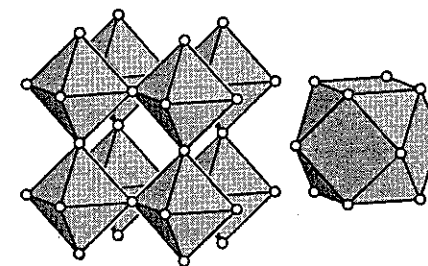


Fig. 6.27. Left: The *J* lattice complex shown as an array of corner-connected regular octahedra. Right: The cuboctahedron “hole” in the packing.

In the cubic structure, the bond angle $\theta = \angle B-X-B = 180^\circ$. If the octahedra are maintained rigid but tilted (thus “crumpling” the array and reducing the bond angle θ) so that $\cos^{-1}(-2/3) = 131.81^\circ < \theta \leq 180^\circ$ each vertex will still have eight nearest neighbors.¹

If all the octahedra (which remain undistorted) are rotated by an angle $\pm\phi$ about a set parallel $\langle 111 \rangle$ axes the arrangement can be converted from the cubic *J* structure ($\phi = 0$) to hexagonal eutaxy (*hcp*) ($\phi = \pm 30^\circ$, symmetry $P6_3/mmc$). If the octahedra are filled the final BX_3 arrangement is PdF_3 (§ 6.1.5). The intermediate and final structures have symmetry $R\bar{3}c$. Referred to a centered hexagonal cell and unit-diameter spheres:

$$a = \sqrt{8\cos\phi}, c = \sqrt{48}. \text{ Centers in } 18e: R \pm (x, 0, 1/4; 0, x, 1/4; \bar{x}, \bar{x}, 1/4), x = (\sqrt{3} - \tan\phi)/\sqrt{12}$$

It is interesting that the *J* structure can be considered to be composed of intersecting kagome layers parallel to all $\{111\}$. The points at any one elevation in the hexagonal structure such as $z = 1/4$ (with $x, y = x, 0; 0, x$ and \bar{x}, \bar{x}) correspond to the points in a hexagonal cell relating the kagome $\rightarrow 3^6$ illustrated in Fig. 5.40 (see also Exercise 10 in Chapter 5). Hexagonal eutaxy corresponds to a stacking of the 3^6 layers. In Fig. 6.28 try to see how collapsing the kagome nets to 3^6 corresponds to rotations of the octahedra alternately clockwise and anti-clockwise about $\{111\}$.

¹For $\theta < \cos^{-1}(-2/3)$ inter-octahedral $X \dots X$ distances will be less than the intra-octahedral distances.

Using the symbols of § 6.1.6, the stacking of kagome layers along [111] is $N_1N_2N_3$.

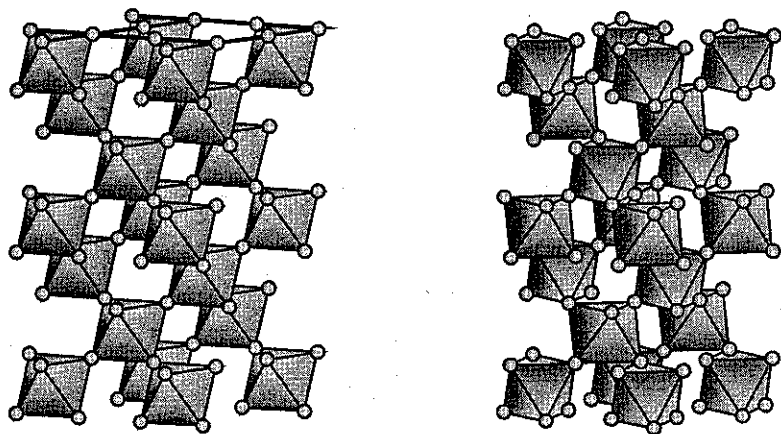


Fig. 6.28. Left: the octahedra of the *J* arrangement shown with [111] vertical on the page. Part of a kagome (3.6.3.6) net in a (111) plane is heavily outlined at the top. Right: the same set of octahedra after rotation as described in the text so that the vertices are hcp. The figure illustrates the transformation $\text{ReO}_3 \rightarrow \text{PdF}_3$.

6.3.6 Another 8-coordination: the pyrochlore packing

Another interesting 8-coordinated arrangement can also be considered as arising from a different array of corner-connected octahedra. We call it the pyrochlore packing as it is an idealization of the octahedral framework in compounds with the pyrochlore structure¹:

pyrochlore $Fd\bar{3}m$, $a = 16/\sqrt{18}$, $\rho = 27\sqrt{2}\pi/256 = 0.468$
 centers in 48 *f*: $F \pm (x, 1/8, 1/8; 1/4 - x, 1/8, 1/8; \bar{x}, 3/8, 3/8; 3/4 + x, 3/8, 3/8)\kappa$, $x = 7/16$

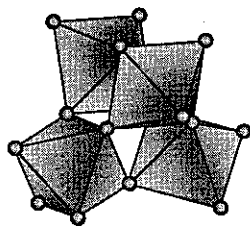


Fig. 6.29a. A "pyrochlore unit" of four octahedra sharing vertices. The space at the center is an "empty" octahedron.

¹Pyrochlore is a mineral of variable composition: $(\text{Ca}, \text{Na})_2(\text{Nb}, \text{Ta})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$.

The structure may be thought of as composed of "pyrochlore units" of corner-sharing octahedra such as illustrated in Fig. 6.29a. Further corner sharing between units produces the structure shown in Fig. 6.29b.

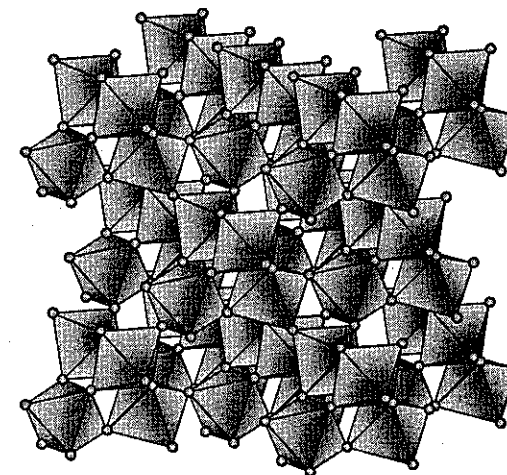


Fig. 6.29b. The pyrochlore packing as corner-connected octahedra. The drawing consists of a face-centered cubic array of the "pyrochlore units" of Fig. 6.29a.

The same arrangement occurs in intermetallic compounds: for example as the *W* arrangement in $\text{Fe}_3\text{W}_3\text{C}$ (with C in the octahedra).

6.3.7 Another 8-coordination: the *S* lattice complex

The final 8-coordinated sphere packing that we mention is another invariant cubic lattice complex (symbol *S*). A formal description for unit diameter spheres is:

S $\sqrt{43}d$, $a = 8/\sqrt{14} = 2.138$, $\rho = 2\pi/a^3 = 0.643$
 Sphere centers in 12 *a*: $I + (3/8, 0, 1/4; 1/8, 0, 3/4)\kappa$

The points of this arrangement divide space up into irregular octahedra (actually metaprisms) and irregular tetrahedra. The metaprisms form non-intersecting rods along $\langle 111 \rangle$ by sharing triangular faces. In Fig. 6.30 these rods are shown in a projection down [111]. The packing of rods in four different directions is the same as in the *garnet* cylinder packing to be described in § 6.7.3. Each metaprism also shares a face with a metaprism in each of three rods not parallel to it, so each metaprism shares a face with five adjacent metaprisms. A high-pressure form of elemental Ga has this structure. It also corresponds to the Th positions in the important Th_3P_4 structure type.

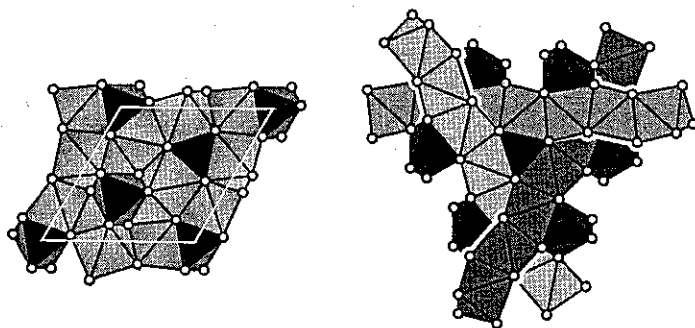


Fig 6.30. Left: The S structure projected down $[111]$. Dark shading indicates $[111]$ rods of face-sharing metaprisms. Right: parts of three rods parallel to the other three $\langle 111 \rangle$ directions are emphasized.

There are four-thirds of an octahedron (metaprism) and one tetrahedron for each sphere in the S packing. In Th_3P_4 , P atoms center the metaprisms. The centroids (equidistant from all six vertices) of the metaprisms are in 16 c : $I + (x, x, x; 1/4+x, 1/4+x, 1/4+x; 1/2-x, \bar{x}, 1/2+x; 1/4-x, 3/4-x, 3/4+x)\kappa$, $x = 1/12$. The real structure of Th_3P_4 (for data see Appendix 5) has x close to this "ideal" value. The centroids of the tetrahedra are in 12 b : $I + (7/8, 0, 1/4; 5/8, 0, 3/4)\kappa$. Note that the tetrahedral sites (12 b) also form an S lattice complex displaced from the 12 a positions by $1/2, 0, 0$. Filling 12 a by A and 12 b by B would give a (hypothetical) 4-coordinated structure AB that is its own antistructure. The tetrahedral sites are far from regular; in the AB structure just described the ABA angles are 99.6° ($4\times$) and 131.8° ($2\times$). Taken together the A and B positions form a 4-connected net known as S^* which is described in § 7.3.12.

There is a sense in which the S structure is intermediate between the primitive hexagonal and cp arrays. Thus consider the division of space into tetrahedra and/or 6-coordinated figures (prisms, metaprisms or antiprisms): (Here N_6 and N_4 are the numbers of six- and 4-coordinated sites per packing atom.)

structure	N_6	N_4
primitive hexagonal	2	0
S (Th_3P_4)	$4/3$	1
eutactic (cp)	1	2
bcc	0	6

6.3.8 7-coordination and a relation between FeSi and NaCl

7-coordinated sphere packings can be obtained in a rather obvious way by prismatic stacking of 5-coordinated layers. We describe such a stacking of $3^3.4^2$ nets in § 6.4.2 and a stacking of $3^2.4.3.4$ nets in § 6.4.3.

Another, less obvious, 7-coordinated packing, again for spheres of unit diameter is:

$$Pa\bar{3}, a = 4/(\sqrt{15} - \sqrt{3}) = 1.868, \rho = 0.6802$$

$$\text{Sphere centers in } 8c: \pm(x, x, x; (1/2+x, 1/2-x, \bar{x})\kappa, x = (\sqrt{5} - 1)/8 = 0.155$$

Note that for $x = 1/4$ we have a primitive cubic structure with a doubled cell edge (8 lattice points). The transformation from the primitive cubic structure to the $Pa\bar{3}$ structure (and *vice versa*) involves displacements along all four $\langle 111 \rangle$ directions and is rather difficult to illustrate; the neighbors of the points in one unit cell are shown in the top part of Fig. 6.31.

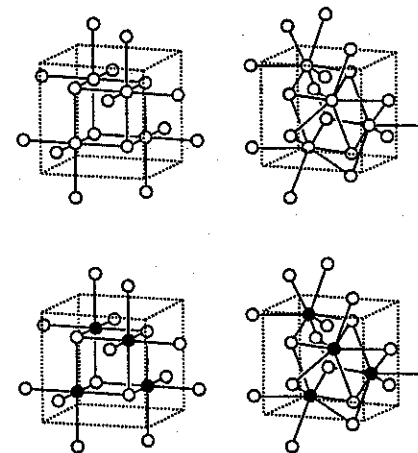


Fig. 6.31. Top: the $Pa\bar{3}$ 7-coordinated structure (right) compared with the primitive cubic structure (left). Bottom: alternately coloring the points in these structures produces NaCl (left) and FeSi (right).

We have seen that the anions in **fluorite** (CaF_2) are in a primitive cubic array. In PdF_2 recovered from high pressure (under which conditions it probably is **fluorite**) the F array is the $Pa\bar{3}$ structure. For crystallographic data for PdF_2 see Appendix 5.¹

If the eight points in 8 c of $Pa\bar{3}$ are alternately colored black and white in such a way that (e.g.) those at x, y, z are black and those at $1-x, 1-y, 1-z$ are white, the symmetry is lowered to $P2_13$ and the two sets of points are at 4 a : $x, x, x; (1/2+x, 1/2-x, \bar{x})\kappa$. this corresponds to the situation in idealized FeSi with $x_{\text{Fe}} = 1-x_{\text{Si}}$. (In the real structure of FeSi , $x_{\text{Fe}} = 0.136$, $x_{\text{Si}} = 0.844$ —see Appendix 5). Similarly coloring the points of the primitive cubic array produces NaCl . We have therefore derived a simple relationship between these last two structures as also shown in Fig. 6.31.

¹The reported symmetry of this form of PdF_2 is actually $P2_13$, but the parameters are very close to what they would be for $Pa\bar{3}$ symmetry [A. Tressaud & G. Demazeau, *High Temp. High Press.* **16**, 303 (1984)] and these are given in Appendix 5.

6.3.9 6-coordination: the *T* lattice complex and cristobalite

Structures with lower coordination numbers are better described as nets [systems of points (atoms) connected by edges (bonds)]. However we will consider here a few 6-coordinated sphere packings. The first is with spheres at the points of a simple cubic lattice. Note that a cube is a special case of a rhombohedron (with $\alpha = 90^\circ$). It should be clear that a cube of unit edge can be smoothly distorted to a rhombohedron with $\alpha = 60^\circ$ (a primitive cell of *fcc*) so we have a simple way of transforming from simple cubic to face-centered cubic. The intermediate symmetry is $R\bar{3}m$ and as long as $\alpha > 60^\circ$ there are only six nearest neighbors. Therefore, this 6-coordinated sphere packing can approach arbitrarily close in density to that of closest packing (12-coordinated).

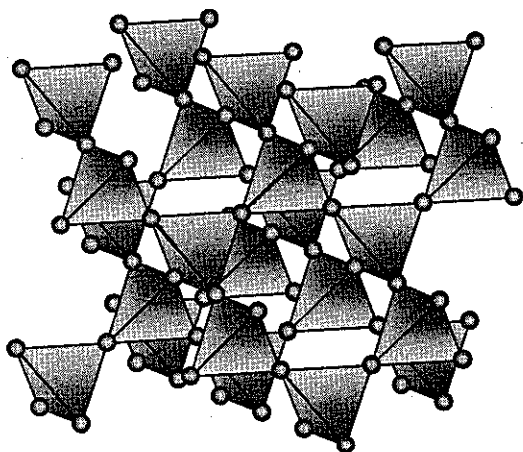


Fig. 6.32. The *T* structure shown as corner-connected tetrahedra.

A second 6-coordinated packing we discuss here has centers of spheres at the points of another invariant cubic lattice complex (symbol *T*).

T $F\bar{4}3m$, $a = \sqrt{8}$, $\rho = 0.370$. Sphere centers in 16 *c*: $F + (0,0,0); (0,1/4,1/4)\kappa$

This is another pattern that occurs in a wide variety of crystal structures. It is the oxygen positions of an idealized high-cristobalite (β -cristobalite) form of SiO_2 , so it is sometimes (a little misleadingly) called the cristobalite arrangement. Other notable occurrences are at the sites of the octahedrally-coordinated atoms in the spinel structure and the pyrochlore structure, and the Cu atoms in the MgCu_2 structure (§ 6.6.3). The structure can be considered as made up of corner-connected tetrahedra as shown in Fig. 6.32. Examination of the figure will show that the points fall on kagome (3.6.3.6) nets parallel to $\{111\}$ as they do in the *J* structure. However now the kagome nets normal to any one $\langle 111 \rangle$

direction alternate with 3^6 nets with twice the spacing between points. The empty space (not in the tetrahedra) in the structure is made up of a packing of truncated tetrahedra, accordingly the structure can be considered as arising from a packing of regular tetrahedra and truncated tetrahedra.¹

Using the symbols of § 6.1.6, the stacking of atom layers normal to $[111]$ in the *T* structure is $N_1n_3N_2n_1N_3n_2\ldots$ —the same as that of the Al atoms in the spinel structure.

The *T* structure can be collapsed by concerted rotations of the tetrahedra about $\bar{4}$ axes to produce denser arrangements (in much the same way as the *J* structure is converted to *hcp* by rotations of octahedra) as illustrated in Fig. 6.33. Let *B* represent the centers of the tetrahedra and *X* the vertices. Analytical descriptions of these transformations are, in terms of $u = \cos\phi$, $s = \sin\phi$ and $t = \tan\phi$ (ϕ is a rotation angle discussed below):

(i) *T* \rightarrow cubic eutaxy:

$$\bar{4}2d, a = 2u, c = \sqrt{8}$$

$$X \text{ in } 8d: I + (x, 1/4, 1/8; \bar{x}, 3/8, 1/8; 3/4, x, 7/8; 1/4, \bar{x}, 7/8), x = t/4$$

$$B \text{ in } 4a: I + (0,0,0; 1/2,0,3/4)$$

When $\phi = 0^\circ$ the structure is the cubic *T* pattern described with a body-centered tetragonal cell. When $\phi = 45^\circ$ it is *ccp* described with a doubled cell ($c = 2a$). Note that the density increases by a factor of two in going from *T* to *ccp*.

If atoms *A* are in positions $4b: I + (0,0,1/2; 1/2,0,1/4)$ we have stoichiometry ABX_2 . If $\phi = 45^\circ$, both *A* and *B* are tetrahedrally coordinated by *X* and we have a superstructure of sphalerite (ZnS); an example is chalcopyrite, CuFeS_2 . If *A* is larger than *B*, then $\phi [= \tan^{-1}(4x)]$ is smaller, allowing the $\{A\}X_4$ tetrahedron to expand, thus for CdSiP_2 , $x = 0.21$ ($\phi = 40^\circ$).

(ii) *T* \rightarrow 11-coordinated.

$$P4_12_12, a = 1 + u, c = \sqrt{8}u$$

$$X \text{ in } 8b: (x, y, z; y, x, \bar{z}; \bar{x}, \bar{y}, 1/2 + z; \bar{y}, \bar{x}, 1/2 - z; 1/2 - x, 1/2 + y, 1/4 - z; 1/2 - y, 1/2 + x, 1/4 - z; 1/2 + x, 1/2 - y, 3/4 - z; 1/2 + y, 1/2 - x, 3/4 - z),$$

$$x = u/(2 + 2u), y = s/(2 + 2u), z = (1 + t)/8$$

$$B \text{ in } 4a: (x, x, 0; \bar{x}, \bar{x}, 1/2; 1/2 - x, 1/2 + x, 1/4; 1/2 + x, 1/2 - x, 3/4),$$

$$x = (1 + u + s)/(4 + 4u)$$

This $P4_12_12$ structure is actually an idealization (regular tetrahedra) of the anion positions in the low-cristobalite form of SiO_2 . $\phi = 0^\circ$ corresponds to *T* and $\phi = 45^\circ$ corresponds to the 11-coordinated packing described in § 6.3.1. Just as there are compounds ABX_2 with $\bar{4}2d$ symmetry, there are also ternary compounds with $P4_12_12$ symmetry. Examples include LiAlO_2 and NaAlO_2 with different values of ϕ . If $A = B$ we have the structure of β - BeO , which we meet again in § 7.3.3. Cristobalite is intermediate,

¹This structure is just one of an infinite number of ways of packing these polyhedra (see the discussion of the MgCu_2 and the MgZn_2 structures in § 6.6.3).

with $\phi \approx 20^\circ$ at room temperature.¹ Note that, like the quartz form of SiO_2 , cristobalite exists in enantiomorphic forms with symmetry either $P4_12_12$ or $P4_32_12$.

