Sphere Packings and Space Filling by Congruent Simple Polyhedra

M. O'KEEFFE

Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA. E-mail: mokeefe@asu.edu

Abstract

14-coordinated tetrahedral packings of symmetry-related spheres in which all the holes are tetrahedral are described. The corresponding dual structures with vertices in the holes of the original structure form four connected nets that subdivide space into congruent simple polyhedra. Six tetrahedrally packed sphere packings and seven polyhedron packings are described and coordinates of vertices given. Examples are given of packings of combinations of two or more of the space-filling polyhedra.

1. Introduction

Sphere packings are of considerable interest in crystal chemistry as structures of intermetallic compounds and have been extensively studied for that reason. Many examples are given by O'Keeffe & B. G. Hyde (1996; referred to as OKH hereinafter). The holes in such a packing are sites at which the shortest distance to the centers of the nearest spheres is a local maximum (Conway & Sloane, 1988). In the familiar closest sphere packings, the holes are of two types: tetrahedral and octahedral. In crystal chemistry, special interest attaches to sphere packings in which all the holes are tetrahedral; these structures are here called tetrahedrally packed (t.p.). The b.c.c. sphere packing is the only t.p. structure in which all the tetrahedra are congruent (Sommerville, 1923), however very many t.p. structures are known in which there is more than one kind of sphere and more than one kind of tetrahedron. A special class of structures consists of those in which the tetrahedron packing is restricted to configurations in which five or six tetrahedra meet at an edge; these are known as tetrahedrally close-packed (t.c.p.) structures. The classic work describing such structures is that of Frank & Kasper (1958, 1959) and they are often referred to as Frank–Kasper structures. They have special coordination figures of 12, 14, 15 and 16 coordination and serve as the crystal structures of some of the more important known intermetallic phases (for a review, see Shoemaker & Shoemaker, 1986). Many other intermetallic crystal structure types are t.p., a well known example is that of CuAl$_2$ (OKH, p. 255) in which there is 10 and 15 coordination.

As Frank & Kasper explicitly recognized, each tetrahedron of a t.p. structure necessarily has four other tetrahedra sharing its faces, so the dual structure derived by placing vertices at the tetrahedron centers forms a 4-connected net.† Such nets may also be considered as a packing of simple polyhedra (those in which exactly three faces meet at each vertex), which, in the case of the duals of the Frank–Kasper structures, have faces that are restricted to pentagons and hexagons. Some of these structures are well known in chemistry as the structures of clathrate hydrates and clathrasils (see *e.g.* OKH, p. 333). They have also become of interest as model structures for foams especially since the discovery by Weaire & Phelan (1994a) that a foam based on the structure known as the type I hydrate (dual of the A15 or Cr$_3$Si structure) has the lowest surface area of any known structure of uniform volume bubbles, thus refuting a conjecture of Kelvin (described in the next paragraph) that had stood unchallenged for over 100 years (Weaire, 1997). Recent discussions, with references, of the importance of Frank–Kasper and related t.c.p. phases and their duals to problems of packing and space filling and to biological structure include those by Sadoc & Mosseri (1996), Charvolin & Sadoc (1996) and Rivier & Aste (1996).

The Kelvin structure is derived as the dual of the body-centered cubic (b.c.c.) sphere packing, in which the centers of the spheres divide space into six tetrahedra per sphere with either four or six tetrahedra meeting at each edge. As all the spheres are equivalent, the 4-connected net of the tetrahedron centers corresponds to a packing of congruent polyhedra; in this case, Archimedean truncated octahedra. Kelvin's conjecture was that the structure of a minimum energy foam of uniform bubbles would be topologically equivalent to this polyhedron packing. To chemists, the net of the packing is familiar as the framework of the aluminosilicate sodalite, for which it is usually named (OKH, p. 315). In order to take into account the fact that the tetrahedra in a b.c.c. structure have unequal edges, one must count the eight first and six second neighbors in the b.c.c. structure as part of the coordi-

---

† Notice that mathematicians use the term 'dual' of a lattice to refer to another lattice that (in the case of primitive lattices) crystallographers and solid-state physicists call the 'reciprocal' lattice. In this sense, the duals of the body-centered lattices referred to below are also body-centered tetragonal with $c^*/a^* = 2^{1/2}a/c$. If $c/a = 2^{1/4}$, the lattice is isodual (Conway & Sloane, 1994).

nation sphere, and the structure is considered as (8+6) coordinated. The dual structure is derived from a packing of polyhedra (truncated octahedra) with eight hexagonal and six quadrangular (square) faces. Notice that the polyhedra are Voronoi polyhedra that contain all points closer to a given sphere center than to any other, and that their vertices are at the holes of the structure. The coordination number is equal to the number of faces of the Voronoi polyhedron (Frank & Kasper, 1958). It is simple to show (OKH, p. 409) that in a t.p. structure the number of tetrahedral holes per sphere is $\langle Z \rangle/2 - 1$ where $\langle Z \rangle$ is the average coordination number (average number of faces on the Voronoi polyhedra).