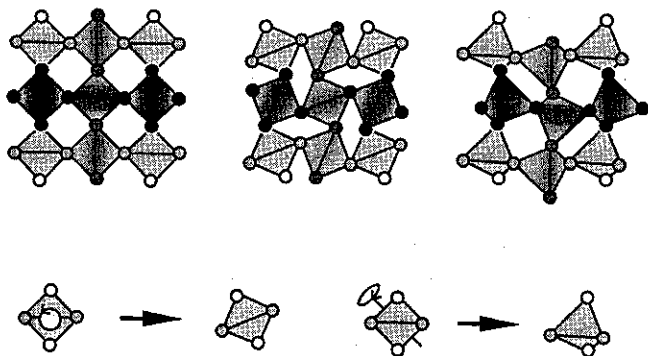


Fig. 6.33. Partial "collapse" of the ideal cristobalite (top left) to the $\bar{1}42d$ structure (top middle) and to the $P4_12_12$ structure (top right). The structures are projected down c and the centers of the tetrahedra are at heights differing by $c/4$. $\phi = 22.5^\circ$ in the two derived structures. The lower part of the figure shows how a tetrahedron appears in projection after rotation about a $\bar{4}$ axis.

There is a third way (with symmetry $Pna2_1$) to collapse the T structure by concerted rotations of tetrahedra, this time to give **hcp**, but in the intermediate arrangement the structure has two crystallographically-distinct spheres.²

6.3.10 Another 6-coordination: the Y lattice complex

Our last sphere packing with 6-coordination is also cubic:

$$P2_13, a = \sqrt{[1/(8x^2 - 2x + 1/2)]}, 0 \leq x \leq 1/4$$

Sphere centers in 4 a : $(x, x, x); (1/2+x, 1/2-x, \bar{x})\kappa$

If $x = 0$ (or $1/4$ or $1/2$ or $3/4$) the arrangement is face-centered cubic (cubic eutaxy) with 12-coordination. If x is changed from 0 then there are six nearest and six next-nearest neighbors. Increasing $|x|$ from 0 corresponds to displacing the centers of spheres along all four $\langle 111 \rangle$ directions (cf. the $Pa\bar{3}$ 7-coordinated packing described in § 6.3.8 above). The density is a minimum for $|x| = 1/8$ at which point the unit cell parameter (for equal spheres)

¹Note that if we consider the $(\text{Si})\text{O}_4$ tetrahedra in cristobalite to be rigid, compression along c will require ϕ to increase (to decrease c), and hence a will decrease also. Materials that behave in this way (contracting in a direction normal to an applied compressive stress) are rather rare, but cristobalite is one. In terms of elasticity theory, it is said that it has a negative Poisson's ratio.

²For a detailed account of these transformations, and their relevance to crystal chemistry, see M. O'Keeffe & B. G. Hyde, *Acta Crystallogr.* B32, 2923 (1976).

is $\sqrt{8/3}$ and the density is $\sqrt{3/2}\pi/8 = 0.481$. The symmetry is now $P4_332$ and the sphere centers are on the invariant cubic lattice complex $+Y$ with coordinates $(1/8, 1/8, 1/8; 5/8, 3/8, 7/8)\kappa$. Fig. 6.34 (which might be compared with Fig. 6.31) shows unit cells of **ccp** (using $x = 1/4$) and $+Y$ for comparison. The six neighbors of $+Y$ are at the vertices of a trigonal metaprisim (symmetry 32) as indicated in the figure.

The **Fe** (or **Si**) atoms in **FeSi** are close to the $+Y$ packing. As we saw in § 6.3.8 converting the **Fe** and **Si** arrays to two inter-penetrating **ccp** arrays produced **NaCl**. But two inter-penetrating **ccp** arrays also describes **sphalerite** (**ZnS**, see § 6.1.2), the difference is that in **NaCl** the two arrays are displaced by $1/2, 1/2, 1/2$; in **sphalerite** they are displaced by $1/4, 1/4, 1/4$ (or $3/4, 3/4, 3/4$). Thus the transformation $+Y \rightarrow \text{ccp}$ can also be used to describe **FeSi** \rightarrow **sphalerite**. A description of the three structures in terms of a $P2_13$ cell is:

NaCl	$x_{\text{Na}} = 0.25$	$x_{\text{Cl}} = 0.75$
FeSi	$x_{\text{Fe}} = 0.15$	$x_{\text{Si}} = 0.84$
ZnS	$x_{\text{Zn}} = 0.0$	$x_{\text{S}} = 0.75$

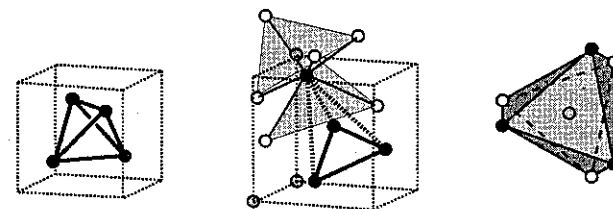


Fig. 6.34. Left: a unit cell of **ccp**. Center: a unit cell (filled circles) of $+Y$; the neighbors of one point are shown as open circles and the two equilateral faces of the trigonal metaprisim formed by those points are lightly shaded. Right: the same coordination metaprisim viewed down a 3-fold axis.

6.4 Sphere packings with cube and trigonal prism sites as stackings of two-dimensional nets

Many of the sphere packings in crystal structures are simply described as a stacking of planar nets; particularly 3^6 and 4^4 . If we remove the restriction to closest packings of such layers, structures can be generated with sites that are trigonal prisms or cubes. Here we extend our notation for describing structures based on closest packing to include these other packings also. We give many examples of real structures based on the idealized sphere packings; crystallographic data for these compounds are collected in Appendix 5.

6.4.1 Non-close-packed stackings of 3^6 nets

We have already discussed closest packings as a stacking of 3^6 nets in positions labeled

A, B or C. We did not allow sequences involving two layers in the same position. In a sequence AB the spacing between layers of unit-diameter spheres is assumed to be (at least close to) $\sqrt{2/3} = 0.816$. A sequence AA requires layers to be (close to) unit distance apart and indeed the symbol $A (= AAA\dots)$ could be taken to stand for a primitive hexagonal lattice sphere packing ($c/a = 1$). Allowing like letters to repeat generates trigonal prismatic sites between the layers. For AA these sites are at positions β and γ at the same level and together they form a 6^3 net within the layer as shown in Fig. 6.35. For AIB_2 (Greek letters now for B, and parentheses enclose sites at the same level) the sequence is $A(\beta\gamma)A(\beta\gamma)A\dots$ showing that B atoms fill *all* the trigonal prism sites of a primitive hexagonal AI structure and form a 6^3 (honeycomb) net, as described in § 5.3.5.

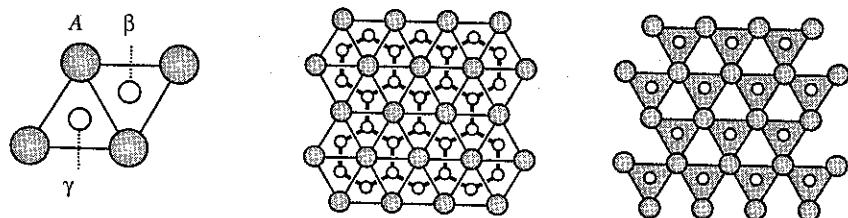


Fig. 6.35. Left: The position A of a cp layer and two trigonal prism sites α and β between two A layers. Center: illustrating that the β and γ sites together for a 6^3 net. Right: the pattern of trigonal prisms when just the β sites are occupied.

Fig. 6.35 also shows the pattern of trigonal prisms when one half of the trigonal prism sites are occupied. A simple structure of this type is WC which may be written (with Greek letters for C) $A\beta A\beta A\dots$. As shown in Fig. 6.36, the $\{C\}W_6$ trigonal prisms form infinite columns by sharing their triangular faces.¹ It might be noted that the structure is its own antistructure so there are also $\{W\}C_6$ trigonal prisms.

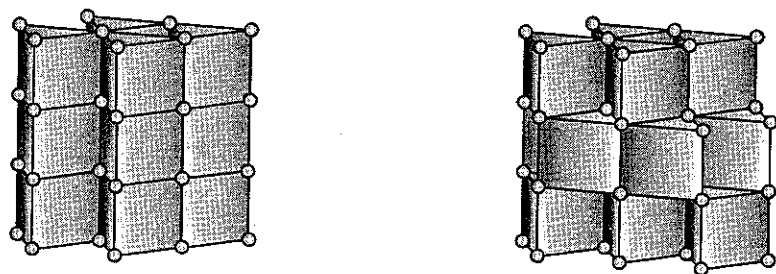


Fig. 6.36. Left: WC as $\{C\}W_6$ trigonal prisms. Right: NiAs as $\{As\}Ni_6$ trigonal prisms.

¹Note that B and C are notations for layer positions, but B and C are symbols for chemical elements!

NiAs was described earlier (§ 6.1.5) in terms of hcp As and can be coded (with Greek letters for Ni) as $B\alpha C\alpha B$; the structure with symbols for cations and anions reversed is $A\beta A\gamma A\dots$. The layers of trigonal prisms are the same as in WC, but now adjacent layers are staggered so that trigonal prisms share only edges between the layers as illustrated in Fig. 6.36.

We next consider some patterns in which stackings of the AA type containing trigonal prism sites are mixed with those of the AB type that contain tetrahedral and octahedral holes. Special interest attaches to slabs AA with half the trigonal prism holes filled, and to slabs AB with either all the octahedral holes or all the tetrahedral holes filled. Fig. 6.37 shows these three kinds of slab. Notice that the faces of the polyhedra occupy one half of the triangles in a cp layer (cf. Fig. 6.35, right); a consequence is that slabs of these sorts can be joined without polyhedra sharing faces, as in the structures to be described next. Notice that an isolated octahedral or trigonal prism slab of X between two cp Y layers has stoichiometry XY_2 ; when the Y are shared between two slabs the contribution to the overall stoichiometry is $XY_{2/2} = XY$. An isolated tetrahedral layer has stoichiometry X_2Y_2 and a slab sharing Y with adjacent slabs contributes $X_2Y_{2/2} = X_2Y$ to the overall stoichiometry. We have already discussed (§ 6.1.5) La_2O_3 with hcp La and alternating octahedral slabs (OLa) and tetrahedral slabs (O_2La).



Fig. 6.37. From left to right: parts of layers of trigonal prisms, octahedra and tetrahedra.

Two 10-coordinated packings with the same density are: $AABB\dots$ and $AABBCC\dots$

$$AABB \quad P6_3/mmc, a=1, c=2+\sqrt{8/3}=3.63, \rho=2\pi(\sqrt{18}+\sqrt{27})=0.6657$$

$$\text{Centers in } 4f: \pm(1/3, 2/3, z; 1/3, 2/3, 1/2-z), z=1/(4+\sqrt{24})=0.112$$

We have in fact met this structure as the Ti packing in TiP (see § 6.1.5, especially Fig. 6.13, p. 220). With Greek letters for P the packing is $A\gamma B\alpha B\gamma A\beta A\dots$. P(1) is in octahedral holes (γ) between A and B layers. P(2) is in trigonal prismatic holes: β between AA layers and γ between BB layers. The combined P packing $\gamma\alpha\gamma\beta\dots$ corresponds to *hc* close packing (but note that the packings cannot correspond simultaneously to *ideal* $AABB$ cation packing and *ideal* *hc* anion packing as the two packings have incompatible spacing requirements).

The same cation packing is found in Sc_2O_2S which may be coded with Greek letters for O,S as $A\beta\alpha B\gamma B\alpha\beta A\gamma\dots$. This shows that the tetrahedral sites between AB layers are filled (these are O atoms) and one-half the trigonal-prismatic sites between AA and BB layers are filled (these are S atoms).¹

¹If one wants to be completely explicit, the elemental symbols could be used as subscripts.

In the TiP and Sc_2O_3 structures the filling of sites in the trigonal prism layers is dictated by the requirement that the trigonal prisms do not share triangular faces with occupied octahedra (in TiP) or occupied tetrahedra (in Sc_2O_3) in adjacent layers. In the hexagonal structures of MoS_2 and NbS_2 the anion packing is $AABB$ but the interstices in the AB slab are empty so there are isolated trigonal prism layers and it does not matter very much therefore which set of sites is filled in these layers. In the $2H_a$ structure of NbSe_2 the sequence is $A\gamma AB\gamma B\dots$ and in the $2H_b$ structure of MoS_2 the sequence is $A\beta AB\alpha B\dots$.

In the structure of BaCu , Ba has the same ($AABB$) packing, with Cu in *all* the trigonal prism sites: with Greek letters for Cu, the stacking sequence is $A(\beta\gamma)AB(\alpha\gamma)B$. Notice that the Cu atoms are on 6^3 nets and the structure could be described as an intergrowth of AlB_2 slabs BaCu_2 with cp slabs Ba.

The second 10-coordinated sphere packing ($AABBCC$) is rhombohedral:

$$AABBCC \quad R\bar{3}m, a = 1, c = 3 + \sqrt{6}. \text{ Centers in } 6c: R \pm (0, 0, z), z = 1/(6 + \sqrt{24}) = 0.092$$

The S atoms in $3R \text{ MoS}_2$ have this arrangement; with Greek letters for Mo the sequence is $A\beta AB\gamma BC\alpha C$. The pattern of filling of trigonal prisms destroys the center of symmetry and there are two kinds of S atom in the structure (for data see Appendix 5).

There are other ways of stacking parallel 3^6 nets.¹ Adjacent layers can be stacked so there are only two contacts for each sphere with neighbors in an adjacent layer. Fig. 6.38 indicates the appropriate positions, labeled D, E and F . Notice that positions D, E and F are only relevant for stacking over an A layer. For unit spheres in contact the spacing between layers such as AD is $\sqrt{3}/2 = 0.866$.

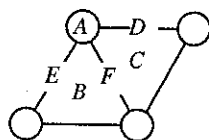


Fig. 6.38. Illustrating positions for stacking 3^6 nets. A, B and C are the same as shown in Fig. 6.1.

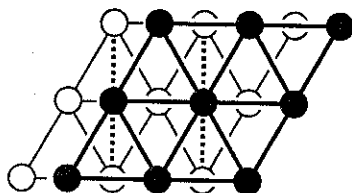


Fig. 6.39. bct projected on (110) showing the AD stacking of 3^6 nets (filled and open circles respectively). The cell outlined by dotted lines is a face centered tetragonal cell $\sqrt{2}a \times \sqrt{2}a \times c$ (a is the edge of the body-centered tetragonal cell). c is horizontal on the page.

¹See also A. F. Wells *Structural Inorganic Chemistry* [5th Ed. Oxford (1984), Chapter 4].

A sequence such as $ADAD\dots$, illustrated in Fig. 6.39, corresponds to a 10-coordinated sphere packing (6 neighbors in each layer and 2 above and 2 below) and is, in fact, our old friend bct (§ 6.3.2). The nets are (110) layers of the body-centered cell (shown in Fig. 6.21, p. 230) or (100) layers of a face-centered cell (indicated in Fig. 6.39).

The 10-coordinated sequence $ADEF$ is closely related to bct (which is AD) and has the same density. The structure is orthorhombic:

$$ADEF \quad Fddd, a = 1, b = \sqrt{3}, c = \sqrt{12}. \text{ Sphere centers in } 8a: F \pm (1/8, 1/8, 1/8)$$

γ -Pu has this structure (see Exercise 9). Fig. 6.40 (which should be compared with 6.39) illustrates the structure projected on (001).

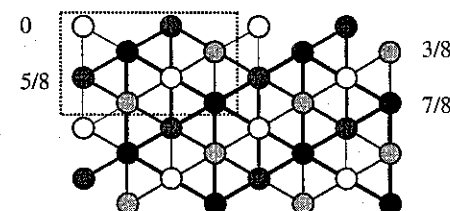


Fig. 6.40. The 4-layer sequence $ADEF$ of stacked 3^6 layers with $Fddd$ symmetry projected down c . (b is horizontal on the page). Numbers are elevations in units of c .

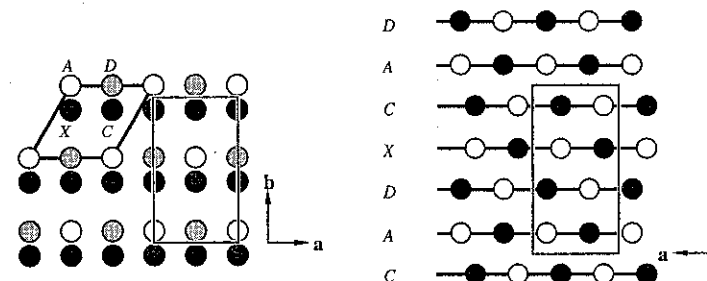


Fig. 6.41. An 11-coordinated sphere packing obtained by stacking 3^6 nets as described in the text. Left: projected on (001) (b vertical on the page). Depth of shading indicates increasing elevation. Right: projected on (100). Open and filled circles represent sphere centers with $x = 0$ and $1/2$. The orthorhombic unit cell is outlined (c vertical on the page).

There are many other possibilities, but they are not very common in crystal chemistry. One of the simpler is the sequence of two close-packed layers, say BA followed by D which, in turn, is followed by another close-packed layer. This fourth layer is not in a position to which we have yet applied a label; it is shown in Fig. 6.41 where it is labeled X . This is an 11-coordinated sphere packing; for example, a sphere in an A layer has 6

neighbors in the layer, 3 in the *B* layer and 2 in the *D* layer. The crystallographic description of this packing is:

$$Cmca, a = 1, b = \sqrt{3}, c = \sqrt{(8/3) + \sqrt{3}}, \rho = 4\pi(9 + \sqrt{72}) = 0.719$$

Sphere centers in 8 *f*: $C \pm (0, y, z; 0, y, 1/2 - z), y = 1/6, z = 3/\sqrt{2} - 2$

The density is the same as that of the tetragonal 11-coordinated sphere packing of § 6.3.1; it would be nice to know if a less dense 11-coordinated packing exists.

6.4.2 Non-close-packed stackings of 4^4 nets

Recall that *ccp* can also be described as a stacking of 4^4 nets. A number of other sphere packings (not *closest* sphere packings) can also be so described. It is convenient now to recognize four positions for the layers: *A*, *B*, *C* and *D* as shown in Fig. 6.42.¹

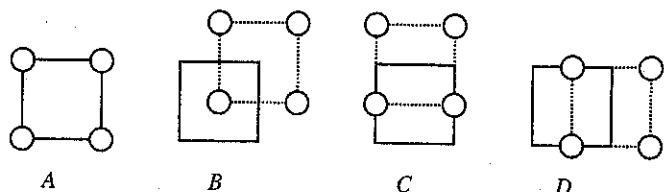


Fig. 6.42. The four relative positions for stacked 4^4 nets. The full lines outline a square cell.

A pair of layers packed *AB* (or, equivalently, *CD*) corresponds to a (100) slice of *ccp* and for unit spheres, the spacing between layers is (ideally) $1/\sqrt{2}$.² Such a slab contains tetrahedral sites. The octahedral sites of *ccp* lie in the *A* and *B* layers, so the slab also contains half octahedra (square pyramids). Thus to have octahedral sites a three-layer sequence such as *ABA* is necessary. The tetrahedral sites lie in the plane half way between *A* and *B* in both the *C* and *D* positions (see Fig. 6.43). The slab with filled sites could therefore be coded (using Greek letters for the tetrahedral sites) as $A(\gamma\delta)B$ with parentheses again being used to enclose atoms at the same level. This unit is a very common element of crystal structures and we refer to it as a *tetragonal tetrahedral layer* (to distinguish it from the hexagonal slab of tetrahedral sites between two 3^6 layers). It is a (100) layer of *fluorite*. Notice that the tetrahedral sites are on a 4^4 net of twice the density (dotted lines on the left in Fig. 6.43).

Such layers occur in the litharge form of *PbO* with O in the tetrahedral sites and the mackinawite form of *FeS* (indeed they are sometimes called mackinawite layers) with Fe in

tetrahedral sites. The overall cation packing in *PbO* is approximately *ccp* as the sequence is $A(\gamma\delta)BA(\gamma\delta)B\dots$ but in the real material the inter-layer spacings are not exactly the ideal values.

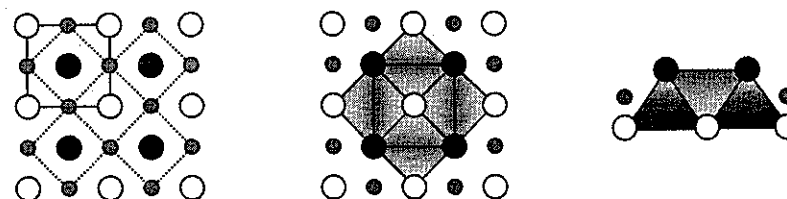


Fig. 6.43. Left: plan view of two 4^4 layers of spheres (open and filled large circles) stacked *AB*; the smaller circles indicate the location of tetrahedral sites between the layers. Center: some of the tetrahedra are shown. Right: the same in elevation.

PbFCl (matlockite) is an important example of a structure type with tetragonal tetrahedral layers, and as it is one of the most commonly-occurring of all ternary structures we digress a little to describe it here. The structure goes under several names and we also use **BaMgSi** for anti-structure compounds in which **Ba** + **Mg** replace **Cl** + **F**; in *Pearson's Handbook* (Book List) it is called **Cu₂Sb**. It is related to **PbO** in the sense that there are (**PbF**) tetragonal tetrahedral layers with stoichiometry **Pb₂F₂** but they are now interwoven with two layers of **Cl** on 4^4 nets. Now the tetrahedral layers are further apart, and in isostructural compounds like **LaOX** (*X* = Cl, Br, I) with layers of {O}La₄ tetrahedra of almost constant size, the interlayer spacing is determined by the size of the interlayer atoms *X*.

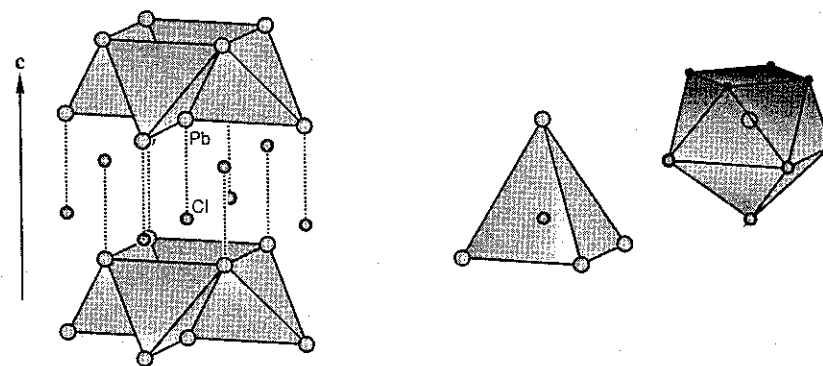


Fig. 6.44. The structure of **PbFCl**. Left: showing the layers of edge-sharing {F}Pb₄ tetrahedra with Cl atoms in intervening layers. Right: showing the {Cl}Pb₅ and {Pb}Cl₅F₄ coordination polyhedra around the two atoms identified with labels on the left. F atoms (not shown on the left) are small filled circles.

¹There should be no risk of confusion with the symbols for stacking 4^4 nets with those for stacking 3^6 nets as long as it is made clear to which one refers. *Parallel* 3^6 and 4^4 nets of equal-sized spheres are incommensurate so mixed stackings do not normally occur.

²Beware! If the spacing between the layers is $1/2$ one has an element of *bcc*.

Figure 6.44 illustrates the structure of PbFCl . F is in a $\{\text{F}\}\text{Pb}_4$ tetrahedron and Cl is in a $\{\text{Cl}\}\text{Pb}_5$ square pyramid. The Pb coordination is an irregular square antiprism with a small F_4 square face and a larger Cl_4 square face; this larger face is capped by a fifth Cl to give Pb a 9-coordination, $\{\text{Pb}\}\text{Cl}_5\text{F}_4$.

We return now to a discussion of further packings of 4^4 layers. A sequence such as AC with spacing $\sqrt{3}/2$ will generate an element of primitive hexagonal packing, in fact a $(10\bar{1}0)$ layer, and a continuing sequence AC... (or AD... or BC... or BD...) is primitive hexagonal with the 6 axes of the trigonal prisms perpendicular to the stacking direction as can be seen from Fig. 6.45.

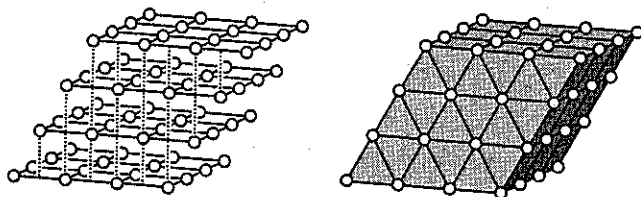


Fig. 6.45. Illustrating that non-close-packed stacking of 4^4 layers can generate a primitive hexagonal array. Left: a sequence of 4^4 layers. Right: the trigonal prismatic sites are shaded.

A sequence such as AA, with unit spacing between the layers, corresponds to a slice of primitive cubic in what should be an obvious way.

We now describe some other stackings of 4^4 layers which correspond to packings of equivalent spheres and which are encountered in crystal chemistry. As discussed above they can contain trigonal prism and cube sites as well as tetrahedral sites between two layers that are in closest packing. We assume the interlayer spacings to be those for spheres in contact.

ACBD: This corresponds to a packing of trigonal prisms with their axes pointing in two orthogonal directions (and normal to the stacking directions). The symmetry is $I4_1/amd$ (with the 4-fold axis parallel to the stacking direction) so the prisms do not have 6-fold axes in the structure. We have described this 8-coordinated packing in § 6.3.5 (see Fig. 6.26).

ABCD. This is a 10-coordinated sphere packing (it has the same density as the 10-coordinated stackings of 3^6 nets described above) and might be considered an intergrowth of **ccp** (the AB and CD parts) with primitive hexagonal (the BC and DA parts). The symmetry is now orthorhombic:

ABCD $Cmcm$, $a = c = 1$, $b = \sqrt{2} + \sqrt{3}$. Centers in 4 c: $C \pm (0, y, 1/4)$, $y = (3 - \sqrt{6})/4$

This packing is found as the structure of one of the high-pressure polymorphs of Ga. If the trigonal prism sites (between the BC and DA layers) are filled, the important **CrB** structure type (**B** in the trigonal prisms) is obtained. In **UBC**, in addition to **B** in the hexagonal prisms (of U), there are C atoms in the square pyramids.

The structure is shown in three ways in Fig. 6.46, first as a stacking of 4^4 nets,

secondly with the trigonal prisms shaded in, and finally as a projection down **a**. In the last case the trigonal prism centers are indicated; notice that they form zig-zag rods parallel to **c**.

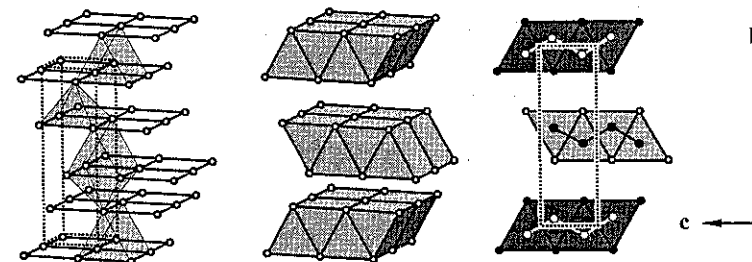


Fig. 6.46. Illustrating an ABCD stacking of 4^4 layers (**CrB** packing). In the middle the trigonal prism layers are shaded. On the right the structure is shown in projection on (100) (light and dark shading is used to differentiate prisms with centers at $x = 0$ and $x = 1/2$). The trigonal prism sites are shown as larger circles connected by lines to their nearest neighbors.

We digress to describe a related 10-coordinated sphere packing of the same density that is not however usefully described as a stacking of layers. In this structure we again have trigonal prisms, but now in columns (rather than slabs) and the sphere packing corresponds to the Fe atom positions in (idealized) **FeB** (**B** is in the trigonal prisms). Fig. 6.47 compares the two packings. In both structures the trigonal prism centers form zig-zag rods which are normal to the plane of projection in Fig. 6.47.

FeB packing $Pnma$, $a = 1.9062$, $b = 1$, $c = 1.6506$
Sphere enters in 4 c: $\pm(x, 1/4, z)$; $1/2+x, 1/4, 1/2-z$, $x = 0.1811$, $z = 0.1583$

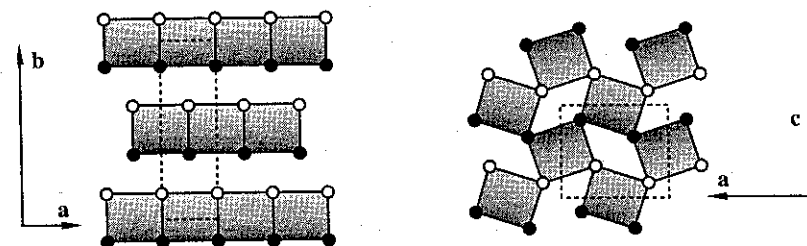


Fig. 6.47. Left: the **CrB** sphere packing (of **Cr**) projected on (001) (compare fig. 6.46). Open and filled circles are at $z = 1/4$ and $3/4$ respectively. Right: the **FeB** sphere packing (of **Fe**) projected on (010). Open and filled circles are at $y = 1/4$ and $3/4$ respectively. In both cases shaded rectangles are columns of trigonal prisms sharing square faces.

ACDABDCB: This is another 10-coordinated sphere packing of the same density and can similarly be considered as an inter-growth of alternate layers of **ccp** and primitive

hexagonal. It is tetragonal:

ACDABDCB $I4_1/amd$, $a = 1$, $c = \sqrt{8} + \sqrt{12} = 6.293$

Sphere centers in 8 c : $I \pm (0, 1/4, z)$; $0, 3/4, 1/4 + z$, $z = \sqrt{3}/[8(\sqrt{2} + \sqrt{3})] = 0.0688$

This occurs as the Mo packing in α -MoB (with again B in the trigonal prismatic sites, now between AC, DA, BD and CB). In contrast to the previous case (ABCD, CrB), the trigonal prisms "point" in two different directions as shown in Fig. 6.48 (which should be compared with the middle of Fig. 6.46). β -MoB is CrB.

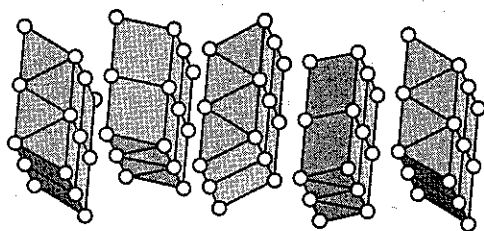


Fig. 6.48. Illustrating an ACDABDCB stacking of 4^4 layers (c is horizontal).

AABB: This is a 9-coordinated sphere packing and might be considered an intergrowth of ccp (the AB and BA parts) with primitive cubic (the AA and BB parts). The symmetry is tetragonal:

AABB

$I4/mmm$, $a = 1$, $c = 2 + \sqrt{2}$, $\rho = 2\pi/(6 + \sqrt{18}) = 0.6134$

Sphere centers in 4 c : $I \pm (0, 0, z)$, $z = 1/\sqrt{8} = 0.3536$

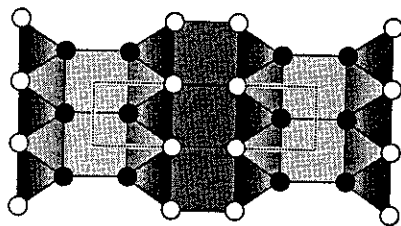


Fig. 6.49. A projection of the AABB stacking of 4^4 layers of Te atoms in Th_2TeN_2 showing the layers of tetrahedra (centered by N) and cube sites (centered by Te). The projection is down a with c running across the page. The cube centers are at $x = 0$ and $x = 1/2$ (differentiated by light and darker shading).

In Th_2TeN_2 N atoms are between the AB and BA slabs of Th, forming tetragonal tetrahedral layers (cf. Fig. 6.43) with stoichiometry N_2Th_2 . The Te atoms are between the AA and BB layers of Th. Using Greek letters for Te and N, the structure is $A\beta A(\gamma\delta)B\alpha B(\gamma\delta)$. An idealized version (with regular tetrahedra and cubes) is shown in

Fig. 6.49. Th_2TeN_2 is a member of the largest of all groups of ternary structure types. It is usually named for the antistructure compound ThCr_2Si_2 (in which Th and Cr play the role of Te and N in Th_2TeN_2) but in *Pearson's Handbook* (Book List) it is called **BaAl₄**. The structure type is similar to **PbFCl** in having tetragonal tetrahedral layers and a wide range of cla according to the size of the atom between the layers (in the "cube" sites).

ACCA: This is a 7-coordinated sphere packing and is an intergrowth of primitive cubic and primitive hexagonal. The symmetry is orthorhombic:

ACCA

$Cmmm$, $a = c = 1$, $b = 2 + \sqrt{3} = 2.7321$

Sphere centers in 4 j : $C \pm (0, y, 1/2)$, $y = 1/(4 + \sqrt{12}) = 0.1340$

The ACCA packing is that of Fe in the Fe_2AlB_2 structure. Al fills the cube sites (between AA and CC layers of Fe) and B fills the trigonal prism sites (between AC and CA layers). The structure may be also considered as a prismatic stacking of $3^3 4^2$ nets as shown in Fig. 6.50.

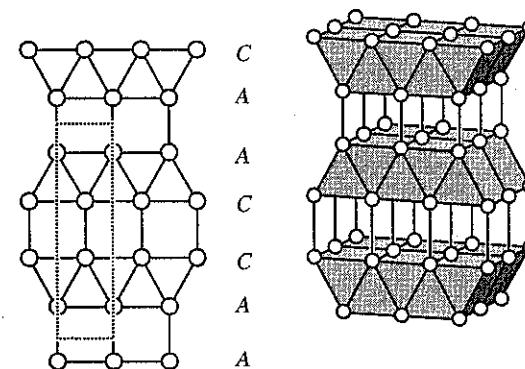


Fig. 6.50. ACCA stacking of 4^4 nets of Fe in Fe_2AlB_2 . Left: viewed normal to the stacking direction (vertical on the page). Right: as a clinographic projection. The trigonal prism sites (filled by B) are shaded, and the cubes (occupied by Al, not shown) are outlined.

6.4.3 Stacked $3^2.4.3.4$ nets

Stacking of $3^2.4.3.4$ layers produces 7-coordinated sphere packings with a variety of interstitial sites—cubes, square antiprisms (better *metaprisms*), trigonal prisms and tetrahedra—and many crystal structures are based on filling some or all of the interstitial sites in these packings. In this section we briefly describe some of the simpler such structures (crystallographic data for real materials are in Appendix 5).

For a prismatic stacking (i.e. one directly above the other) of $3^2.4.3.4$ layers the formal description for spheres of unit diameter is:

$P4/mbm$, $a = \sqrt{2 + \sqrt{3}} = 1.932$, $c = 1$, $\rho = 0.5612$
 Sphere centers in 4g: $\pm(x, 1/2+x, 0; 1/2-x, x, 0)$, $x = 1/\sqrt{16 + \sqrt{192}} = 0.1830$

The interstices in the sphere packing are cubes and trigonal prisms. In LiY_2Si_2 , Li is in all the cube sites and Si in all the trigonal prism sites of the Y packing as shown in Fig. 6.51. Notice that the atoms in the trigonal prism sites come together in pairs (Si_2 in LiY_2Si_2). The structure is usually called U_3Si_2 .

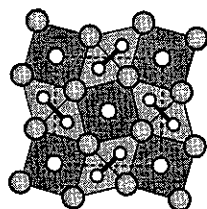


Fig. 6.51. Prismatic stacking of $3^2.4.3.4$ nets projected on (001) showing the cube sites (darker shaded) and trigonal prismatic sites that occur in pairs (joined by heavy lines).

Another stacking of $3^2.4.3.4$ nets is of rather common occurrence in crystal structures. Now the nets in each layer are displaced by $1/2, 1/2, 1/2$ to make a two-layer stacking as shown in Fig. 6.52. The structure is tetragonal (a and x are the same as for the previous structure):

$I4/mcm$, $a = 1.932$, $c = \sqrt{2\sqrt{3}} = 1.861$
 Sphere centers in 8h: $I \pm (x, 1/2+x, 0; 1/2-x, x, 0)$, $x = 0.1830$

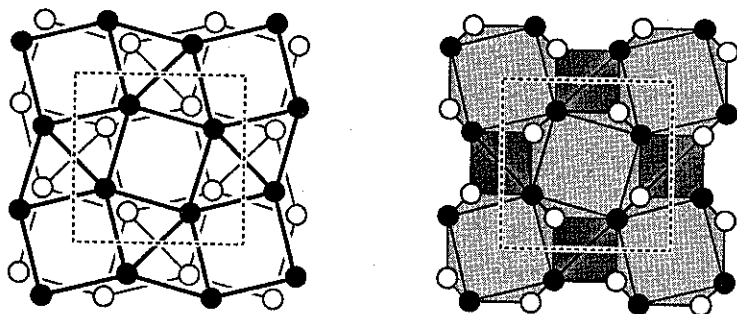


Fig. 6.52. A sphere packing generated by stacking alternating layers of $3^2.4.3.4$. Left: showing the nets. Right: emphasizing the square metaprisms and some of the tetrahedra (darker shaded). The projection is on (001) of the tetragonal cell. Empty and filled circles are at $z = 0$ and $1/2$ respectively.

A notable feature of the structure is the columns of face-sharing square metaprisms. Note also the tetrahedra centered at $1/2, 0, 1/2$ and $0, 1/2, 1/2$. An example of the occurrence of this packing is the Al arrangement in CuAl_2 in which Cu atoms center the Al₈ metaprisms so that linear -Cu-Cu- rods run parallel to c . In PtPb_4 only half the Pb₈ metaprisms are filled by Pt (those in alternate layers perpendicular to c). In contrast, in TaTe_4 , Ta fills only the Te₈ metaprisms centered at $0, 0, z$ forming isolated rods of face-sharing {Ta}Te₈ metaprisms with their axes parallel to c . In KInTe_2 , in addition to {K}Te₈ metaprisms, there are {In}Te₄ tetrahedra (the tetrahedral sites are also shown in Fig. 6.52).

A third stacking of $3^2.4.3.4$ nets is also important in crystal chemistry. Pairs of prismatically-stacked nets are displaced by $1/2, 1/2, 1/2$ to produce a four-layer sequence, and the structure may be thought of as an intergrowth of the previous two. The symmetry is the same as in the previous sequence:

$I4/mcm$, $a = 1.9318$, $c = 3.8612$
 Centers in 16f: $I \pm (x, 1/2+x, z; 1/2-x, x, z; x, 1/2-x, 1/2-z; 1/2+x, x, 1/2-z)$, $x = 0.1830$, $z = 0.1295$

Layers of square metaprism and tetrahedral sites alternate with layers containing trigonal prism and cube sites. In Cr_5B_3 , Cr(2) atoms are in this sphere packing with Cr(1) in the cubes, and B atoms fill the square metaprisms and the trigonal prisms. In PdGa_5 the same packing of Ga(2) atoms occurs, now Ga(1) are in the cube sites, Pd in the metaprisms and the trigonal prisms are empty.

6.5 A summary of sphere packings

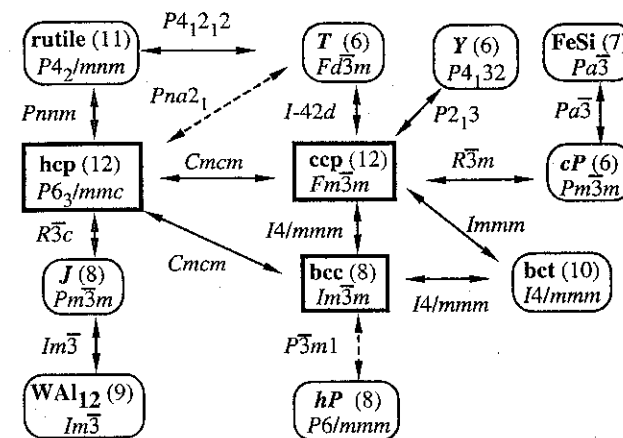


Fig. 6.53. Some of the structural relationships discussed in this chapter (arrows). Numbers in parentheses are coordination numbers. Notice the central positions of ccp and bcc.

The diagram (Fig. 6.53) indicates some of the sphere packings and transformations between them that we have discussed. In the diagram the lines indicate a transformation path of the symmetry indicated; a broken line indicates that in the intermediate structure there is more than one kind of sphere (i.e. they are not all equivalent to each other). Attention is drawn to the central position occupied by **ccp**. Note that **cco** (symmetry *Cmcm*, see § 6.3.3) is not shown but is intermediate between **hcp** and **ccp**.