If the Kelvin problem is reformulated as that of finding the minimum surface area structure of bubbles of equal volume and of equal pressure, it is possible that the solution will correspond to an assembly of congruent bubbles (Kusner & Sullivan, 1996; reprinted in Weaire, 1997). Such bubbles will be simple polyhedra and will have at least 14 faces (Kusner, 1992). This is one of the reasons for describing some other packings of congruent polyhedra with 14 faces and the associated (dual) sphere packings.

Another reason for interest in these structures is that some also appear in a chemical context as atomic arrangements in crystals, and the existence of other structures not yet found in nature provides a powerful incentive to the synthetic chemist. In fact, the technique of generating 4-connected network structures as the duals of t.p. structures is of considerable utility in designing such structures. Well known examples, which involve structures described by OKH (p. 335), are the clathrate hydrate structures known as type I and type II, which consist of packings of polyhedra with five- and six-sided faces. These are the duals of the A15 (Cr_3Si) and C15 ($MgCu_2$) structures, both of which are Frank–Kasper phases. Another example is provided by the 4-connected net of the clathrasil known as sigma-2 (or SGT), which is derived from a packing of two kinds of polyhedra: those with twelve pentagonal faces and six hexagonal faces, and those with six pentagonal faces and three quadrangular faces. The dual structure is that of $ThSi_2$ and the hexagonal faces correspond to Th–Th 'contacts', the pentagonal faces to Th–Si contacts and the quadrangular faces to Si–Si contacts. It is noted below, however, that not all 4-connected nets of polyhedron packings are the duals of sphere packings.

In this paper, I start with the body-centered tetragonal (b.c.t.) lattice packing of which the body-centered cubic (b.c.c.) and face-centered cubic (f.c.c.) lattice packings are special cases. I then describe some (10+4)-coordinated t.p. sphere packings related to a third special case of b.c.t. Space-filling polyhedra and their packings are derived from these structures. An alternative approach to enumeration of space-filling polyhedra starting from cubic closest packing (c.c.p.) results

in the identification of five different space-filling polyhedra. Seven distinct packings of equivalent polyhedra are identified. Examples are also given of packings involving combinations of two or more of these polyhedra.

2. Sphere packings and holes in b.c.t. and related lattices

A well known transformation (the Bain relationship, see e.g. OKH, p. 229) relates the b.c.c. to the f.c.c. structure of cubic closest packing (c.c.p.). This involves distortion to a body-centered tetragonal lattice with $c/a > 1$ ($c/a = 1$ for b.c.c.). When $c/a = 2^{1/2}$, the structure becomes the 12-coordinated c.c.p.; at this point, groups of four tetrahedral holes merge into octahedral holes. With $c/a > 2^{1/2}$, the coordination is (4+8). Now the octahedra become elongated and each octahedral hole is split into two at the centers of square pyramids. There are now two square-pyramidal and two tetrahedral holes per sphere. In the well known $ThCr_2Si_2$ structure type [the most populous of all ternary inorganic crystal structure types (Pearson, 1985)], Si and Cr fill these holes in a packing of Th.

In c.c.p., the Voronoi polyhedron is a rhombic dodecahedron and the vertices of the polyhedron packing are 4- and 8-connected; in b.c.t. with $c/a > 2^{1/2}$, the Voronoi polyhedron is an elongated dodecahedron and the vertices of the polyhedron packing are 4- and 5-connected. Therefore, neither of these structures gives rise to a 4-connected net or to a space filling by simple polyhedra. If c.c.p. is subject to an opposite distortion to b.c.t. with $c/a < 2^{1/2}$, the octahedra surrounding octahedral holes are compressed so that one diagonal is shorter than the other two. The octahedral holes are now split into four tetrahedral holes with the short diagonal of the octahedron forming one edge and the structure is t.p. For $1 < c/a < 2^{1/2}$, the coordination is (8+4+2). For $c/a = 1$ (b.c.c.), the coordination is (8+6). Continuing the compression along **c**, one has for $(2/3)^{1/2} < c/a < 1$ that the coordination is (8+2+4), and for $c/a = (2/3)^{1/2}$ the coordination is (10+4). These coordination changes with cell-edge ratio are summarized in Fig. 1. T.p. (10+4)-coordinated sphere packings are of particular interest in the context of this paper and are discussed next.
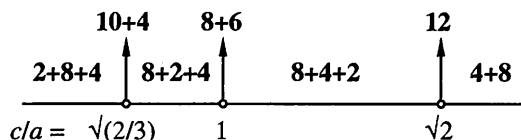

Fig. 1. Variation of coordination number with axial ratio for b.c.t. lattices. $(p + q + r)$ indicates that there are p nearest, q next-nearest, and r next-next-nearest neighbors; and a total of $p + q + r$ faces on the Voronoi polyhedra of the lattice points.