6.6 Some packings of two kinds of spheres

Here we describe some structures of simple binary intermetallic compounds. They are of interest both as the structures of large groups of compounds and as components of more complex structures. As an example we cite the fact that **MgCu₂** (§ 6.6.3) is the structure of many intermetallic compounds and also of the cation array (**MgAl₂**) in **spinel**, **MgAl₂O₄**.

6.6.1 Cu₃Au and Ni₃Sn

Cu₃Au is a simple ordered derivative of **ccp**. The original *fcc* structure is replaced by a primitive cubic one (symmetry *Pm $\bar{3}$ m*) with **Au** at 0,0,0 and **Cu** at (0,1/2,1/2) κ . The structure should be familiar: the **Cu** arrangement is the *J* structure described in § 6.3.5 and **Au** is in the cuboctahedral holes of this structure. (see Fig. 6.27).

(111) planes of **Cu** are kagome (3.6.3.6) nets and **Au** centers the hexagons of the nets so that the combined (111) nets are 3⁶. Fig 6.54 shows how the nets are stacked; using the symbolism of § 6.1.6, the stacking of kagome nets is *N₁N₂N₃...*

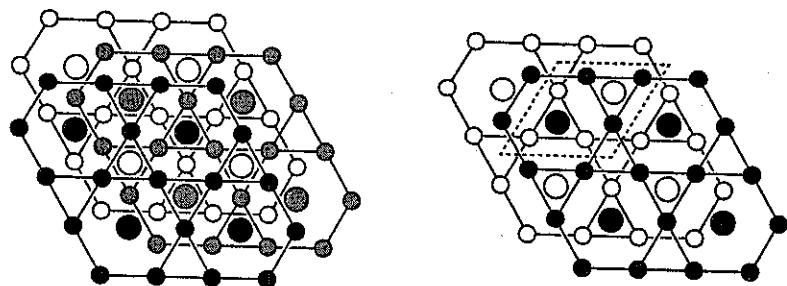


Fig. 6.54. Left: the cubic stacking of **Cu₃Au** nets projected down [111]. Larger circles are **Au**. Open, shaded and filled circles are at different levels: 0, 1/3 and 2/3 respectively in units of **a + b + c**. Right: the stacking of nets at $z = 1/4$ and $3/4$ (open and filled circles) in **Ni₃Sn**. Larger circles are **Sn**.

Ni₃Sn is the analogous structure derived by ordering of **hcp**. **Ni** atoms form kagome (3.6.3.6) layers with **Sn** centering the hexagons. The layers are therefore like (111) layers in **Cu₃Au** but now the stacking of kagome nets is hexagonal: *N₁N₂...* as also shown in

Fig. 6.54. For the ideal structure with atoms *d* apart:

Ni₃Sn	<i>P6₃/mmc</i> , $a = 2d$, $c = \sqrt{(8/3)}d$, $c/a = \sqrt{(2/3)} = 0.816$
	Ni in 6 <i>h</i> : $\pm(x, 2x, 1/4; x, \bar{x}, 1/4; 2\bar{x}, \bar{x}, 1/4)$, $x = -1/6$
	Sn in 2 <i>c</i> : $\pm(1/3, 2/3, 1/4)$

Note that empty **Ni₆** octahedra (with centers at 0,0,0 and 0,0,1/2) share faces and form isolated rods parallel to **c**. Contrast **Cu₃Au** in which the empty **Cu₆** octahedra share vertices only (Fig. 6.27 again).

In the cubic high-temperature form of **BaTiO₃** the **BaO₃** arrangement is **AuCu₃** (**Ti** in the **O₆** octahedra). In **BaNiO₃** the **BaO₃** arrangement is **SnNi₃** (**Ni** in the **O₆** octahedra). These oxide structures are often referred to as cubic and hexagonal **perovskite** respectively. For crystallographic data see Appendix 5; cubic **perovskite** was described in § 5.3.4.

6.6.2 CuZn (β -brass), CuAu and MoSi₂

The simplest ordering of **bcc** is **CuZn** in which **Cu** is at the origin (0,0,0) and **Zn** at the body center (1/2,1/2,1/2) of a cubic cell. Notice that the structure is primitive cubic (symmetry *Pm $\bar{3}$ m*). The structure is also that of **CsCl** which is often used as the eponymous compound, but as it is much more common for intermetallic compounds we prefer the name **CuZn** or **β -brass** (**CuZn** is **β -brass**). Notice that the structure is its own antistructure and each atom is coordinated by eight of the other kind at the corners of a cube (Fig. 6.55).

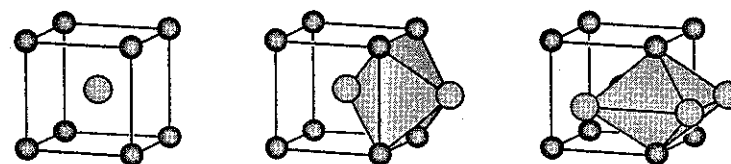


Fig. 6.55. Left a unit cell of **CuZn** (smaller, darker-shaded circles are **Cu**). Middle: a **Cu₄Zn₂** octahedron. Right a **Cu₂Zn₄** octahedron.

It may be recalled that in **bcc** the octahedra around octahedral sites fill space twice over (see § 6.2)—in **CuZn** there are two sets of octahedra: **Cu₄Zn₂** [at (0,1/2,1/2) κ] and **Cu₂Zn₄** [at (0,0,1/2) κ] as shown in Fig. 6.55. Each set of octahedra exactly fills space. In cubic **perovskite** **BaTiO₃** the cation arrangement (**BaTi**) is **CuZn** and the anions are in **(O)Ba₄Ti₂** octahedra.

Alternate {100} layers of **CuZn** are 4⁴ nets of **Cu** and **Zn** which are stacked *AB* (cf. § 6.4.2). For the structure to have cubic symmetry the layers must be *a/2* apart, where *a* is the unit cell edge of the 4⁴ layers. If the layers are instead $\sqrt{2}a/2$ ($\approx 0.71a$) apart the structure is an ordering of **ccp** and the structure is referred to as **CuAu**. The symmetry is tetragonal (*P4/mmm*) and **Cu** is at 0,0,0 and **Au** at 1/2,1/2,1/2 so that **CuZn** is the special

case of CuAu with $c/a = 1.0$; $c/a = \sqrt{2} = 1.414$ corresponds to an ideal ordering of **ccp**. The general case is called **CuAu**; examples of actual compounds are (with c/a in parentheses): FeNi (1.41), CuAu (1.31), PtZn (1.22), NiZn (1.08) and MnHg (1.01).

In MoSi_2 the atoms are again on 4^4 nets in the sequence MoSiSi along c . The stacking alternates AB so the structure has the six-layer repeat $A_{\text{Mo}}B_{\text{Si}}A_{\text{Si}}B_{\text{Mo}}A_{\text{Si}}B_{\text{Si}}$.

MoSi_2 $I4/mmm$
 Mo in 2 a : $I + (0,0,0)$
 Si in 4 e : $I \pm (0,0,z)$ with $z \approx 1/3$

a is the spacing of the 4^4 nets. If $c/a = 3\sqrt{2} = 4.23$ the structure is a superstructure of **ccp** and if $c/a = 3$ it is a superstructure of **bcc**. Many compounds have axial ratios between these two values. A third possibility is a superstructure of **bct** for which $c/a = 3\sqrt{(2/3)} = \sqrt{6} = 2.449$. For MoSi_2 $c/a = 2.45$ so clearly in this case the structure should be considered as a superstructure of the 10-coordinated **bct** packing. In Volume II of this series we adduce several examples of ionic compounds with MoSi_2 cation packing; K_2MgF_4 is a good example (for data see Appendix 5).

6.6.3 MgCu_2

MgCu_2 is often cited as an example of a structure that is based on an efficient packing of spheres of two sizes. The Cu arrangement is the T sphere packing of § 6.3.9 (see Fig. 6.32) which can be described as an array of vertex sharing Cu_4 tetrahedra. The space not occupied by Cu_4 tetrahedra consists of truncated tetrahedra, and it is useful at the outset to see how these two polyhedra can combine to fill space. Fig. 6.56 shows how two truncated tetrahedra and two tetrahedra can be assembled into a large 60° rhombohedron. This is in fact a primitive cell of the T structure. It is also a primitive cell of MgCu_2 if Cu is in the T positions and Mg centers the truncated tetrahedra (see also Fig. 6.58 below). Mg is coordinated by the twelve Cu and also by four Mg capping the hexagonal faces of the truncated tetrahedron. This 16-vertex coordination figure was identified as the Friauf polyhedron in § 5.1.7 (see Fig. 5.12). As shown below, Cu is 12-coordinated in a $\{\text{Cu}\}\text{Cu}_6\text{Mg}_6$ icosahedron (Fig. 6.57).



Fig. 6.56. Two tetrahedra and two truncated tetrahedra combining to make a 60° rhombohedron (right).

The formal description of the structure is:

MgCu_2 $Fd\bar{3}m$. Mg in 8 a : $F \pm (1/8, 1/8, 1/8)$ (lattice complex $D = \text{diamond}$)
 Cu in 16 d : $F \pm (1/2, 1/2, 1/2 ; 1/2, 1/4, 1/4) \times$ (lattice complex T)

Fig. 6.57 shows the structure projected on (100). On the left, just the atom positions are shown, and most people will find that figure somewhat uninformative. However, in the center a Cu_{12} truncated tetrahedron around one Mg is picked out and on the right a Cu_6Mg_6 icosahedron around one Cu is similarly depicted.

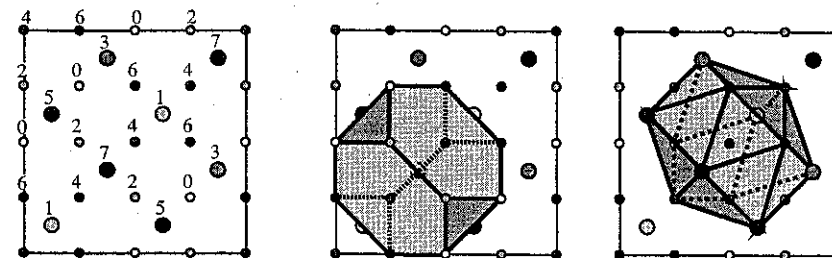


Fig. 6.57. Left: MgCu_2 projected on (100). Larger circles are Mg and numbers are elevations in multiples of $a/8$. The intensity of shading is proportional to elevation. Center, an $(\text{Mg})\text{Cu}_{12}$ truncated tetrahedron and right, a $\{\text{Cu}\}\text{Cu}_6\text{Mg}_6$ icosahedron picked out. Polyhedron edges obscured by front faces are shown as broken lines.

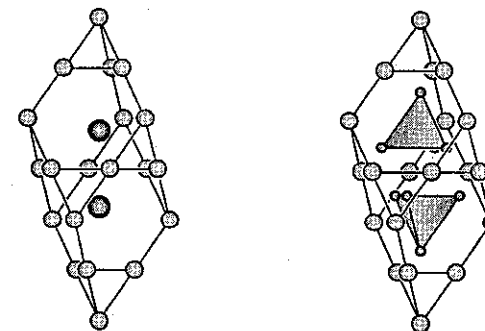


Fig. 6.58. Left: a primitive cell of MgCu_2 (larger circles are Mg). Right: a primitive cell of MgAl_2O_4 shown as $\{\text{Mg}\}\text{O}_4$ tetrahedra and Al atoms.

The structure can also be considered as a space-filling by tetrahedra (not all regular). These are of three sorts: per MgCu_2 unit there are 4 MgCu_3 tetrahedra (these are made up of an Mg and a triangular Cu_3 face of the surrounding truncated tetrahedron), 12 Mg_2Cu_2 tetrahedra and one regular Cu_4 tetrahedron. Structures which are space fillings of tetrahedra are sometimes referred to as "topologically close packed."

We mentioned earlier (§ 6.1.6) that in **spinel** (MgAl_2O_4) the cation array is MgCu_2 and indeed to get **spinel** from MgCu_2 all that has to be done is to fill all the MgCu_3 tetrahedra with anions so that in MgAl_2O_4 there are $\{\text{O}\}\text{MgAl}_3$ tetrahedra. It is not

immediately obvious that this results in $\{\text{Mg}\}\text{O}_4$ tetrahedra, $\{\text{Al}\}\text{O}_6$ octahedra and (approximately) **ccp** O! For this aspect of the structure refer back to § 6.1.6, especially Fig. 6.17 (p. 223). Fig. 6.58 compares primitive cells of MgCu_2 and MgAl_2O_4 .

Close packed structures may be described as built up of rhombohedral units consisting of an octahedron and two tetrahedra (Fig. 6.4). Similarly, there is a family of structures built up of different stackings of the rhombohedral unit consisting of two centered truncated tetrahedra and two tetrahedra (Fig. 6.56). Fig. 6.59 illustrates the simpler possibilities. By analogy with close packing, the stacking in MgCu_2 can be described as *c*; the stacking in MgZn_2 is then *h* and in MgNi_2 it is *hc* (see Fig. 6.59). The structures collectively are known variously as as "Friauf-Laves phases" or just "Laves phases."¹

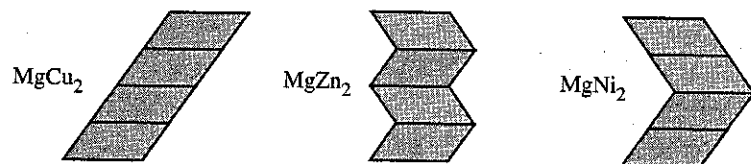


Fig. 6.59. The stacking of rhombohedral units in MgCu_2 , MgZn_2 and MgNi_2 .

6.6.4 Cr_3Si (A15)

The structure known as A15² or Cr_3Si has a number of features in common with MgCu_2 . The atoms are in fixed positions (on the sites of invariant lattice complexes) so the structure is completely determined by the cubic cell constant. Space is again divided up into irregular tetrahedra, so it is another example of a topologically close-packed structure.

Cr_3Si $Pm\bar{3}n$. Si in 2 *a*: 0,0,0 ; 1/2,1/2,1/2 (bcc)
Cr in 6 *c*: $\pm(1/4,0,1/2)\kappa$ [or 6 *d*: $\pm(1/4,1/2,0)\kappa$] (lattice complex *W*)

The structure is illustrated in Fig. 6.60. Notice the non-intersecting rods of Cr atoms along $\langle 100 \rangle$; we describe a related cylinder packing with the same symmetry below [§ 6.7.3 (a)]. The Cr atoms form icosahedra with symmetry $m\bar{3}$ about the Si; this icosahedron was described in § 2.5.7 (see Fig. 2.25, p. 54). It is a good exercise to identify the icosahedron in projection as shown in Fig. 6.61.

Figure 6.61 also shows the coordination figure about Cr; it should be identified as the 14-vertex polyhedron obtained by capping the hexagonal faces of a hexagonal antiprism. The coordination of Cr is $\{\text{Cr}\}\text{Si}_4\text{Cr}_{10}$; the closest neighbors of Cr are two other Cr at a

¹After the German crystallographer F. Laves, who contributed significantly to the understanding of intermetallic structures of this and related types. "Laves" is pronounced with two syllables: "La-ves."

²In *Strukturbericht* (the predecessor of *Structure Reports*) simple structures were assigned symbols. *An* represents elemental structures such as A1 = **ccp**, A2 = **bcc**, A3 = **hcp**, etc. A form of W metal (or W_3O ? = " β -tungsten") was early reported to be Cr_3Si and although this is no longer believed to be correct, the designation A15 is still used for this structure type. The designations B1 = NaCl and B2 = CsCl (CuZn) are also still used on occasion.

distance of $a/2$.

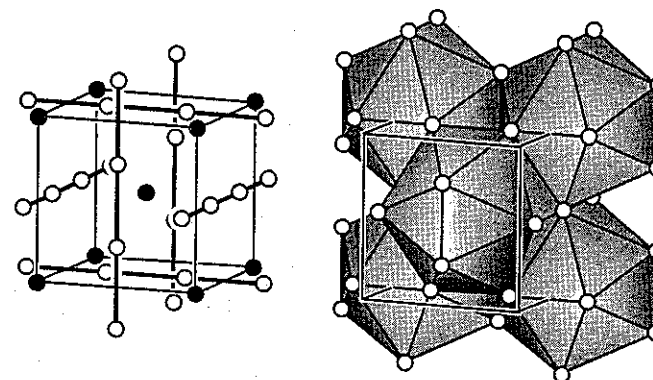


Fig. 6.60. Cr_3Si (Cr are open circles, Si are filled circles). Left: emphasizing the Cr rod packing. Right: showing some of the $\{\text{Si}\}\text{Cr}_{12}$ icosahedra (note the two orientations of the icosahedra).

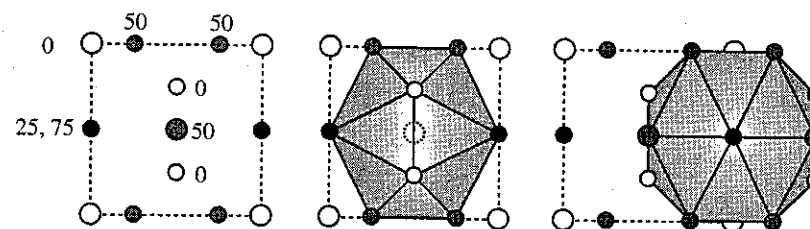


Fig. 6.61. Left: a unit cell of Cr_3Si projected on (001), numbers are heights in multiples of $c/100$. Larger circles represent Si. The shading scheme now indicates elevations. Center: The icosahedron centered at 1/2, 1/2, 1/2 is picked out. Right: The polyhedron around a Cr at $z = 1/4$.

Superconducting compounds with this structure are of considerable interest as many have high critical temperatures. Nb_3Ge ($T_c = 23.2$ K) has the highest superconducting transition temperature of any known material other than the copper-oxide superconductors.

The cation array in **garnet** oxides such as $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ is an ordered derivative of Cr_3Si with $(\text{Ca}_{3/2}\text{Si}_{3/2})$ in the Cr positions and Al in the Si positions. Indeed the complicated garnet structure is completely generated by putting O atoms in all the Ca_2AlSi tetrahedra of the cation array. In Volume II of this series we will show that many other complex oxide structures are conveniently described as intermetallic structures "stuffed" with O atoms.¹

¹For an earlier account of this topic see M. O'Keeffe & B. G. Hyde, *Structure and Bonding* 61, 77 (1985).

6.7 Cylinder (rod) packings¹

Crystal structures are often conveniently described as sphere packings, with atoms instead of spheres, but sometimes we want to consider the packing of larger units. Atoms (or spheres) are *point* objects in the sense that they have zero-dimensional periodicity and crystals are three dimensional in the sense that they have three-dimensional periodicity. We have already described three-dimensional structures (sphere packings) as packings of *layers*, which are objects with two-dimensional periodicity, and we do so again in following chapters. The symmetry of layers is described by the layer groups (Appendix 1).

Sometimes it is convenient to consider structures as a packing of rods, which are objects with one-dimensional periodicity. These have the symmetries of the rod groups (Appendix 1).² The highest symmetry rod is the infinite cylinder; here we describe some packings of equivalent (symmetry-related) cylinders. In application to crystal chemistry, we replace the cylinders with *rods* of atoms. Examples of rods are strings of atoms, atoms at the vertices of rods of polyhedra (e.g. octahedra sharing opposite faces), atoms forming helices (as commonly found for rods of S atoms).

In the symmetrical packings we describe, symmetry axes coincide with the cylinder axes and are therefore non-intersecting. A line (such as a cylinder axis) corresponds to the locus of all points of a univariant lattice complex. For example $0,0,z$ or $\pm(0,0,z)$ corresponds to a line along *c* if *z* is allowed to take all possible values. In the same way $\pm(0,0,z)\kappa$ corresponds to lines along *a*, *b* and *c* and intersecting at $0,0,0$ (also at $1,0,0$; etc.); this cannot correspond to a cylinder packing as the lines intersect. In general the location of axes is given as the line of intersection of two planes. The intersection of planes $x = x_0$ and $y = y_0$ is written as x_0, y_0, z where *z* can have any value. Likewise $1/3+u, 2/3+u, u$ indicates the line of intersection of the planes $x = z + 1/3$ and $y = z + 2/3$. Unit cell parameters are given for cylinders of unit diameter.

In descriptive crystal chemistry the cubic rod packings are of most importance and are met repeatedly in that connection.

6.7.1 Cylinders with parallel axes

If cylinders are packed with axes parallel to *c*, a cross-section $z = \text{constant}$ will just be a circle packing. In particular the closest packing of equal cylinders will be a hexagonal packing (i.e. based on a 3^6 net):

$P6/mmm$, $a = 1$. Cylinder axes along $2c$: $\pm(0,0,z)$. Rod symmetry $p6/mmm$

The fraction of space occupied by the cylinders (the density) is the same as for closest

¹For more on this topic see M. O'Keeffe & S. Andersson, *Acta Crystallogr.* A33, 914 (1977) and M. O'Keeffe, *Acta Crystallogr.* A48, 879 (1992).

²The reader anxious to learn about rod symmetries will find some good examples in this section. The less ambitious can skip the parts dealing with this topic. After all we got through § 6.4 (on the stacking of layers) without discussing layer groups (although the temptation to do so was strong). The reason was in part due to the fact that most of our "layers" were only one atom thick.

circle packing $\rho = \pi/\sqrt{12} = 0.9070$. The rod symmetry $p6/mmm$ is that of an infinite column of hexagonal prisms stacked along the hexagonal axis. (*p* stands for the one-dimensional lattice).

An example of this packing is provided by the helical rods of P in NaP (compounds such as KP, NaAs and RbSb are isostructural) illustrated in Fig. 6.62. The rods have a 4-fold repeat so the axis is approximately a 4_1 axis and all the helices are of the same hand. In this structure, the P-P bond length is 2.24 Å, and the P-P-P angles are 112° and 115°. LiP, LiAs, NaSb and KSb have a related structure containing helices of P of both hands. For crystallographic data see Appendix 5. Elemental Se has 3_1 helices in the same rod packing.

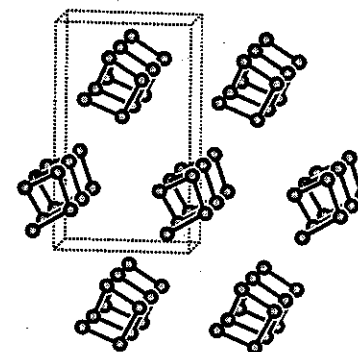


Fig. 6.62. The helical rods of P in NaP viewed at an angle slightly tilted from a 2_1 axis.

Further cylinder packings can be derived from other regular and Archimedean tessellations. The least dense packing, based on 3.12^2 , has density $\rho = \sqrt{3}\pi/(7 + 4\sqrt{3}) = 0.3907$.

6.7.2 Cylinders with axes in parallel planes

Here we describe packings of layers of cylinders in contact. They will all have the same density, $\rho = \pi/4 = 0.7854$. Cylinder axes lie along non-intersecting 2-fold rotation axes.

(a) Two-layer tetragonal. Here cylinder axes lie in layers perpendicular to *c*; for $z = 0$ the axes run in the $[100]$ direction, for $z = 1/2$, they lie in the $[010]$ direction. Thus the rods run along *a* through $0,0,0$ and along *b* through $0,0,1/2$; see Figs. 6.63 and 6.64. Note that we give unit cell parameters for a packing of cylinders of unit diameter; in a crystal structure the rod symmetry is $pmmm$ (which is the symmetry of, for example, an infinite stack of bricks) and the axial ratio c/a will not, in general, be equal to 2.

$P4_2/mmc$, $a = 1$, $c = 2$

Cylinder axes along $4c$: $\pm(x,0,1/2; 0,x,0)$. Rod symmetry $pmmm$

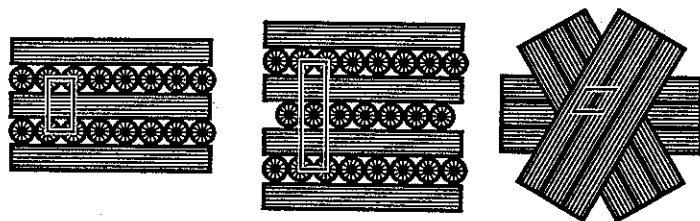


Fig. 6.63. Left: a two-layer tetragonal cylinder packing. Center: a four-layer tetragonal cylinder packing. *c* is up the page in both cases. Right: a three-layer hexagonal cylinder packing viewed down *c*. (See also Fig. 6.64 for the first two cases).

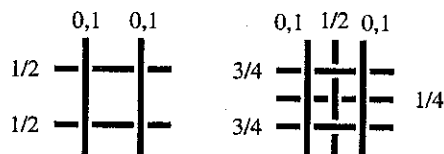


Fig. 6.64. Left: axes of a two-layer tetragonal cylinder packing. Right: axes of a four-layer tetragonal cylinder packing. The view is down *c* and the numbers are the elevations of the axes in units of *c*.

(b) Four-layer tetragonal. Rods run along *a* through 0,3/4,1/4 and 0,1/4,3/4 and along *b* through 0,0,0 and 1/2,0,1/2 (this description assures that there is a center of symmetry at 0,0,0). The arrangement should be apparent from Figs. 6.63 and 6.64.

$$I4_1/amd, a = 1, c = 4$$

Axes along 0,*x*,0 ; *x*,1/4,3/4 ; 1/2,*x*,1/2 ; *x*,3/4,1/4 derived from

16 *h*: 1 ± (0,*x*,*z* ; 0,1/2-*x*,*z* ; 1/4+*x*,1/4,3/4+*z*, 3/4-*x*,1/4,3/4+*z*), *z* = 0

Rod symmetry *pmcm*

A digression on rod symmetry: The rods in the four-layer structure (b) run along 2₁ axes parallel to *a* and *b* of *I4₁/amd*. Consider the rod along *a*: it lies in the mirror plane normal to *b* and is normal to the mirror plane normal to *a*. The rod also lies in the *a* glide plane normal to *c*.¹ The symbol for the rod symmetry group is accordingly *pmma*. However in the rod groups it is conventional to take the translation direction as (with subscript “*r*” for the rod) *c_r*. Making the substitution *a_r* = *b*, *b_r* = *c*, *c_r* = *a*, the rod symmetry group with these new axes becomes *pmcm* as given above. The full symbol is *p 2₁/m 2/c 2₁/m*. An infinite crankshaft or zig-zag (see § 7.3.5) has this symmetry. End digression.

A beautiful example of this cylinder packing is found in the structures of $Hg_{3-x}MF_6$ (*M* = As, Sb, Nb, Ta and *x* is typically about 0.12). The As compound is known as “alchemist’s gold.” Isolated {*M*}F₆ octahedra are surrounded by disordered rods of Hg atoms in positions 16 *h* of *I4₁/amd* with *z* ≈ 0 as shown schematically in Fig. 6.65. Remarkably,

¹It is a good exercise to get a copy of the *International Tables* and verify these statements.

the stoichiometric compound Hg_3NbF_6 has a simple layer structure with 3⁶ layers of Hg alternating with layers of isolated {Nb}F₆ octahedra.¹

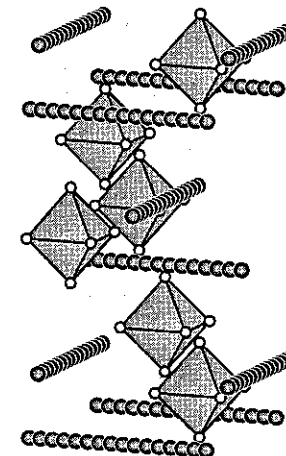


Fig. 6.65. The structure of $Hg_{2.88}SbF_6$ illustrated as {Sb}F₆ octahedra and rods of Hg atoms. The Hg atoms are disordered along the rods shown.

(c) Three-layer hexagonal. Rods run along *a* through 0,0,0 along *a* + *b* through 0,0,1/3 and along *b* through 0,0,2/3. The arrangement of cylinders should be apparent from Fig. 6.63.

$$P6_222, a = 1, c = 3$$

Axes along 6 *g*: (±*x*,0,0 ; *x*,*x*,1/3 ; *x*,*x*,1/3 ; 0,±*x*,2/3). Rod symmetry *p222*

6.7.3 Cubic cylinder packings

These are rather important as they sometimes form the basis for a description of cubic crystal structures that are otherwise difficult to describe. They are named for structures in which they are conspicuous features. We describe four packings and an intergrowth structure. The cylinder axes correspond to non-intersecting symmetry axes in cubic space groups (see § 3.3.6, p. 74) which are either (i) 2-fold or 4-fold axes parallel to <100> or (ii) 3-fold axes parallel to <111>. In the second case, the fact that the cylinder axes are inclined to each other makes structures based on this structural principle difficult to illustrate satisfactorily in projection. The most important packings are those named *β-W* and *garnet* [(a) and (b) below]. Cubic space groups with non-intersecting 3-fold axes are listed on p. 83.

¹See I. D. Brown *et al.*, *Inorg. Chem.* **23**, 405 (1984) and references therein.

(a) β -W (Figs. 6.66 and 6.67)

$$Pm\bar{3}n, a = 2, \rho = 3\pi/16 = 0.5890$$

Axes along 12 g : $\pm(x, 0, 1/2; 1/2+x, 0, 1/2)\kappa$. Rod symmetry $p4_2/mmc$

In the β -W structure of A_3B (also known as $A15$ or Cr_3Si —see § 6.6.4), strings of A atoms lie on the cylinder axes along $\langle 100 \rangle$ at $(u, 0, 1/2)\kappa$. (The B atoms in A_3B are at cell corners and at the body center and are in icosahedral coordination by A). The cylinder axes correspond to the 4_2 axes of $Pm\bar{3}n$.

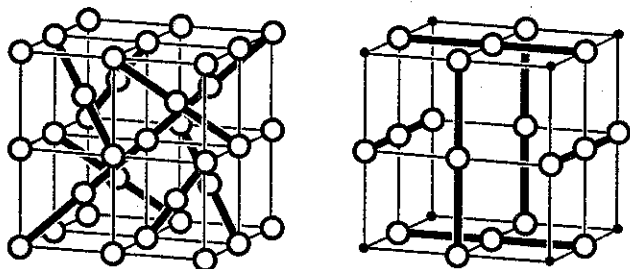


Fig. 6.66. Two cubic cylinder packings. Left: garnet. Right: β -W. The heavy lines indicate the locations of the cylinder axes. The open circles serve only to indicate high symmetry points on the rods.

(b) garnet (Fig. 6.66)

$$Ia\bar{3}d, a = \sqrt{8}, \rho = \sqrt{3}\pi/8 = 0.6802$$

Axes along 32 e : $1 \pm (x, x, x; 1/4+x, 1/4+x, 1/4+x; 1/2-x, 1/2+x, x; 3/4-x, 1/4+x, 3/4+x; x, 1/2-x, 1/2+x; 3/4+x, 3/4-x, 1/4+x; 1/2+x, x, 1/2-x; 1/4+x, 3/4+x, 3/4-x)$
Rod symmetry $p\bar{3}c1$

In this cubic cylinder packing, cylinders are parallel to body diagonals of a cubic cell. Now they lie on non-intersecting $\bar{3}$ axes, i.e. along $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}\bar{1}]$ and $[\bar{1}11]$.

In the garnet structure of $Ca_3Al_2Si_3O_{12}$ the cylinders are to be replaced by rods of alternating $\{Al\}O_6$ octahedra and empty O_6 trigonal prisms sharing opposite triangular faces. It might be noted that the centers of the octahedra are at $\bar{3}$ sites so they are trigonal antiprisms, but the absence of $\bar{6}$ axes means that the trigonal "prisms" are not strictly regular prisms (they are slightly twisted towards being metaprisms in the garnet structure). As discussed in Appendix 2, a rod of alternating regular octahedra and trigonal prisms has symmetry $p6_3/mmc$; but the 6_3 axis is incompatible with cubic symmetry.

(c) β -Mn (Fig. 6.67):

$$I4_132, a = 4, \rho = 3\pi/32 = 0.2945$$

Axes: $1/4, 0, u; 3/4, 1/2, u; u, 1/4, 0; u, 3/4, 1/2; 0, u, 1/4; 1/2, u, 3/4$.
Rod symmetry $p4_122$

A third cylinder packing is derived from β -W by removal of one-half of the cylinders. We call this the β -Mn cylinder packing as that otherwise enigmatic structure is simply described in terms of rods of face-sharing Mn_4 tetrahedra with this cylinder packing. Fig. 6.67 shows the β -W and the β -Mn packings, the former with a cell with doubled edge. The symmetry of the β -Mn packing is $I4_132$ and the axis equations are obtained by substituting $1/4, 0, u$ in the general positions 48 i . The cylinder axes lie along the 4_1 axes of this space group; the substitution $3/4, u, 0$ puts the cylinder axes on the 4_3 axes. Combination of the two enantiomorphs of the β -Mn packing recovers the β -W packing.

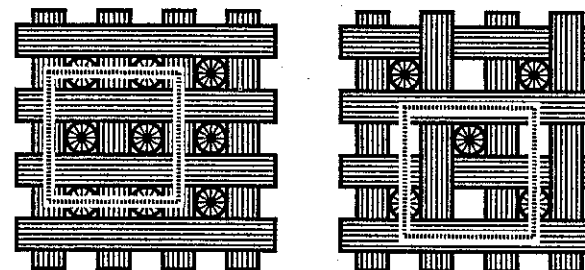


Fig. 6.67. The β -W (left) and β -Mn (right) cylinder packings. The true cell edge for β -W has half the edge of that shown.

(d) $SrSi_2$ (Fig. 6.68):

$$I4_132, a = 6\sqrt{2}, \rho = \sqrt{3}\pi/72 = 0.0756$$

Axes: $1/3+u, 2/3+u, u; 1/6+u, 2/3-u, u; 2/3+u, 5/6+u, -u; 5/6-u, 5/6+u, u$.
Rod symmetry $p3_12$

A fourth cylinder packing is obtained by removing eight-ninths of the cylinders of the garnet packing. We call it the $SrSi_2$ packing because the Si atoms in that structure form 3_1 (or 3_2) helices with axes corresponding to those of the cylinder packing (see § 7.2). The positions of the cylinder axes (3_1) are obtained by substituting $1/3+u, 2/3+u, u$ in the general positions 48 i of $I4_132$. The enantiomorphous structure with cylinders on 3_2 axes is obtained by the substitution $2/3+u, 1/3+u, u$. A sketch of the packing viewed down one of the 3_1 axes is shown in Fig. 6.68.

(e) γ -Si:

$$Ia\bar{3}d, a = 6\sqrt{2}$$

3_1 axes $1/3+u, 2/3+u, u; 1/6+u, 2/3-u, u; 2/3+u, 5/6+u, -u; 5/6-u, 5/6+u, u$
 3_2 axes $2/3+u, 1/3+u, u; 5/6+u, 1/3-u, u; 1/3+u, 1/6+u, -u; 1/6-u, 1/6+u, u$.
Rod symmetry $p3_12$ and $p3_22$

The $SrSi_2$ packing is very open, and the two enantiomorphs can intergrow without

contact (so the intergrowth structure is not a *stable* cylinder packing). In the γ -Si polymorph of silicon (§ 7.3.12), the Si atoms fall on 3_1 and 3_2 helices with axes corresponding to this intergrowth structure. The cylinder axes are now obtained by the substitution of $1/3+u, 2/3+u, u$ in the general positions of $Ia\bar{3}d$.

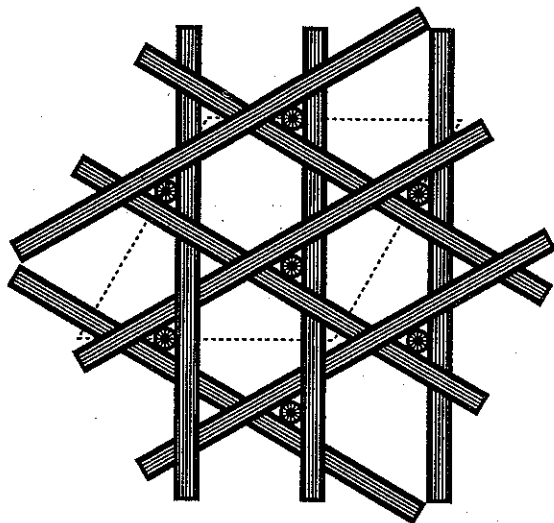


Fig. 6.68. The SrSi_2 cylinder packing viewed down $[111]$. Note that for clarity only a few cylinders not parallel to the projection axis are shown.

6.8 Notes

6.8.1 Symmetries of arrays of closest packed spheres

The space groups for arrays corresponding to closest sphere packings are $Fm\bar{3}m$ (only for *ccp*), $P6_3/mmc$, $P6_3mc$, $P\bar{6}m2$, $R\bar{3}m$, $R3m$, $P\bar{3}m1$ and $P3m1$. A useful discussion and table has been published [A. L. Patterson & J. S. Kasper, *International Tables*, vol. II] that allows the symmetry of complex sequences to be determined. In many crystal structures one or more sets of atoms are only approximately in closest packing and the symmetry may be lower.

The ideal symmetry is readily determined from the Zhdanov symbol (§ 6.1.3) of the packing from the rules given here, which should be applied in the order given until the space group is determined. In using the rules be sure to note that a sequence such as 2211 refers to ...221122112211... and could equally be written 1221 or 2112.

(a) Determine if there is a center of symmetry: This is revealed by symmetry of certain

numbers in the succession of numbers. Thus 2111 can be written:

$$\dots(2)1(1)1(2)1(1)1(2)\dots$$

where the numbers in parentheses are located symmetrically. There will always be zero (no center of symmetry) or two such numbers (centrosymmetrical) in the symbol. Note that if the symbol contains just two numbers (as in 11 or 41) each number is symmetrically surrounded, and that in e.g. 2112 no number is symmetrically surrounded.

(b) If the first half of the symbol is the same as the second half the symmetry is either $P6_3/mmc$ (centrosymmetric) or $P6_3mc$ (non-centrosymmetric). Thus 11 (*hcp*) and 121121 have symmetry $P6_3/mmc$ and 123123 has symmetry $P6_3mc$.¹

(c) If the symbol can be written so that the second half of the symbol is the reverse of the first half, but there is no center of symmetry, the symmetry is $P\bar{6}m2$. An example is 2112.

(d) The Zhdanov symbol always has an even number of terms: $N_1N_2N_3N_4\dots N_n$ (n even). If the symmetry has not yet been determined [in (b) or (c)], subtract the sum of the even terms from the sum of the odd terms i.e.: $N_1 + N_3 + \dots + N_{n-1} - (N_2 + N_4 + \dots + N_n)$.

If the result is either zero or a multiple of 3 the symmetry is trigonal (but not rhombohedral): either $P\bar{3}m1$ (centrosymmetric) or $P3m1$ (non-centrosymmetric). Thus 41 has symmetry $P\bar{3}m1$ and 5211 has symmetry $P3m1$.

If the result is neither zero nor a multiple of three the symmetry is rhombohedral: either $R\bar{3}m$ (centrosymmetrical) or $R3m$ (non-centrosymmetrical). Thus 21 (*hfc*) has symmetry $R\bar{3}m$ and 3211 has symmetry $R3m$.

6.8.2 Neighbors, coordination sequences, and identifying packings

It should be noted that closest sphere packings differ in numbers of n th geometrical neighbors. For unit diameter spheres the number of neighbors at a given distance are listed for the first few shells of *ccp* and *hcp* below. Generally such numbers cannot be used to distinguish packings in crystal structures, as the arrangement often only approximates an ideal sphere packing, and the numbers of geometrical neighbors rapidly lose any relation to those in the ideal packing.

distance	1	$\sqrt{2}$	$\sqrt{8/3}$	$\sqrt{3}$	$\sqrt{11/3}$	2
ccp	12	6	0	24	0	12
hcp	12	6	2	18	12	6

In Chapter 7 we discuss *coordination sequences* which represent the numbers of *topological* neighbors in shells. In the context of sphere packings, a second topological neighbor of a sphere is one (other than the reference sphere) in contact with first neighbors; third neighbors are those (other than first neighbors) that are in contact with second neighbors; and so on. The number of k th neighbors in *this* sense is n_k . It is interesting that n_k for $k > 1$ is greater for *hcp* than for *ccp*. For *hcp* the sequence is 12, 44, 96... for *ccp*

¹The symbols for these packings could be abbreviated $\langle 1 \rangle$, $\langle 12 \rangle$ and $\langle 123 \rangle$ respectively.

it is 12, 42, 92.... Be sure to distinguish *topological* neighbors (discussed here) with *geometrical* neighbors (discussed in the previous paragraph).