3. T.p. (10+4)-coordinated sphere packings

The b.c.t. structure with $c/a = (2/3)^{1/2} = 0.816\ldots$ is a well known (see *e.g.* Hellner, 1986; Wells & Chamberland, 1987; Koch & Fischer, 1992) (10+4)-coordinated structure that is called b.c.t. by OKH (p. 229). Each lattice point has ten neighbors at a distance c and four further neighbors at a. An interesting feature of the b.c.t. structure is that there are close-packed 3^6 layers parallel to {110} although the stacking of the layers is not close packed, rather each sphere in one layer is over the midpoint of the line joining the centers of two contiguous spheres in the layer below. As shown in Fig. 2, the centers of spheres in each layer may be placed in one of three equivalent positions with respect to the layers below. In the figure they are labeled D, E and F with respect to an initial layer at A (see *e.g.* Wells, 1984, p. 149; OKH, p. 246). The derived packings can be described in a manner analogous to the familiar method of describing closest packings.

In closest packing, two kinds of layer are identified. One, labeled h, has similar layers on both sides such as B in the sequence ABA. The second, labeled c, has different layers one each side such as B in the sequence ABC. The two distinct packings of one kind of sphere are h (h.c.p.) and c (c.c.p.) and all packings can be characterized by a sequence of h's and c's.

A similar system can be used for the 10-coordinated packings but now there are three possibilities. A layer D in a sequence ADA has the same layer on each side, let us call it s. On the other hand, layers D in sequences ADE and ADF have different layers on each side, the layers differing by being rotated by $\pm120°$ with respect to each other. The two possibilities are enantiomers, so they are labeled r and l (right and left). The possible packings of one kind of sphere (*i.e.* those in which all spheres are related by symmetry) can now be expressed as s, r (or l), rl and $rrll$.

The sphere centers in three of these packings correspond to invariant lattice complexes so they are labeled by the symbols (I, Q and D) used for such structures
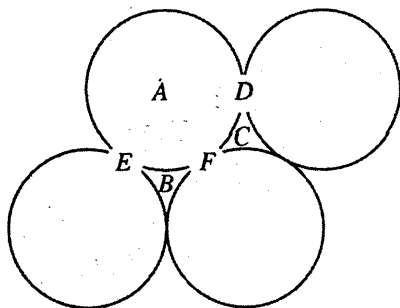

Fig. 2. Positions for stacking 3^6 layers of spheres above a layer in position A. B and C are positions for closest packing. D, E and F are the positions for the 10-coordinated sphere packings discussed in the text.

(Fischer & Koch, 1983; Hellner, 1986).† The fourth is derived as a combination of the previous two and is labeled DQ. It appears to have been overlooked in earlier discussions of sphere packings of which I am aware.

The simplest packings involving two kinds of sphere are rs and $rsls$. Coordinates for these packings are also given below where they are also labeled as IQ and ID, respectively. Lattice parameters are given for unit diameter spheres. In each case, a sphere has ten neighbors in contact and four further away at a distance $(3/2)^{1/2}$ times the diameter, and in each case the centers divide space into six tetrahedra per sphere. I, D and Q correspond to packings 9, 10 and 11 of Koch & Fischer (1992).

$s = I$, layer sequence $AD\ldots$ symmetry $I4/mmm$, $a = (3/2)^{1/2}$, $c = 1$, $c/a = 0.816\ldots$, sphere centers at $2(a)$: $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. This is the b.c.t. structure and I is the symbol for a body-centered lattice.

$r = Q$, layer sequence $ADE\ldots$, symmetry $P6_422$ (or the enantiomorph $P6_222$), $a = 1$, $c = 3 \times 3^{1/2}/2$, $c/a = 2.598\ldots$, sphere centers at $3(d)$: $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{5}{6}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{6}$. The 3^6 layers are normal to c. For $c/a \simeq 1$, the structure (now 4-coordinated) is that of the Si atoms in quartz – hence the label Q. If the $P6_422$ structure describes r, then the $P6_222$ enantiomorph describes l.

$rl = D$, layer sequence $ADEF\ldots$, symmetry $Fddd$, $a = 1$, $b = 3^{1/2}$, $c = 2 \times 3^{1/2}$, sphere centers at $8(a)$: $\pm(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}; \frac{5}{8}, \frac{5}{8}, \frac{1}{8}; \frac{1}{8}, \frac{5}{8}, \frac{5}{8}; \frac{5}{8}, \frac{1}{8}, \frac{5}{8})$. The 3^6 layers are normal to c. For $a = b = c$, the positions of the sphere centers correspond to the diamond structure – hence the label D.

$rrll = DQ$, layer sequence $ADEAFEDF\ldots$, symmetry $Fddd$, $a = 1$, $b = 3^{1/2}$, $c = 4 \times 3^{1/2}$, sphere centers at $16(g)$: $\frac{1}{8}, \frac{1}{8}, z$; *etc.*, $z = 5/16 = 0.3125$. The 3^6 layers are normal to c.

$rs = IQ$, layer sequence $ADAEAF\ldots$, symmetry $P6_422$ (or the enantiomorph $P6_222$), $a = 1$, $c = 3 \times 3^{1/2}$. Q (r) spheres at $3(a)$: $0, 0, 0$; *etc.*, I (s) spheres at $3(d)$: $\frac{1}{2}, 0, \frac{1}{2}$; *etc.* The 3^6 layers are normal to c.

$rsls = ID$, layer sequence $ADAE\ldots$, symmetry $Cccm$, $a = 1$, $b = 3^{1/2}$, $c = 2 \times 3^{1/2}$, D (r or l) sphere centers at $4(a)$: $0, 0, \frac{1}{4}$; *etc.*, I (s) sphere centers at $4(e)$: $\frac{1}{4}, \frac{1}{4}, 0$; *etc.* The 3^6 layers are normal to c.

The I structure is close to that of elemental Pa and the D structure is close to that of γ-Pu. The structures are also found (with tripled unit cells due to atomic ordering) in a large family of silicides and germanides as follows: $I \rightarrow$ MoSi$_2$, $Q \rightarrow$ CrSi$_2$, $D \rightarrow$ TiSi$_2$ (see *e.g.* Pearson, 1972; Hellner, 1986).

OKH (p. 231) describe another (10+4)-coordinated sphere packing (called by them c.c.o.) derived from I by

---

† Unfortunately, 'D' is used in two contexts in this section. The notation is well established in both instances: for positions in sphere packing (*e.g.* Wells, 1984) and for the lattice complex (*e.g.* Fischer & Koch, 1983). As long as the reader bears in mind the two uses, no confusion should occur.

periodic twinning. To generate this structure, and another related one, it is useful to consider the I structure in terms of its {101} layers. Viewed normal to (101), the I structure is made up of distorted 4^4 layers stacked in a five-layer sequence in such a way that each sphere in a layer is in contact with three spheres in each of the layers on either side as shown in Fig. 3. The c.c.o. structure is made up of the same layers in a two layer repeat [b.c.t. and c.c.o. are the packings labeled 3-4*-3 I and 3-4*-3 II by Wells & Chamberland (1987)]. The symmetry is $Cmcm$ and, for spheres of unit diameter, $a = (3/2)^{1/2}$, $b = (5/2)^{1/2}$, $c = (12/5)^{1/2}$. Sphere centers are at $4(c)$: $0, y, \frac{1}{4}$ etc. with $y = 3/10$. It transpires that the net corresponding to the centers of the tetrahedra in this structure is topologically identical to the Kelvin structure although the 10-coordinated packings are distinct in the two cases.

The c.c.o. structure suggests the construction of another (10+4)-coordinated sphere packing from a related distorted 4^4 net as shown in Fig. 4. The symmetry is $Pnma$ and I call it O (for orthorhombic). For unit diameter spheres, $a = 15^{1/2}/2$, $b = (12/5)^{1/2}$, $c = 1$. Sphere centers are at $4(c)$: $x, \frac{1}{4}, z$; etc. with
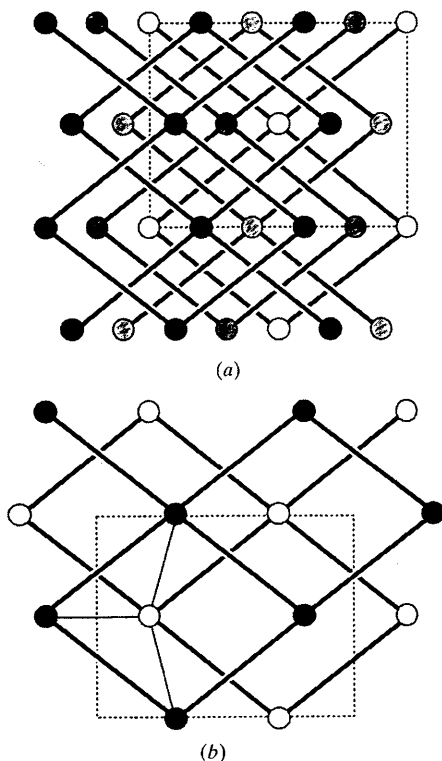
$x = 7/20$, $z = 7/8$. It is interesting, but perhaps not obvious, that the five-layer stacking of such layers analogous to that shown in the top part of Fig. 3 produces the D structure described above.

In all structures of this section, each sphere has ten equidistant neighbors and four more at a distance $(3/2)^{1/2}$ times greater. The packing density is the same: the fraction of space filled by the spheres is $\rho = 2\pi/9 = 0.698\ldots$, cf. $\rho = \pi/3 \times 2^{1/2} = 0.740\ldots$ for closest packing and $\rho = 3^{1/2}\pi/8 = 0.680$ for b.c.c. There are six tetrahedral holes per sphere and their centers define a 4-connected net corresponding to a space filling by 14-face polyhedra. These nets are described below.

Many other 10-coordinated sphere packings are known (OKH). Examples from crystal chemistry are the metal structures of CrB, FeB and MoB, and the anion structures in Ti_5Te_4 and two polymorphs of MoS_2; these are not t.p. structures.