For *lattice* sphere packings [*cP*, *cI*, *cF*, *tI* (**bct**) and *hP* (*c/a* = 1)] with *N* first neighbors there is a simple expression for the numbers of topological neighbors:

$$n_k = (N - 2)k^2 + 2 \quad (6.1)$$

Some other equations are (brackets indicate rounding down to an integer):

$$\text{hcp} \quad n_k = [21k^2/2 + 2] \quad (6.2)$$

$$\text{cco} \quad n_k = [17k^2/2 + 2] \quad (6.3)$$

Once the nearest neighbors of atoms in a structure have been identified (for example, on the basis of interatomic distance) the coordination sequence for each atom is uniquely defined and the packing can often be identified from the coordination sequences even when the arrangement departs significantly from the ideal geometry. In particular each kind of atom in a **cp** structure (*h*, *c*, *hc*, etc.) has a unique coordination sequence and this fact may be exploited to determine the nature of the packing.¹

6.8.3 Close packing or polyhedron packing? An unsolved problem

Many "ionic" crystal structures are based on approximately **cp** arrangements of cations and/or anions (and just as importantly, many are not). The well known structures of spinel (MgAl_2O_4) and olivine (Mg_2SiO_4) are examples in which the anion arrangement is approximately **ccp** and **hcp** respectively. A popular view (to which we do not subscribe) is that the reason for such structures occurring is that "large" anions are close packed (why, for heaven's sake?) and the "small" cations fit more-or-less snugly in the tetrahedral and/or octahedral interstices. One objection to this proposal is that many (e.g. oxide) structures are *not* based on **cp** arrays, or if they are, they are often **cp cation** arrays; but nevertheless one is lead to ask why so many structures based on **cp** (or better eutaxy) do occur.

A possible answer is as follows. The most common coordination figures found in oxides and related materials are $\{M\}X_4$ tetrahedra and $\{M\}X_6$ octahedra [even in compounds which are not based on **cp** such as enstatite (MgSiO_3)]. In order to make a crystal of the appropriate stoichiometry, the individual polyhedra must be condensed together by sharing corners and/or edges and/or faces. To take a concrete example: MgAl_2O_4 is constructed of $\{Mg\}O_4$ tetrahedra and $\{Al\}O_6$ octahedra combined in the ratio 1:2 and sharing O atoms so that there are four O atoms per MgAl_2 . With regular polyhedra of equal edges it is conjectured that *any* periodic way of combining them subject to the foregoing constraints will result in a **cp** array of O atoms.

The unsolved (we think) problem which we offer the reader is this: What stoichiometries

¹The program EUTAX does this for a number of simple structures. Users of this program might like to find the **cp** array of the I atoms in Exercise 11. Note that the numbers in the coordination sequence are largest for **hcp** and smallest for **ccp** (i.e. all other **cp** structures have intermediate values).

and combinations of octahedra and tetrahedra will lead inexorably to the polyhedron vertices being on a **cp** (i.e. eutactic) array?

In applications to crystal chemistry additional constraints might be added, such as not allowing tetrahedra to share faces (which would allow their central atoms to come rather close together), and to eliminate configurations that result in very asymmetric coordinations around the polyhedron vertices [see E. W. Gorter, *J. Solid State Chem.* **1**, 279 (1970).]

The term "close packing" is sometimes used rather loosely. For example in a discussion of the stability of the feldspar structure (specifically sanidine = KAlSi_3O_8) in a well known text it is stated that the oxygen atoms "approximate rather crudely to cubic close packing...perhaps this relative compactness contributes to the stability." The feldspar structure is based on a framework of corner-sharing O_4 tetrahedra and it would therefore be expected (see § 6.8.5) that each O atom will have six near neighbors and indeed this is the case. The six nearest neighbors of O atoms in sanidine are in the distance range 2.60-2.74 Å (corresponding to tetrahedron edges) and the next six neighbors are in a distance range of 3.30-4.48 Å.

6.8.4 More on the relationship between **bcc** and **hcp**: AuCd

In § 6.3.3 we described a relationship between **bcc** and **hcp**. Some metallic elements such as Ti and Zr have both structures (the high temperature or β form is **bcc**) and the transition occurs very nearly at constant volume. The orthorhombic cells given in § 6.3.3 become in units of $V^{1/3}$ for **bcc**: *a*, *b*, *c* = 0.794, 1.122, 1.122 and for **hcp**: *a*, *b*, *c* = 0.707, 1.225, 1.154, so that the transformation from **bcc** on cooling requires about a 10% decrease in *a* and a 10% increase in *b*. In **CuZn** compounds alternate {100} layers of **bcc** are **Cu** and **Zn**; some of these transform at low temperatures to a superstructure of **hcp** by the mechanism described. Fig 6.69 shows the resulting structure which is called **AuCd**, as the martensitic transformation has been well studied in that compound. In the binary compound the symmetry is *Pmma* and the unit cell is derived from the one described here by (0 0 1 / 1 0 0 / 0 1 0). Data for two forms of AuCd are given in Appendix 5. The low temperature form is close to ideal **hcp**; the 12 shortest distances are 2.89-3.16 Å.

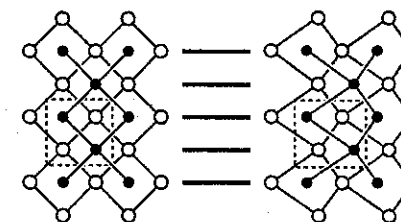


Fig 6.69. Left: the **CuZn** structure projected on (001). Right: the **AuCd** structure plotted on (010) of the *Pmma* cell with *c* horizontal on the paper. Heavy lines mark the position of (110) planes of **CuZn** that become **cp** planes in **AuCd**. If all the atoms were the same this figure would also illustrate the relationship of **bcc** (left) to **hcp** (right). Compare Fig. 6.24 (p. 232).

6.8.5 More sphere packings

A complete enumeration of sphere packings would be a big task and has not been done to our knowledge. Cubic sphere packings have been enumerated by W. Fischer [*Zeits. Kristallogr.* 138, 129 (1973); 140, 50 (1974)] who found no examples with 10- or 11-coordination. An article on sphere packings is in the *International Tables C*. The study of lattice sphere packings in N -dimensional space is an active area of research in mathematics—see Appendix 2.

Here we describe some additional structures confined (so far!) to fewer crystal structure types than most of the structures described above.

Another 10-coordinated sphere packing, and the Ti_5Te_4 structure

Cubes with four faces capped by square pyramids (half octahedra) can be packed as shown in Fig. 6.70. The cubes share their uncapped faces to form rods parallel to c of a tetragonal cell, and the pyramids, which cap the other four faces of the cubes, share edges. The structure is less dense than the other 10-coordinated sphere packings described in this chapter:

$$I4/m, a = \sqrt{[17/(14 - \sqrt{128})]} = 2.5156, c = 1, \rho = (56 - 32\sqrt{2})\pi/51 = 0.6619$$

Centers in 8 h : $I \pm (x, y, 0; \bar{y}, x, 0)$, $x = (6 - \sqrt{2})/17 = 0.2697$, $y = (7 - \sqrt{32})/17 = 0.0790$

The Te arrangement in Ti_5Te_4 is quite close to this packing. The Ti atoms center all the cube faces, so the Ti arrangement consists of rods of octahedra sharing opposite vertices. About a dozen compounds (e.g. V_5S_4 , Ta_5Sb_4) have the same structure.

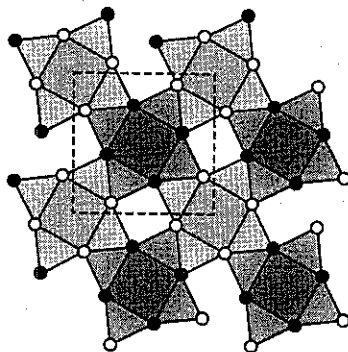


Fig. 6.70. A 10-coordinated sphere packing projected down the c axis. Open circles are at $z = 0$ and filled circles are at $z = 1/2$.

If the cubes with capped faces are deformed into cuboctahedra the result is a

9-coordinated packing corresponding to ccp with 1/5 of the atoms removed (compare with another 9-coordinated packing described below). The parameters would now be $a = \sqrt{5}$, $c = \sqrt{2}$, $a/c = 1.58$ $x = 3/10$, $y = 1/10$ and the sites at 4 d : $I + (0, 1/2, 1/4; 1/2, 0, 1/4)$ are in regular tetrahedra. In β - BaFe_2S_4 , $a/c = 1.45$, S atoms are in 8 h with $x = 0.301$, $y = 0.120$, Ba centers the cuboctahedra of S and Fe is in the S_4 tetrahedra (for data see Appendix 5). $\text{Ga}_2\text{Te}_5 = \text{Te}(1)\text{Ga}_2\text{Te}(2)_4$ is iso-structural [with Te(1) playing the role of Ba and Te(2) playing the role of S].

Some 9-coordinated sphere packings

One symmetrical arrangement is:

$$I\bar{4}3m, a = \sqrt{8}. \text{Centers in } 24 \text{ } g: I + (x, x, z; \bar{x}, x, \bar{z}; x, \bar{x}, \bar{z}; \bar{x}, \bar{x}, z)\kappa, x = 3/8, z = 1/8$$

This arrangement represents a way of removing 1/4 of the spheres of cubic eutaxy so that each sphere has nine neighbors (compare the 8-coordinated J arrangement, which can also be described as cubic eutaxy with 1/4 of the spheres removed). The density is accordingly $\rho = \pi/\sqrt{32} = 0.5554$. This packing is a special case of the anion packing in the mineral sodalite discussed under 6-coordinated sphere packings below (p. 274).

A second 9-coordinated sphere packing that occurs in a variety of contexts (for example as the Al arrangement in WAl_{12}) is also discussed below (p. 278) as an example of a sphere packing with icosahedral interstices. Fischer's compilation, referred to above, includes two other examples of 9-coordination with cubic symmetry.

Another 8-coordinated sphere packing: the NaZn_{13} structure

About 50 compounds, mostly $M\text{Zn}_{13}$ and $M\text{Be}_{13}$ (here M is a "big" atom from the first three columns of the periodic table) have the NaZn_{13} structure (for crystallographic data see Appendix 5). We describe it here, as it is an elegant example of how an apparently complex structure is built up from very simple principles.

We start by assembling an infinite structure by joining together snub cubes ($3^4.4$) sharing square faces in every possible direction; every polyhedron of one hand (recall the symmetry of a snub cube is 432) is joined in this way to six polyhedra of the other hand. Each vertex of this assembly will have eight nearest neighbors, so it may be considered an 8-coordinated sphere packing. A formal description is:

$$Fm\bar{3}c, a = 4.5704, \rho = 0.5265$$

Sphere centers in 96 i : $F \pm (0, \pm y, z; 1/2, \pm z, y)\kappa, y = 0.1761, z = 0.1141$
 Snub cube centers in 8 a : $F \pm (1/4, 1/4, 1/4)$
 Icosahedron centers in 8 b : $F + (0, 0, 0; 1/2, 1/2, 1/2)$

As well as the large holes at the centers of the snub cubes (filled by Na in NaZn_{13}) with symmetry 432, there are holes surrounded by 12 equidistant spheres forming almost regular icosahedra with symmetry $m\bar{3}$. In NaZn_{13} , Zn atoms center these icosahedra

forming Zn_{13} groups. (The unit cell therefore contains $96 + 8 = 104$ Zn atoms and 8 Na atoms, i.e. eight NaZn_{13} units.) In the real structure the free parameters for Zn are quite close to the ideal ones given above.

Figure 6.71 shows a beginning of the packing of snub cubes. The place where an icosahedron can nestle between the snub cubes should be identified. The figure also shows a snub cube sharing triangular faces with eight icosahedra (note that the latter occur in two different orientations). The triangular faces of the snub cube and the darker-shaded faces of the icosahedra are equilateral triangles. The icosahedron edges parallel to the cubic axes are about 4% longer than the others.

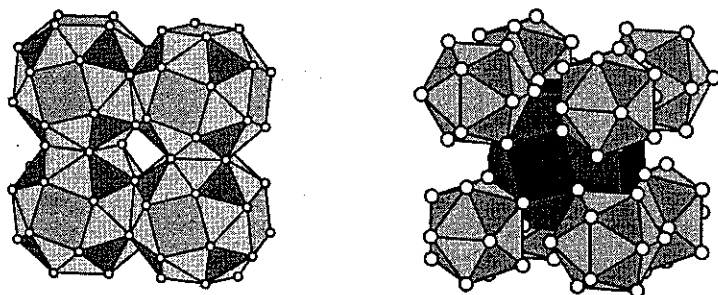


Fig. 6.71. Left: snub cubes (two of each hand) sharing square faces. Right: a snub cube (darker shaded and mostly obscured) sharing triangular faces with icosahedra as in the NaZn_{13} structure.

A remarkable example of this structure is in a rare form of opal from Brazil. Two different-sized spheres of silica pack as Na and Zn. (Common opals have one size of sphere in cp). The spheres are now much bigger than atoms: about $0.5 \mu\text{m}$ [see J. V. Sanders & M. J. Murray, *Nature* **275**, 201 (1975) and *Phil. Mag.* **42**, 721 (1980)].

More 6-coordinated sphere packings

Frameworks of corner-connected (regular) tetrahedra such as the T structure are 6-coordinated sphere packings. The O atoms in quartz (§ 3.6) form another such framework. The O atoms in the sodalite structure are also an example. For reference we give coordinates for regular tetrahedra of unit edge length. The centers of tetrahedra (here labeled Si for convenience) are on a W^* net:

$$\begin{aligned} \text{Im}\bar{3}m, a &= 2 + \sqrt{2} = 3.4142, \rho = 0.3157 \\ \text{Sphere centers (O) in } 24 h: &I + (0, \pm x, \pm x)\kappa, x = 1/\sqrt{8} = 0.3536 \\ \text{Tetrahedron centers (Si) in } 12 d: &I \pm (1/4, 0, 1/2)\kappa \end{aligned}$$

This is a special high-symmetry, low-density case of a more general 6-coordinated packing with symmetry $I4_3m$, in which the tetrahedron centers remain in the same positions (also labeled $12 d$) but the vertices are in positions $24 g: I + (x, x, z; \bar{x}, x, \bar{z}; \bar{x}, \bar{x}, z$

$x, \bar{x}, \bar{z})\kappa$. For a 6-coordinated sphere packing (regular tetrahedra sharing vertices), $x = \sqrt{(z^2 + 1/8)}$ with $0 \leq z < 1/8$. When $z = 0$ we regain the $\text{Im}\bar{3}m$ structure with an Si-O-Si angle of 160.57° . In real sodalites (alumino-silicates) the bond angle is typically 140° corresponding to $z \approx 0.06$. When $z = 1/8$ the structure is the 9-coordinated structure referred to above, and the Si-O-Si angle would then be 109.48° .

Figure 6.72 shows a fragment of the structure in its minimum and maximum density forms. For unit tetrahedron edge length, the unit cell parameter is $a = 3.142$ in the minimum density form and $a = 2.818$ in the maximum density form and the density has increased by about 39%.¹

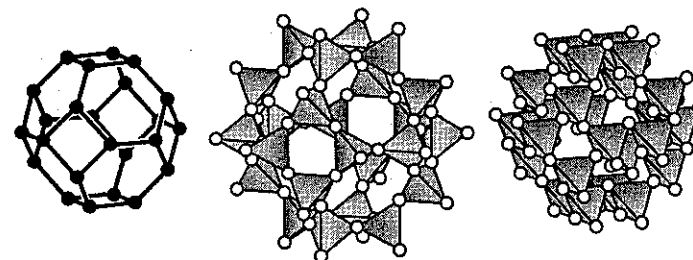


Fig. 6.72. Left: a truncated octahedron. Middle: A corner-connected array of tetrahedra (centered at the vertices of the truncated octahedron) as in the low-density, high-symmetry version of the sodalite anion structure. Right: the collapsed, high-density version of the same structure.

Yet another framework of regular tetrahedra has tetrahedron centers, T , on lattice complex S^* ($3/8, 0, 1/4$; etc. of $Ia\bar{3}d$). The vertices, X (sphere centers) are given by:

$$\begin{aligned} Ia\bar{3}d, a &= 2\sqrt{(2-\sqrt{3})} = 3.8637, \rho = 0.4357 \\ X \text{ in } 48 g: &(1/8, x, 1/4-x; \text{etc.}), x = 1/2 - \sqrt{3}/8 = 0.2835; T-X-T = 150^\circ \end{aligned}$$

An important elemental structure type is that of β -Sn (white tin). Here we give parameters for a slight idealization with six equal distances:

$$I4_1/amd, a = \sqrt{15}/2, c = 1, \rho = 0.5585. \text{ Sphere centers in } 4 a: I \pm (0, 3/4, 1/8)$$

Except for the unit cell parameters this structure has the same description as the 8-coordinated structure described in § 6.3.4 (p. 234). The two structures are very different though; in β -Sn $c/a = 0.516$, in the 8-coordinated structure $c/a = 3.46$. This again emphasizes the fact that in non-cubic structures axial ratios should be carefully considered before concluding that two structures are the same (or related). In fact the same positions of $I4_1/amd$ with $c/a = 1.414$ corresponds to the diamond structure.

We could have devoted a section of this chapter to space-filling packings of polyhedra.

¹The relevance of this structure and its transformations to crystal chemistry has been the subject of much discussion. Three papers on the topic appeared in *Acta Crystallogr.* **A37**, 1-17 (1981).

We have seen, for example, how space-filling packings of tetrahedra and octahedra give rise to eutactic arrangements; and the *T* structure may be considered a packing of tetrahedra and truncated tetrahedra. In the next chapter we will meet 4- and 5-connected structures that arise from other packings of regular and/or Archimedean polyhedra. Here are two 6-coordinated examples involving rhombicuboctahedra (3.4³, Fig. 5.5) which we call *rco*'s for short.

An *rco* has two kinds of square faces: There are six having edges in common only with other squares; these are parallel to the faces of a cube. Joining *rco*'s through these faces will result in a structure in which the centers of the *rco*'s are on a primitive cubic lattice and the remaining space is a labyrinth of face-sharing cubes and cuboctahedra. Crystallographic data are:

- (a) Cubes, cuboctahedra (3.4.3.4) and *rco*'s (3³.4):

$$Pm\bar{3}m, a = 1 + \sqrt{2} = 2.4142, \rho = 0.4465$$

$$\text{Sphere centers in } 12 \text{ } i: (0, \pm x, \pm x) \kappa, x = 1/(2 + \sqrt{2}) = 0.2929$$

We illustrate the structure in three ways in Fig. 6.73. Note particularly that if we consider just the packing of cubes and cuboctahedra (so that the "empty" space consists of *rco*'s) we have a continuous three-dimensional surface tiled with polygons. We will discuss such *infinite polyhedra* in the next chapter (see also Appendix 3). In this example all the vertices are equivalent and are 3.4².3.4².

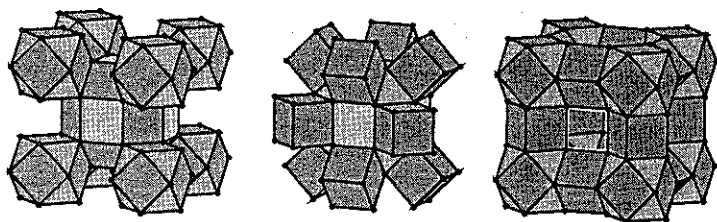


Fig. 6.73. Space filling by cubes, cuboctahedra and *rco*'s. Left: the combination of cuboctahedra and *rco*'s. Center: the combination of cubes and *rco*'s. Right: the combination of cubes and cuboctahedra.