4. Derivation of some space-filling polyhedra

In an alternative approach to identification of candidates for space-filling polyhedra, I start with the holes of c.c.p. with two tetrahedral and one octahedral hole per lattice point (sphere center). Each octahedron can be divided into four tetrahedra by a diagonal; as there are three equal diagonals, there are three sets of four possible tetrahedral sites per octahedron as shown in Fig. 5. Each f.c.c. lattice point is surrounded by eight tetrahedral sites and six octahedral sites, the latter along the $\pm x$, $\pm y$ and $\pm z$ directions. To generate a simple polyhedron with 24 vertices (14 faces) surrounding a lattice point, 16 additional vertices must be added to the tetrahedral sites. This means selecting one each of each of the three sets of four possible tetrahedral sites per octahedral site in such a way that an appropriate polyhedron is generated. Two examples
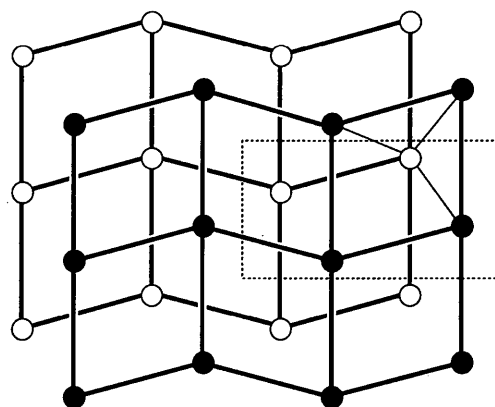

(a)

(b)

Fig. 3. (a) The positions of sphere centers in (101) layers of the I (b.c.t.) 10-coordinated sphere packing. In this projection, there are five positions for the layers. (b) The c.c.o. 10-coordinated sphere packing as a two-layer stacking of the same layers. The view is along c of the $Cmcm$ unit cell (b horizontal) and the two layers differ in elevation by $c/2$. Lighter lines connect one point to its nearest neighbors in an adjacent layer.

Fig. 4. The positions of sphere centers in (010) layers of the O 10-coordinated sphere packing. A unit cell is outlined (a is horizontal). The two layers differ in elevation by $b/2$ and lighter lines connect one point to its nearest neighbors in an adjacent layer.
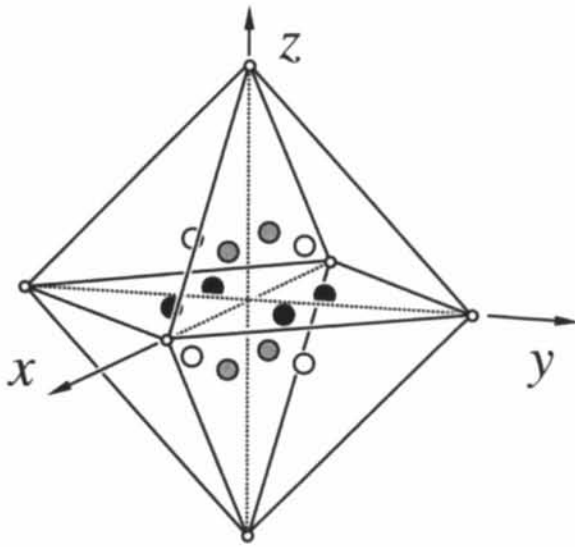
Fig. 5. The three sets of four tetrahedral sites derived from subdivision of an octahedron.

of the procedure are shown in Fig. 6. In the first case, all six sets of four sites in planes normal to **z** are chosen. The polyhedron is topologically equivalent to the Kelvin polyhedron (truncated octahedron) and is labeled K.

To help in identifying polyhedra, they are assigned a code $pqr(s)$. In this code, p, q and r are the numbers of selected sets of four tetrahedral sites normal to **z**, **x** and **y**, respectively, and s is the number of quadrangular faces of the polyhedron (all polyhedra have only four-, five- and six-sided faces; the number of five-sided faces is $12 - 2s$ and the number of six-sided faces is $2 + s$). The code for the Kelvin polyhedron is 600(6). The second example in Fig. 6 has a code 420(2). This is in fact the second of two space-filling polyhedra described by Williams (1968) so it is labeled W_2 (Williams called it the β-tetrakaidecahedron).

There are two sequences of polyhedra that can be generated in this way (Fig. 7). In the first sequence, the two sets of four tetrahedral sites normal to **z** in the $\pm z$ directions are selected and the labels x and y are arbi-
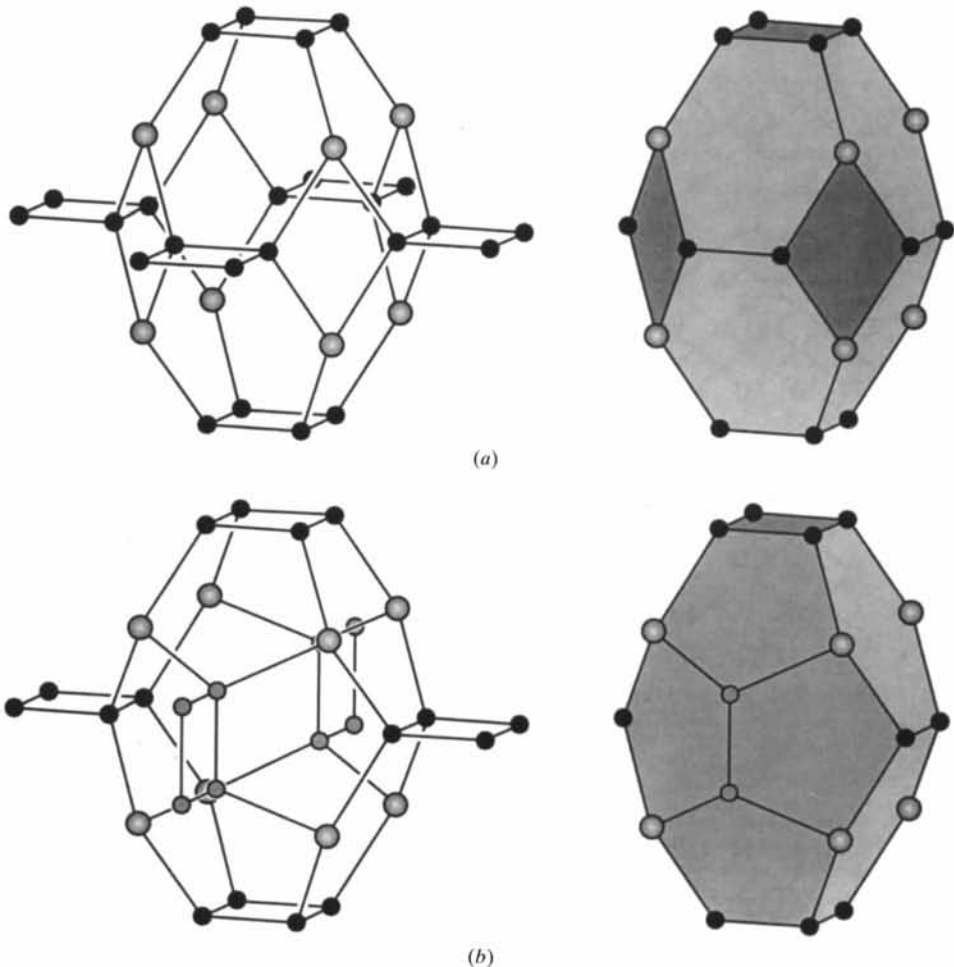

(a)

(b)

Fig. 6. Two space-filling polyhedra derived by the procedure described in the text. (a) The K polyhedron, (b) the W_2 polyhedron.

trary. In the second sequence, the set normal to **z** in the +z direction and the set normal to **y** in the +y direction are chosen. The requirement of 14 faces per polyhedron limits the possibilities to those shown in Fig. 8. As far as I can determine, only five of these polyhedra are space filling, and those that do not appear to be space filling are labeled X. It seems possible that a proof that a polyhedron does not fill space could be difficult, but it is noted that the space-filling possibilities identified are all those that have a zero in the code (see Fig. 7).

K and W_2 are described above. W_1 was also illustrated by Williams (1968). The polyhedron labeled O I have not found discussed before but, as shown below, it does fill space. The polyhedron labeled K' was described by Weaire & Phelan (1994b), who called it a 'twisted Kelvin cell'; it was also identified as a space filler by Aste et al. (1996). It turns out that it corresponds to the Voronoi polyhedron of r and l layers of the (10+4)-coordinated t.p. sphere packings described above.