- (b) Tetrahedra, cubes and *rco*'s:

$$Fm\bar{3}m, a = 2 + \sqrt{2} = 3.4142, \rho = 0.4210$$

$$\text{Sphere centers in } 32 \text{ } f: F \pm (x, x, \pm x) \kappa, x = 1/(4 + \sqrt{8}) = 0.1464$$

An *rco* has also twelve square faces with two edges in common with triangles. Joining them by these faces produces a structure in which the centers of the *rco*'s are on a face-centered cubic lattice. The remaining space consists of cubes and tetrahedra (1 and 2 respectively per *rco*) sharing vertices. Fig. 6.74 should provide sufficient information for model builders to proceed.

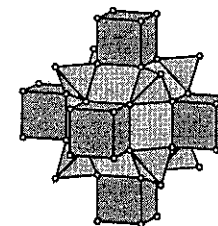


Fig. 6.74. Part of a space filling by cubes, tetrahedra and *rco*'s.

This is the O arrangement in compounds $\text{Ag}_7\text{O}_8\text{X}$ (X is a monovalent anion such as F^- or NO_3^- which is in the center of the *rco*). Ag atoms are of two kinds: those centering the cubes (8-coordinated by O) and those centering the square faces (4-coordinated) of the *rco* that are not shared with cubes.

Another 6-coordinated structure is obtained by joining together *rco*'s and octahedra. Each triangular face of each *rco* is shared with an octahedron, and each octahedron shares a pair of opposite faces with *rco*'s (this makes a rather elegant model). We discuss this structure as an example of an infinite polyhedron 3³.4³ in Appendix 3. Data are:

$$Im\bar{3}m, a = 3.8857, \rho = 0.4284$$

$$\text{Sphere centers in } 48 \text{ } k: l + (\pm x, \pm x, \pm z) \kappa, x = 0.3713, z = 0.1893$$

Finally, we consider a fascinating 6-coordinated structure with only two parameters:

$$P4_132, a = 8/[3\sqrt{(7 - \sqrt{33})}] = 2.3800, \rho = 0.4661$$

$$\text{Sphere centers in } 12 \text{ } d: (1/8, x, 1/4 + x; \text{ etc.}), x = (9 - \sqrt{33})/16 = 0.2035$$

In this structure three equilateral triangles twisted as in a three-bladed propeller meet at a point. There are two next-nearest neighbors at a distance 1.23 times the shortest distance. If all eight neighbors are counted, the structure may be described as a three-dimensional framework of corner-connected metaprisms. Three fifths of the Mn atoms in β -Mn have this arrangement; the remaining two fifths cap the equilateral triangular faces of the metaprisms, forming almost regular tetrahedra.

6.8.6 Sphere packings with icosahedra: WAl_{12} and AuZn_3

Strictly regular icosahedra are incompatible with crystallographic symmetry (which precludes the presence of 5-fold axes); but nature is very clever at designing periodic structures that feature *almost* regular icosahedra. Here we discuss two structures that may be considered as derived from the *J* structure (§ 6.3.6, Fig. 6.27) and which arise in a variety of contexts.

The *J* structure, considered as a packing of octahedra (sharing vertices with each other) and cuboctahedra (sharing faces), contains one of each polyhedron and a total of three

vertices per unit cell. If the cubic cell edge is doubled there will be 8 ($= 2 \times 2 \times 2$) of each polyhedron in the larger cell. We can take the octahedron centers to be at $\pm(1/4, 1/4, 1/4; 1/4, 3/4, 3/4)\kappa$ in this cell and the cuboctahedron centers to be at $0,0,0; 1/2, 1/2, 1/2$ and $(1/2, 0, 0; 1/2, 1/2, 0)\kappa$. The first two cuboctahedra (centered at the cell origin and body center each with 12 vertices) are isolated from each other and account for the $8 \times 3 = 24$ vertices in the doubled cell of the J structure. Let's now convert these two cuboctahedra to icosahedra as indicated in Fig. 2.25 (p. 54), and arrange them so that the shortest distance between vertices of neighboring icosahedra are the same as their edge lengths. It is remarkable that the transformation can be much more elegantly, and informatively, described in terms of concerted rotations of the corner-connected octahedra of the structure (which remain regular) as illustrated in Fig. 6.75. The resulting structure has symmetry $Im\bar{3}$.

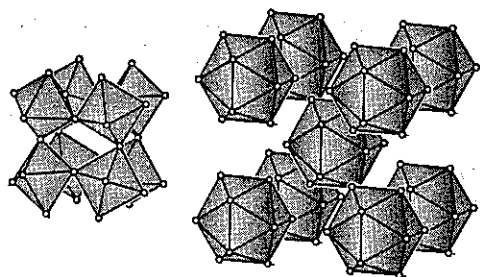


Fig. 6.75. The Al array in WAl_{12} . Left: as vertex-sharing octahedra. Right: as a body-centered array of icosahedra.

The octahedra are rotated about axes parallel to $\langle 111 \rangle$. Let the angle of rotation (the same for every octahedron) be ϕ . The structure is described as follows:¹

$$Im\bar{3}, a = (8\cos\phi + 4)/\sqrt{18}. \text{ Vertices in } 24g: I \pm (0, y, \pm z)\kappa, \\ y = (3\cos\phi - \sqrt{3}\sin\phi)/(8\cos\phi + 4), z = (3\cos\phi + \sqrt{3}\sin\phi)/(8\cos\phi + 4)$$

For regular icosahedra the rotation angle is given by $\tan\phi = \sqrt{3}(\tau - 1)/(\tau + 1) = 22.2^\circ$ and $y = 3/[4(1 + \tau + \sqrt{2})] = 0.1860$, $z = \tau y = 0.3010$. [Here, as usual, $\tau = (\sqrt{5} + 1)/2$.]

Centering the octahedra with atoms B produces stoichiometry BX_3 . It is interesting that at ordinary pressure ReO_3 has the simple cubic structure with $\phi = 0$, but under pressure it suddenly crumples to produce the body-centered structure with $\phi > 0$.²

Centering the icosahedra of X with atoms A produces stoichiometry AX_{12} and we have

¹Readers who are anxious to derive this and related results for themselves should apply the rotation matrix of Eq. 2.3 (§ 2.5.1) to a point originally at $0, 1/4, 1/4$ ($\phi = 0$).

²As the mechanism of compression changes from bond compression (initially), to buckling (angle bending), the bulk modulus (inverse of compressibility) of ReO_3 decreases with pressure [see B. Batlogg *et al.*, *Phys. Rev. B* 29, 3762 (1984)]. For materials with just one mode of compression, the bulk modulus invariably increases with pressure.

the structure of WAl_{12} which has coordinates very close to the ideal ones given here (see Appendix 5 for data).

What happened to the other six cuboctahedra originally ($\phi = 0$) in the unit cell? Four of their vertices have moved close to the center to produce rectangles with edges in the ratio 1:1.07 (i.e. almost square). A large family of oxides, typified by $CaCu_3Ti_4O_{12}$, is known in which Ca centers the icosahedra of the collapsed structure, Cu centers the rectangles and Ti centers the octahedra. Centering just the icosahedra and octahedra produces stoichiometry AB_4X_{12} ; many compounds of this type are known, examples are $LaFe_4P_{12}$ and $LaFe_4Sb_{12}$.

Considered as a sphere packing, the ideal X arrangement, with regular icosahedra, is 9-coordinated, although as mentioned above, each point has a tenth neighbor just 1.07 times as far away. Also to be noted is that although regular icosahedra are possible, icosahedral symmetry is not; in fact the symmetry at the center of the icosahedra is $m\bar{3}$.

The structure we have described represents just the most symmetrical way of collapsing the J structure by rotations (or tilts) of the octahedra. In Volume II of this series we show how other important structures are derived by different patterns of tilts.

If the icosahedron at the body center of the cell in the above structure is rotated 90° about an axis parallel to a cube edge the symmetry is changed to $Pm\bar{3}n$ and, as before, there are 24 vertices in the unit cell. A new sphere packing with only seven neighbors results if the shortest distance between vertices of neighboring icosahedra is the same as the edge length. This is illustrated in Fig. 6.76. Crystallographic data are:

$$Pm\bar{3}n, a = 1/(2y) = 2.8859, \rho = 0.5232 \\ \text{vertices in } 24k: \pm(0, \pm y, z; 1/2, 1/2 \pm z, 1/2 + y)\kappa, \\ y = 1/2 - \sqrt{(2 + 6\tau)/(4 + 4\tau)} = 0.1733, z = \tau y = 0.2803$$

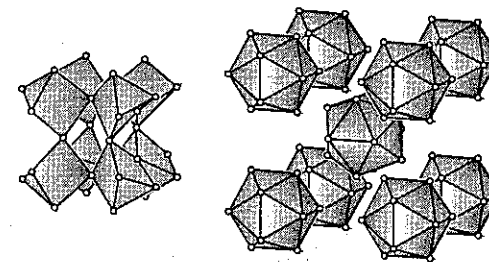


Fig. 6.76. The $Pm\bar{3}n$ arrangement of icosahedra. Left: as an array of corner-connected prisms. Right: the array of icosahedra. Compare with Fig. 6.75.

The array of corner-sharing octahedra in the WAl_{12} structure has now become an array of corner-sharing (somewhat distorted) trigonal prisms. This structure has a nice surprise in store. The unit cell also contains six (again distorted) cuboctahedra with centers at $6c: \pm(1/4, 0, 1/2)\kappa$. If atoms A (at $0, 0, 0$ and $1/2, 1/2, 1/2$) center the X_{12} icosahedra and B center the cuboctahedra, the stoichiometry is AB_3X_{12} . This is in fact the structure of $AuZn_3$ [=

$\text{Au}(1)\text{Au}(2)_3\text{Zn}_{12}$ in which the Zn parameters are quite close to the "ideal" ones given above (see Appendix 5 for crystallographic data).

The AB_3 arrangement in AB_3X_{12} is the very common structure type Cr_3Si or $\beta\text{-W}$ (§ 6.6.4). One form of UH_3 , which we write as $\text{U}(1)\text{U}(2)_3\text{H}_{12}$ has the AuZn_3 structure. We might think of this as Cr_3Si $\text{U}(1)\text{U}(2)_3$ with H in tetrahedral interstices.

There are also some germanides and stannides, e.g. $\text{Pr}_3\text{Rh}_4\text{Sn}_{13}$, in which there are Ge_{13} or Sn_{13} groups obtained by centering the icosahedra. Pr atoms are in the cuboctahedra of Sn, and Rh atoms are in the trigonal prisms of Sn (for data see Appendix 5).

The symmetry of the AuZn_3 structure should lead us to expect (see § 6.8.10) to find a rod packing based on the $\beta\text{-W}$ cubic cylinder packing. Fig. 6.77 illustrates the arrangement of cuboctahedra which consists of rods of face-sharing cuboctahedra packed in this way.

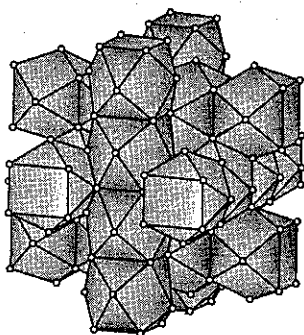


Fig. 6.77. The packing of rods of face-sharing cuboctahedra in the AuZn_3 structure. The rods run parallel to the three cube axes.

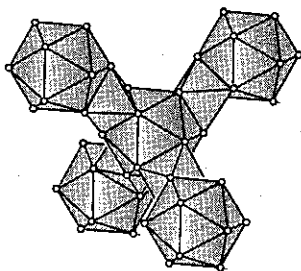


Fig. 6.78. A low density packing of icosahedra and octahedra; an infinite polyhedron 3^7 . Cf. Fig. 6.75.

Finally, we observe that half of the icosahedra of the WAl_{12} structure (Fig. 6.75) could be omitted, leaving each icosahedron with just four neighboring icosahedra and with the centers of the icosahedra arranged as in the **diamond** net (§ 7.3.1). The resulting structure

is illustrated in Fig. 6.78. Note that (excluding the shared face) seven equilateral triangles meet at each vertex so we have an infinite polyhedron 3^7 as discussed in Appendix 3. The structure is a low-density 7-coordinated sphere packing, indeed the least dense that we know of. Crystallographic data for unit edge length are:

$$Fd\bar{3}, a = 5.376, \rho = 0.3235$$

$$\text{Sphere centers in } 96 \text{ g: } (x, y, z, \text{ etc.}), x = 0.0320, y = 1/8, z = 0.2755$$

6.8.7 Cubic invariant lattice complexes

The symbols for some of these complexes (as given in the *International Tables A*) have been given already in this chapter but are summarized here for convenient reference, together with their highest symmetry occurrences. A prefixed "+" or "-" is used for enantiomorphous pairs and an affixed "*" indicates that the lattice complex is derived by combining two lattice complexes (one displaced from the other) with the same symbol but without the affix. In the table below N is the coordination number. The atoms in bold in chemical formulas lie on the lattice complex; the symmetry may be lower in the actual compound (cf. NbO). V^* and Y^{**} (a combination of two Y^*) correspond to two intergrown (but not inter-connected) nets.

complex	space group	position	N	remarks
F	$Fm\bar{3}m$	$4a$	12	face-centered cubic
I	$Im\bar{3}m$	$2a$	8	body-centered cubic
J	$Pm\bar{3}m$	$3c$	8	Fig. 6.27
S	$I\bar{4}3d$	$12a \text{ or } b$	8	Th_3P_4 , Fig. 6.30
P	$Pm\bar{3}m$	$1a$	6	primitive cubic
T	$Fd\bar{3}m$	$16c \text{ or } d$	6	Fig. 6.32
$+Y$	$P4_332$	$4a$	6	FeSi , Fig. 6.34
$-Y$	$P4_132$	$4a$	6	enantiomorph of above
D	$Fd\bar{3}m$	$8a \text{ or } b$	4	diamond, Fig. 7.9
$+V$	$I4_132$	$12c$	4	Fig. 7.36
$-V$	$I4_132$	$12d$	4	enantiomorph of above
J^*	$Im\bar{3}m$	$6b$	4	NbO , Fig. 7.31
W^*	$Im\bar{3}m$	$12d$	4	sodalite, Fig. 7.30
S^*	$Ia\bar{3}d$	$24d$	4	Fig. 7.35
V^*	$Ia\bar{3}d$	$24c$	4	two V nets
$+Y^*$	$I4_132$	$8a$	3	SrSi_2 , Fig. 7.6
$-Y^*$	$I4_132$	$8b$	3	enantiomorph of above
Y^{**}	$Ia\bar{3}d$	$16b$	3	two Y^* nets, Fig. 7.34
W	$Pm\bar{3}n$	$6c \text{ or } d$	2	Cr_3Si , Fig. 6.60

An invariant lattice complex may occur in more than one space group. Thus J also occurs as positions c and d of $P43m$ and (with doubled cell) as positions c and d of $Fm\bar{3}c$.

Other lattice complexes with symbols include ^+Q for the Si atom positions in β -quartz (§ 3.6) with symmetry $P6_222$ and ^-Q for the enantiomorph ($P6_422$), G for a 6^3 layer and N for a $3.6.3.6$ (kagome) layer. We used these last two symbols in § 6.1.6.

6.8.8 Common cubic unit cells for arrays

In § 5.6.12 we discussed common unit cells for plane patterns. There is an analogous problem in three dimensions involving cubic patterns. The smallest cubic supercell of a primitive cell has edges $2a$, i.e. 8 times the volume. The next will have 27 times the volume. The number of symmetry-related points in a cubic cell is a divisor of 192 so in practice, to investigate relationships between cubic structures of symmetry-related points in which a cubic cell is maintained, it is only necessary to consider relationships of this kind between structures with either the same number of points or differing by a factor of eight. There are then six sets of compatible numbers which are:

- (i) 1, 8, 64
- (ii) 2, 16
- (iii) 3, 24, 192
- (iv) 4, 32
- (v) 6, 48
- (vi) 12, 96

We now give some examples of the use of these numbers. The fact that the anions in the spinel structure (§ 3.4) are in 32 e of $Fd\bar{3}m$: $F \pm (x, x, x; (x, 1/4-x, 1/4-x)\kappa)$ (with x typically = 0.26) suggests a possible relationship to ccp with four points per cubic cell [case (iv) above]. The reader is invited to confirm that if $x = 1/4$ the structure is indeed a face-centered cubic lattice described with a $2 \times 2 \times 2$ cell.¹

Another example is provided by the structure of Th_3P_4 which has symmetry $I\bar{4}3d$ with P atoms in 16 c : $I + (x, x, x; 1/4+x, 1/4+x, 1/4+x; (1/2+x, 1/2-x, \bar{x}; 3/4+x, 1/4-x, 3/4-x)\kappa)$ with $x = 0.08$. In this case the reader may confirm that for $x = 0$, the arrangement is body-centered cubic [2 atoms per cell; case (ii) above] described with a $2 \times 2 \times 2$ cell.

Note also the relationship of the cubic 7-coordinated sphere packing of § 6.3.8 (p. 238) with symmetry $Pa\bar{3}$ and eight points per cell to the primitive cubic structure with one per cell [case (i)].

A formal description of the garnet structure of $Ca_3Al_2Si_3O_{12}$ was given in § 3.4. The cubic cell contains 96 O atoms. A well known reference work states that this structure has "oxygen ions in cubic close packing." Reference to case (vi) above shows that this

arrangement with 96 atoms per cubic cell can only be compatible with other cubic structures with 12 atoms per unit cell. In particular it is incompatible with ccp (four per cell). Actually in $Ca_3Al_2Si_3O_{12}$ the first twelve O neighbors of an O atom range in distance from 2.57 - 3.85 Å and the thirteenth neighbor is at 3.89 Å so we can, in any case, discount the claim on those grounds. We can also use the coordination sequence (as described in § 6.8.2) based on the first twelve neighbors to show that the arrangement does not correspond topologically to any cp arrangement.

The Al positions in garnet are in 16 a of $Ia\bar{3}d$ and correspond to bcc (2 per cell) described by a $2 \times 2 \times 2$ cell [case (ii)] and the combination of the Ca and Si positions (24 c and 24 d respectively) corresponds to lattice complex W (6 points per cell) described by a $2 \times 2 \times 2$ cell [case (v)].

Cubic supercells of cubic cells with axes not parallel to the original one may occur, but they are probably not of much interest because of the size of the new cell. A simple example is that obtained by the transformation $(3\ 4\ 0 / -4\ 3\ 0 / 0\ 0\ 5)$ with edge length of $5a$. A cubic supercell with edge an irrational multiple of a (in the same way as a square cell has supercells $\sqrt{2}a \times \sqrt{2}a$ or $\sqrt{5}a \times \sqrt{5}a$) cannot occur however.

6.8.9 Packing of two sizes of sphere: "kissing" numbers

In this chapter, the emphasis has been on sphere packings with one kind of sphere, because these commonly occur in simple crystal structures. However, some structures of intermetallic compounds can be considered as efficient (dense) packings of two or more kinds of sphere of different sizes. The structure of $MgCu_2$ (§ 6.6.3) is an often cited example of an efficient packing of two kinds of sphere and that of $NaZn_{13}$ (§ 6.8.5) is another. Very little systematic research has been done on the problem of classifying packings of spheres of two sizes, but it has an obvious relevance to crystal chemistry and some results would be expected to lead to useful insights into intermetallic structures. For packings of two sizes of circles see L. Fejes Tóth, *Regular Figures* (Pergamon Press, Oxford (1964)). For the packing of two sizes of sphere see M. J. Murray & J. V. Sanders, *Phil. Mag.* A42, 721 (1980). These last authors were interested also in the structures of opals which are packings of (typically micron-sized) silica spheres. In contrast to crystals, opals really are packings of hard spheres.¹

The maximum number of equal spheres that can touch a similar central one is known as the kissing number. It seems astonishing that the answer in three dimensions was once controversial and involved Newton (who correctly said twelve) and Gregory (who thought the answer might be thirteen). However, such questions are difficult to settle to the satisfaction of mathematicians, who are uncommonly hard to please in such matters.

In intermetallic structures, higher kissing numbers are commonly found; for example, in $NaZn_{13}$, Na has 24 equidistant Zn neighbors. In general, in such structures, nature contrives to design an arrangement in which every atom is highly coordinated. At the same time she is tolerant of small variations in interatomic distance—it is this aspect of the topic

¹It is amusing that a *rare* sphere packing (described in the next chapter) also has the same formal description (points in 32 e of $Fd\bar{3}m$) but with $x = 1/(8 + \sqrt{96}) = 0.056...$ so one must be a little cautious. Structures with the same formal description, but differing in the values of one or more parameters, may be very different.