K 600(6) O_h W_1 510(4) C_{2v} X 411(3) C_{2v}

W_2 420(2) D_{2h} X 321(2) C_{2v} X 222(2) D_{4h}

O 420(4) C_s K' 330(4) D_2 X 321(2) C_s

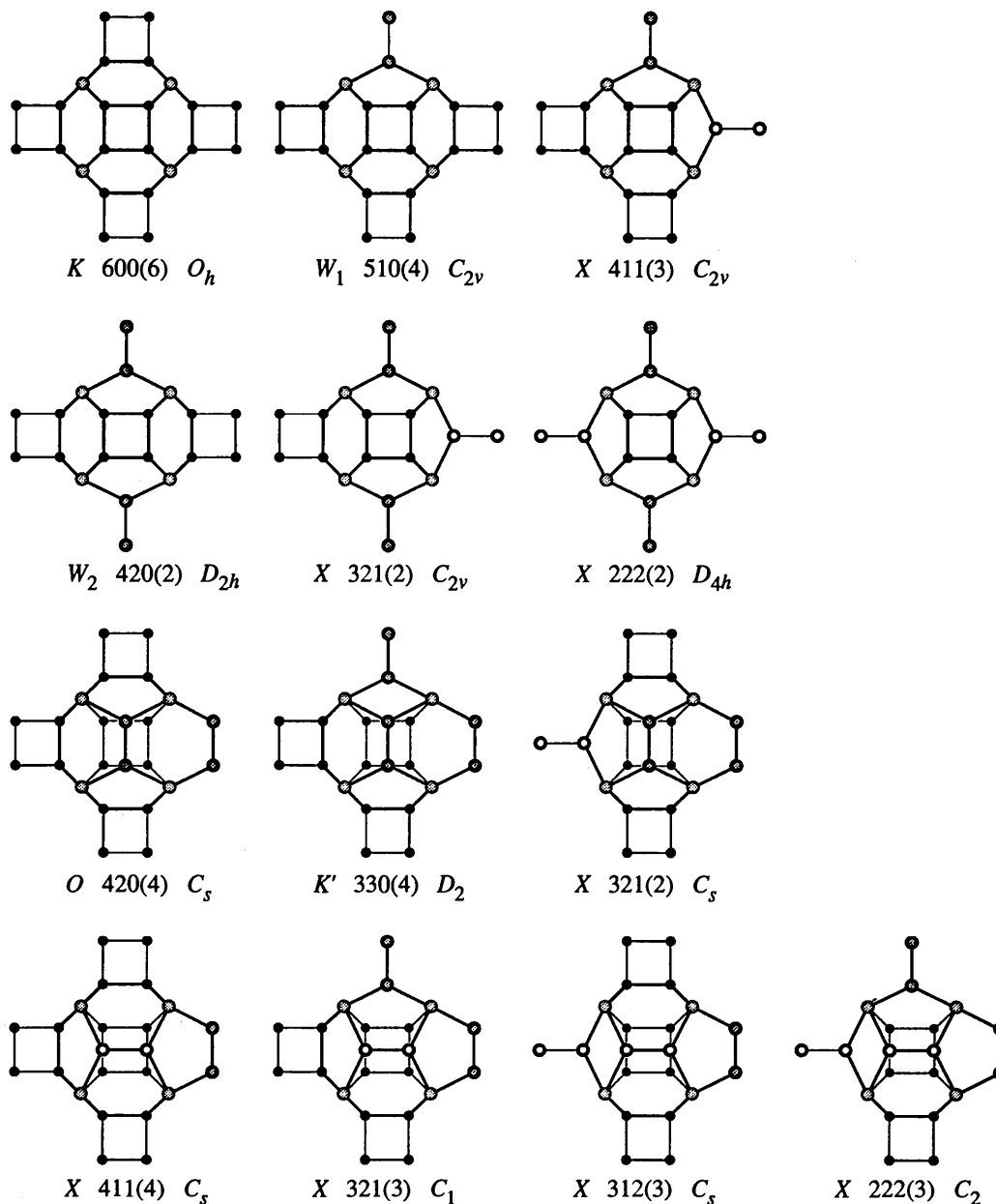X 411(4) C_s X 321(3) C_1 X 312(3) C_s X 222(3) C_2

Fig. 7. The 14-face polyhedra obtained from c.c.p. The eight tetrahedral holes around a central sphere are shown as larger circles and one of the three sets of tetrahedral sites (smaller circles) surrounding an octahedral hole has been selected. Underneath each diagram is a letter symbol used as a name, a numerical code described in the text and the symmetry of the polyhedron.

It might be noted that only a small subset of possible 14-face polyhedra with four-, five- and six-sided faces and 24 vertices appears in Fig. 7. A notable omission is the 'Goldberg' polyhedron, with two six-sided and twelve five-sided faces, that is a conspicuous feature of many clathrate structures. However, it is known that this polyhedron does not fill space (Aste *et al.*, 1996). It would seem to be rash to speculate that other space-filling polyhedra will not be identified, although it is reassuring that the polyhedra corresponding to the t.p. sphere packings described above are all recovered.

5. Space-filling polyhedron packings

Structures derived by packing the polyhedra of the previous section are described next. Coordinates for conformations of the structures with unit edge and with the volume maximized subject to that constraint are given subsequently.

K. The Kelvin (sodalite) structure of packing truncated octahedra is well known (see *e.g.* OKH, p. 316) and not directly illustrated here.

W_1. The W_1 polyhedra pack to form rectangular layers with layer symmetry *cmm*2 (translations along **a** and **b** normal to the 2 axis in the *z* direction, see *e.g.*
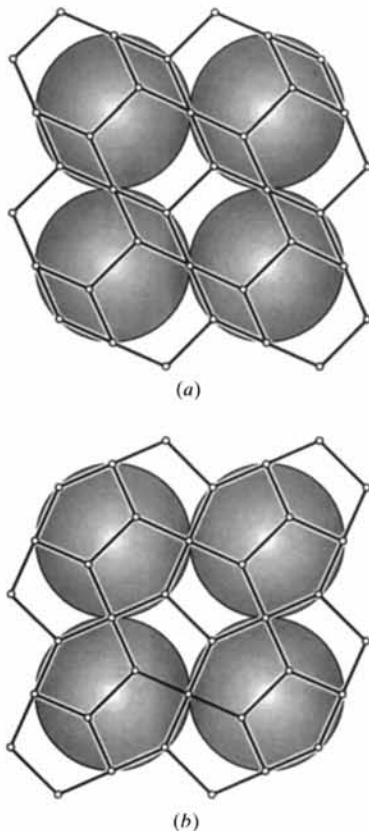

(a)

(b)

Fig. 8. Part of a layer of W_1 polyhedra. (a) and (b) show the same four polyhedra viewed from opposite sides.