¹The "fire" in opal comes from Bragg diffraction of light from the planes in the periodic packing of spheres, in a similar way as crystals diffract X-rays.

which makes it virtually intractable from the point of view of formal geometry.

A related question which is of some importance to crystal chemistry concerns kissing numbers in binary (ternary etc.) compounds (extended structures) in which spheres (atoms) of one kind kiss only spheres of another kind. We call these numbers *heterosphere* kissing numbers. Typically in "ionic" crystals the "cations" have only "anions" as nearest neighbors and *vice versa*, and the question of heterosphere kissing numbers is particularly relevant for this class of compounds.

To take a specific example: in a binary compound A_mB_n (in the strict sense in which all A are equivalent as are all B) with $d(A-B) < d(A-A)$ and $d(B-B)$, what is the maximum possible coordination of A by B ?

We pause first to remark that if the coordination of A by B is p and the coordination of B by A is q , then $pm = qn$. This almost trivial observation turns out to be of some consequence in determining possible coordination numbers in "ionic" crystals.

Our guess, based on observed crystal structures, for the answer to the above question for compounds AB , is that the maximum coordination number (heterosphere kissing number) is 8, and for compounds A_mB_n that the average coordination number (i.e. averaged over all the atoms) can never exceed 8 as long as $d(A-B) < d(A-A)$ and $d(B-B)$.

6.8.10 The occurrence of cubic cylinder packings

s.g.	garnet	γ -Si	β -W ($\times 2$)
	u, u, u	$\frac{1}{3} + u, \frac{2}{3} + u, u$	$0, \frac{1}{4}, u$
$Ia\bar{3}d$	$e, p\bar{3}c1$	$h, p3_12, p3_22$	$f, p4c2$
$I\bar{4}3d$	$c, p3c1$	$e, p3_1, p3_2$	$d, p\bar{4}$
$Ia\bar{3}$	$c, p\bar{3}$	$e, p3_1, p3_2$	$d, pcc2$
$Pa\bar{3}$	$c, p\bar{3}$	$d, p3_1, p3_2$	$d, p1c1$

s.g.	garnet	$SrSi_2$	β -W ($\times 2$)	β -Mn
	u, u, u	$\frac{1}{3} + u, \frac{2}{3} + u, u$	$0, \frac{1}{4}, u$	$\frac{1}{4}, 0, u$
$I4_132$	$e, p3$	$i, p3_12$	$f, p222$	$i, p4_122$
$P4_132$	$c, p3$	$e, p3_22$	$e, p211$	$e, p4_1$
$P4_332$	$c, p3$	$e, p3_22$	$e, p211$	$e, p222_1$
$I2_13$	$a, p3$	$c, p3_1$	$b, p112$	$c, p222_1$
$P2_13$	$a, p3$	$b, p3_2$	$(b, p1)$	$b, p112_1$

s.g.	β -W ($0, \frac{1}{2}, u$ or $\frac{1}{2}, 0, u$)
$Pm\bar{3}n$	g or $h, p4_2/mmc$
$P\bar{4}3n$	h or $g, p4_2c$
$P4_232$	i or $j, p4_222$
$Pm\bar{3}$	f or $g, pmmm$
$P23$	g or $h, p222$

Cubic cylinder packings are of particular interest in the description of complex crystal structures that otherwise resist description. Here (on the previous page) we list the cubic space groups with non-intersecting symmetry axes and the axis locations. The entries in the table are the Wyckoff positions and compatible rod symmetry (Appendix 1). For example we see that the substitution u, u, u in $Ia\bar{3}d$ corresponds to positions e and represents the axes of the **garnet** packing. Rods along these axes have symmetry $p\bar{3}c1$.

Non-intersecting 4-fold or 2-fold axes also occur in the space groups with non-intersecting 3-fold axes. They fall into two sets, each corresponding to the axes of β -W described by a doubled cell. We label this β -W ($\times 2$). Thus, again for $Ia\bar{3}d$, the substitution $0, 1/4, u$ will produce¹ the set $(0, 1/4, u; 0, 3/4, u; 1/2, 3/4, u; 1/2, 1/4, u)$ corresponding to positions $48f$ and rod symmetries will be $p\bar{4}c2$. This set is illustrated as a cylinder packing in Fig. 6.67 with the unit cell (**a** down the page, **b** horizontal and **c** up out of the page) origin appropriately located. The other set of non-intersecting 4-fold axes are 4_1 and 4_3 axes along the lines generated by the substitution $1/4, 0, u$. Please note that the table is appropriate only for the choices of origin made in the *International Tables*.

The β -W structure without a doubled cell occurs in a separate set of space groups as shown. In these space groups the 3-fold axes intersect.

6.9 Exercises

1. Americium is hexagonal:

Am	$P6_3/mmc, a = 3.474, c = 11.25 \text{ \AA}$
	Am(1) in $2a$ $(0, 0, 0; 0, 0, 1/2)$; Am(2) in $2d$: $\pm(1/3, 2/3, 3/4)$

Describe the structure in terms of stacking 3^6 nets (A, B and C) and in terms of h and c .

2. Other **cp** arrays with just two kinds of sphere are:

hcc (6H)	$P6_3/mmc, c/a = 6\sqrt{2/3}$ h in $2b$: $\pm(0, 0, 1/4)$; c in $4f$: $\pm(1/3, 2/3, z; 1/3, 2/3, 1/2-z), z = 1/12$
hhc (9R)	$R\bar{3}m, c/a = 9\sqrt{2/3}$ c in $3a$: $R + (0, 0, 0)$; h in $6c$: $R \pm (0, 0, z), z = 2/9$
$hhcc$ (12R)	$R\bar{3}m, c/a = 12\sqrt{2/3}$ c in $6c$: $R \pm (0, 0, z), z = 5/24$; h in $6c$: $R \pm (0, 0, z), z = 3/8$

3. Mercury has a rhombohedral structure (space group $R\bar{3}m$) with one atom in the unit cell. $a = 2.993 \text{ \AA}$, $\alpha = 70.74^\circ$. What are the distances to the 12 nearest neighbors of a Hg atom? Transform to a face-centered rhombohedral cell (four atoms per cell) for a comparison with face centered cubic. What is α for this cell? [Hint see § 4.4.]

¹The reader who wishes to verify this statement should note, for example, that the line $0, 1/4, u$ is the same line as $0, 1/4, 1/4-u$; it is a line parallel to c passing through $0, 1/4, 0$.

4. What is the arrangement obtained from two interpenetrating *fcc* lattices, one at 0,0,0 and one at $1/2, 1/2, 1/2$. (i.e. a combination of positions 4 *a* and 4 *b* of $Fm\bar{3}m$)? What is the arrangement of points in 8 *c* of $Fm\bar{3}m$ [$F \pm (1/4, 1/4, 1/4)$] ? If we combine all these positions (4 *a*, 4 *b* and 8 *c*) we will have combined four *fcc* lattices (16 points). What is the arrangement now?

5. Positions 16*a* of $Ia\bar{3}d$ are $I + (0,0,0 ; 1/4, 1/4, 1/4 ; 0, 1/2, 1/2 ; 1/4, 1/4, 3/4)\kappa$. What simple arrangement is this?

6. Here are two examples of structures based on *cp*. Note that although they are quite different, they differ only in the numerical values (i.e. they have the same space group and atoms in the same sets of positions—they are *isopuntal*).

- (a) Th_3N_4 $R\bar{3}m$, $a = 3.875 \text{ \AA}$, $c = 27.39 \text{ \AA}$, $c/a = 7.07$
 Th(1) in 3 *a*: $R + (0,0,0)$; Th(2) in 6 *c*: $R \pm (0,0,z)$, $z = 0.222$
 N(1) in 6 *c*, $z = 0.132$; N(2) in 6 *c*, $z = 0.377$

Th is approximately *cp*; what is the stacking sequence? N atoms fill tetrahedral and/or octahedral interstices. Answer (with *A, B, C* for cations and α, β, γ for anions):

hhc Th; sequence = $A \cdot \gamma B \alpha \cdot \beta A \cdot \gamma B \cdot \alpha C \beta \cdot \alpha C \cdot \beta A \gamma \cdot \alpha C \cdot \beta \dots$

- (b) Fe_3S_4 (smythite) $R\bar{3}m$, $a = 3.47 \text{ \AA}$, $c = 34.5 \text{ \AA}$, $c/a = 9.94$
 Fe(1) in 3 *a*: $R + (0,0,0)$; Fe(2) in 6 *c*: $R \pm (0,0,z)$, $z = 0.9171$
 S(1) in 6 *c*, $z = 0.7898$; S(2) in 6 *c*, $z = 0.6270$

S is approximately *cp*; what is the stacking sequence? Fe atoms fill octahedral interstices. Answer (with *A, B, C* for anions and α, β, γ for cations):

hhcc S; sequence = $A \cdot \gamma B \cdot \gamma A \cdot \gamma B \dots C \cdot \beta A \cdot \beta C \cdot \beta A \dots B \cdot \alpha C \cdot \alpha B \cdot \alpha C \dots$

7. The structures of the rutile form of TiO_2 and of CaCl_2 are closely related:

- TiO_2 $P4_2/mnm$, $a = 4.594 \text{ \AA}$, $c = 2.958 \text{ \AA}$
 Ti in 2 *a*: $(0,0,0 ; 1/2, 1/2, 1/2)$
 O in 4 *f*: $\pm(x, x, 0 ; 1/2+x, 1/2-x, 1/2)$, $x = 0.305$
- CaCl_2 $Pnnm$, $a = 6.241 \text{ \AA}$, $b = 6.432 \text{ \AA}$, $c = 4.340 \text{ \AA}$
 Ca in 2 *a*: $(0,0,0 ; 1/2, 1/2, 1/2)$
 Cl in 4 *g*: $\pm(x, y, 0 ; x+1/2, 1/2-y, 1/2)$, $x = 0.275$, $y = 0.325$

Plot both structures in projection down the short axis and compare with Fig. 6.20 (p. 229). What (approximately) is the anion packing?

8. The structure of Mo_2BC is:

- Mo_2BC $Cmcm$, $a = 3.086$, $b = 17.35$, $c = 3.047 \text{ \AA}$
 Mo(1) in 4 *c*: $C \pm (0, y, 1/4)$, $y = 0.3139$; Mo(2) in 4 *c*, $y = 0.0721$
 B in 4 *c*, $y = 0.4731$; C in 4 *c*, $y = 0.1920$

Describe the Mo structure as a stacking of 4^4 nets along *b* using the notation *A, B, C, D* and describe the type of site (octahedron, trigonal prism etc.) occupied by B and C. Compare the B-B and C-C distances in the structure.

9. Pa and $\gamma\text{-Pu}$ are both 10-coordinated:

- Pa $I4/mmm$, $a = 3.932$, $c = 3.238 \text{ \AA}$. Pa in 2 *a*: $I + (0,0,0)$
- $\gamma\text{-Pu}$ $Fddd$, $a = 3.159$, $b = 5.768$, $c = 10.162 \text{ \AA}$. Pu in 8 *a*: $F \pm (1/8, 1/8, 1/8)$

Plot the Pa structure projected on (110). How do the interatomic distances compare with those in the 10-coordinated *bct*? The $\gamma\text{-Pu}$ structure is based on a stacking of 3^6 nets along *c* in the sequence *ADEF* (see Fig. 6.40, p. 247). Calculate the ten shortest interatomic distances in $\gamma\text{-Pu}$. What is the next shortest distance?

10. Ta_3B_4 is orthorhombic:

- Ta_3B_4 $Immm$, $a = 3.29$, $b = 14.0$, $c = 3.13 \text{ \AA}$
 Ta(1) in 2 *c*: $I + (0,0,1/2)$; Ta(2) in 4 *g*: $I \pm (0, y, 0)$, $y = 0.180$
 B(1) in 4 *g*, $y = 0.375$; B(2) in 4 *h*: $I \pm (0, y, 1/2)$, $y = 0.444$

Describe the Ta arrangement as a stacking of 4^4 nets along *b* (as in Exercise 8). What is the coordination of the B atoms? Check your answers by drawing the structure in projection down *a*.

V_3B_4 is isostructural with Ta_3B_4 and VB is isostructural with CrB (p. 250). There is also reported a composition V_5B_6 ($= 2\text{VB} + \text{V}_3\text{B}_4$). Can you guess a possible structure for this last composition? [See Hyde & Andersson (Book List) p. 227.]

11. Many halides have structures with *cp* anions. Some are rather simple (e.g. CdCl_2 , and CdI_2 , § 6.1.5), but others have rather complicated low-symmetry structures. Data in abbreviated form for some iodides are given below.

- ZnI_2 $I4_1/acd$, $a = 12.284$, $c = 23.583 \text{ \AA}$. Zn 32g, 0.3749, 0.3625, 0.0627
 I(1) 16d, 0, 1/4, 0.0047; I(2) 16e, 0.262, 0, 1/4; I(3) 32g, 0.0113, 0.9993, 0.1267
- HgI_2 $P4_2/nmc$, $a = 4.370$, $c = 12.443 \text{ \AA}$. Hg 2a, 1/4, 3/4, 1/4; I 4d, 1/4, 1/4, 0.3891
- BiI_3 $R\bar{3}$, $a = 7.498$, $c = 20.68 \text{ \AA}$. Bi 6c, 0, 0, 0.167; I 18f, 0.342, 0.340, 0.0805
- SnI_4 $Pa\bar{3}$, $a = 12.273 \text{ \AA}$. Sn 8c, 0.125, 0.125, 0.125
 I(1) 8c, 0.252, 0.252, 0.252; I(2) 24d, -0.002, -0.002, 0.253

U ₄	$C2/c$, $a = 13.967$, $b = 8.472$, $c = 7.510$ Å, $\beta = 90.54^\circ$. U 4f: 0,0,152,1/4 I(1) 8f: 0.123,0.118,-0.086; I(2) 8f: -0.134,0.382,0.100
Hf ₄	$C2/c$, $a = 11.787$, $b = 11.801$, $c = 12.905$ Å, $\beta = 116.3^\circ$. All atoms 8f. Hf 0.4244,0.3610,0.3753; I(1) 0.3270,0.3830,0.1309 I(2) 0.4470,0.1351,0.3866; I(3) 0.1898,0.3761,0.3632 I(4) 0.4369,0.6154,0.3808
PrI ₂	$F\bar{4}3m$, $a = 12.360$ Å. All atoms 16 e, x,x,x etc. Pr, $x = 0.3606$; I(1), $x = 0.1115$; I(2), $x = 0.6257$

Identify the anion packings (all are **cp**) and the way the cations occupy the interstices.

12. A tetragonal tetrahedral layer (§ 6.4.2) consists of two 4^4 nets of Y stacked AB , with a 4^4 net of X of twice the density in between [so there are $\{Y\}X_4$ tetrahedra]. The stoichiometry is X_2Y_2 . If n such layers are joined together the stoichiometry is $X_{2n}Y_{n+1}$ (the case $n = \infty$ corresponds to **fluorite** structure X_2Y). In compounds with the KCu_4S_3 structure there are double tetrahedral layers ($n = 2$) of $\{Cu\}S_4$ tetrahedra interwoven with layers of K in $\{K\}S_8$ cubes:

KCu_4S_3	$P4/mmm$, $a = 3.899$, $c = 9.262$ Å, $c/a = 2.38$. K in 1 b: 0,0,1/2 Cu in 4 i: $\pm(0,1/2,z)$; $1/2,0,z$, $z = 0.1603$ S(1) in 1 a: 0,0,0; S(2) in 2 h: $\pm(1/2,1/2,z)$, $z = 0.2944$
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Verify that the S packing consists of 4^4 nets stacked $ABB\dots$ and that Cu atoms are in $\{Cu\}S_4$ tetrahedra. Compare the Cu...Cu distance in the layers with the Cu...Cu distance in elemental Cu (**ccp** with $a = 3.615$ Å). Speculate on the oxidation states of the atoms.

13. $AlCr_2C$ is one of the so-called H phases found for aluminum-transition metal carbides and nitrides. Many other isopuntal compounds are known including examples with two non-metallic components (which are still called H phases):

$AlCr_2C$	$P6_3/mmc$, $a = 2.860$, $c = 12.82$ Å, $c/a = 4.48$. Al in 2 d: $\pm(1/3,2/3,3/4)$ Cr in 4 f: $\pm(1/3,2/3,z)$; $1/3,2/3,1/2-z$, $z = 0.086$; C in 2 a: (0,0,0; 0,0,1/2)
Ti_2SC	$P6_3/mmc$, $a = 3.210$, $c = 11.20$ Å, $c/a = 3.49$. S in 2 d: $\pm(1/3,2/3,3/4)$ Ti in 4 f: $\pm(1/3,2/3,z)$; $1/3,2/3,1/2-z$, $z = 0.099$; C in 2 a: (0,0,0; 0,0,1/2)

Describe the two compounds above in terms of stacking of 3^6 nets (using $ABC, \alpha\beta\gamma$). What (if any) sets of atoms approximate closest packing in each case? What are the coordination polyhedra around S and C? [Compare Ti_2SC with TiP (§ 4.6.3).]

14. Here is a simple packing of unit diameter spheres:

$$I4/mmm, a = 1 + \sqrt{2}, c = \sqrt{2}. \text{Centers in 8 i: } I \pm (x, 0, 0); 0, x, 0, x = 1/(2 + \sqrt{2})$$

Identify the net in the layers normal to c , and the coordination number of the packing.

CHAPTER 7

NETS AND INFINITE POLYHEDRA

7.1 Introduction

In this chapter, in contrast to the last, we discuss some arrays of points with low coordination number, particularly 3- or 4-coordination. These are less usefully considered as sphere packings, and are more commonly described as *nets*. In some cases it is useful to consider the nets as the edges and vertices of packings of polyhedra. As in the previous chapter, the emphasis is mainly on the simpler high-symmetry patterns that occur in a variety of structural contexts. Now a systematic organization is more difficult as nets may be derived and described in more than one way. To improve continuity we have included in the main body of the text some material that might otherwise have been relegated to the Notes. In particular section numbers in this chapter that are marked with an asterisk may be of lesser interest to some readers and may be omitted in a first reading.

The diamond structure is a familiar example of a 4-coordinated (or 4-connected) net and many other 4-connected nets arise as structures of aluminosilicates (including the two most common crystalline materials in the earth's crust: quartz and feldspar). In the latter case the Si (or Al) atoms are the nodes (or vertices) of the net and the -O- bonds are to be considered the links (or edges). The frameworks of zeolites (mainly aluminosilicates and aluminophosphates) are currently of great interest as their catalytic and other properties are largely determined by their structures. Other important 4-connected nets occur in covalent solids and as the hydrogen-bonded networks in polymorphs of ice and in hydrates.

Nets can also have mixed coordination; thus the net describing the atoms in Si_3N_4 (= $ivSi_3^{iii}N_4$), in which Si is connected to four N, and N is connected to three Si, is referred to as (3,4)-connected. An important class of nets with mixed coordination is that corresponding to frameworks of corner-connected octahedra and tetrahedra. For example, in $Fe_2(SO_4)_3$, $\{Fe\}O_6$ octahedra share corners with $\{S\}O_4$ tetrahedra and *vice versa*. The Fe and S atoms are at vertices and the -O- links correspond to edges of a (4,6)-connected net.

We usually describe nets in crystallographic terms. We generally give unit cell parameters and coordinates of vertices that correspond to an idealized conformation in which the edges are of equal length, and in which the volume, subject to this constraint, is a maximum. This conformation is also one of maximum symmetry. Some nets occur in a variety of crystal structures and often then have lower symmetry.

There appears to be no *simple* method of giving a purely topological definition of nets, but a partial topological characterization of 3- and 4-connected nets is nevertheless useful, so we discuss this topic first. A *systematic* description of nets is difficult and efforts to enumerate possibilities have not succeeded in any rigorous manner (many hundreds of 4-connected nets have been described in the literature).

The topology of nets is a source of some fascinating, and mostly unsolved, problems. For comments on these aspects see Appendix 3.