OKH, p. 381 for layer group symmetry). A part of such a layer is shown in Fig. 8. The layer is polar and, in the space-filling packing, pairs of layers of alternating polarity are combined together and then pairs of such double layers are rotated by 90° to produce a centrosymmetric four-layer structure of symmetry $P4_2/ncm$. In the polyhedron packing, the layers are metrically square and the arrangement of the centers of the polyhedra corresponds to a body-centered tetragonal lattice with $c/a > 2^{1/2}$. As explained above, this is not a t.p. structure. The stacking sequence of the polyhedron packing is symbolized $\overrightarrow{W_1} \cdot \overleftarrow{W_1} \ldots$ with arrows indicating the direction of the polar direction of the layers.

W_2. The corresponding layers of W_2 polyhedra look like the lower half of Fig. 8 and the layers have a mirror plane containing the translations (layer symmetry *cmmm*). Alternate layers in the three-dimensional stacking are related by a rotation of 90° to produce a two-layer stacking W_2 with symmetry $P4_2/mnm$. The corresponding sphere packing is again b.c.t., and again the 4-connected net cannot be derived as the dual of a sphere packing.

Intergrowth structures can be formed by interleaving K, W_1 and W_2 layers. The K and W_2 layers will be sandwiched between W_1 layers in sequences $\overrightarrow{W_1} \cdot K \cdot \overleftarrow{W_1} \ldots$ and $\overrightarrow{W_1} \cdot W_2 \cdot \overleftarrow{W_1} \ldots$. The K polyhedron will be distorted from cubic symmetry to a shape similar to that shown in Fig. 6.

O. The *O* polyhedra pack to form rectangular layers, with mirror symmetry in the middle of the layer, of symmetry $p2_1am$ and with polyhedra in two orientations in the layer as shown in Fig. 9. Stacking these layers related by a 2_1 axis in the *z* direction produces a structure with symmetry *Pnam* (*Pnma* in the standard setting). This packing is derived as the dual of the *O* (10+4)-coordinated sphere packing described above.

Perhaps less obvious is that a layer consisting of half K polyhedra and half W_2 polyhedra can intergrow with a layer of *O* polyhedra to produce a structure labeled $KW_2 + 2O$. This *O* layer is different from the layer in the *O*-only packing of the previous paragraph and in fact both layers are oblique as shown in Fig. 10. The
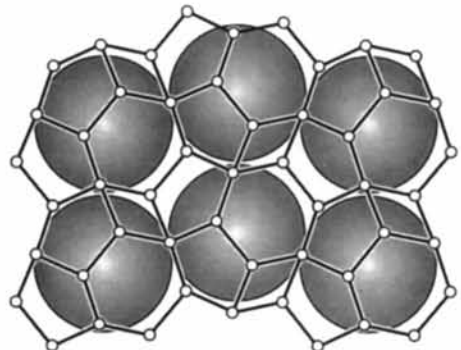

Fig. 9. Part of a layer of *O* polyhedra and the encapsulated spheres.

layers have symmetry $p112/m$ and that of the resulting structure is monoclinic, $P2/m$. Coordinates for this structure are given below.

K'. The last group of structures to be considered are the duals of the (10+4)-coordinated sphere packings derived from stackings of 3^6 layers and involve the K and K' polyhedra. The polyhedron packings consist of hexagonal or pseudo-hexagonal layers of polyhedra encapsulating spheres forming 3^6 layers as shown in Fig. 11. The K' polyhedra are chiral and left (right) forms occur in the l (r) layers of the sphere packing. The possibilities with all polyhedra related by symmetry are labeled K'_D, K'_Q and K'_{DQ}, corresponding to the D, Q and DQ packings.

The rs and $rsls$ packings of two kinds of sphere described above correspond to alternating layers of K and K' polyhedra.

A packing of K polyhedra corresponds to an s layer of the sphere packing. Packing only K polyhedra in the I structure produces a tetragonally distorted version of the sodalite structure (Fig. 11). In the tetragonal ($I4/mmm$) structure, the vertices are of two kinds: four

in $4(d)$: $0, \frac{1}{2}, \frac{1}{4}$ etc. and eight in $8(j)$: $x, \frac{1}{2}, 0$ etc. with $x \approx 0.25$. It is interesting that in $BaPd_2P_4$ (Johrendt & Mewis, 1994) the Ba atoms have the I (b.c.t.) packing with $c/a = 0.87$ [cf. $c/a = 0.816...$ for the (10+4)-coordinated sphere packing] and Pd and P ($x = 0.27$) are in the tetrahedra forming together a tetragonally distorted Kelvin structure. $BaNi_2P_4$ has the same structure (Keimes et al., 1995).

A structure of all K' polyhedra has also been found in chemistry (cf. OKH, p. 334). The Ba atoms in $BaCu_2P_4$ are in the D sphere packing and the Cu and P atoms are at the vertices of the twisted Kelvin polyhedra (compare with $BaPd_2P_4$ discussed above). Indeed, the original (Dünner & Mewis, 1990) illustration of the structure looks not unlike a fragment of a foam of uniform bubbles.

6. Shell structures (coordination sequences)

The shell structure of foams of congruent bubbles is of interest (Aste et al., 1996). A central bubble shares faces with 14 other bubbles. These in turn share faces with n_2 other bubbles and so on – notice that each bubble is counted only once. The sequence of n_k's is the coordination sequence. The cumulative number of bubbles within a topological distance k from a central one is c_k;
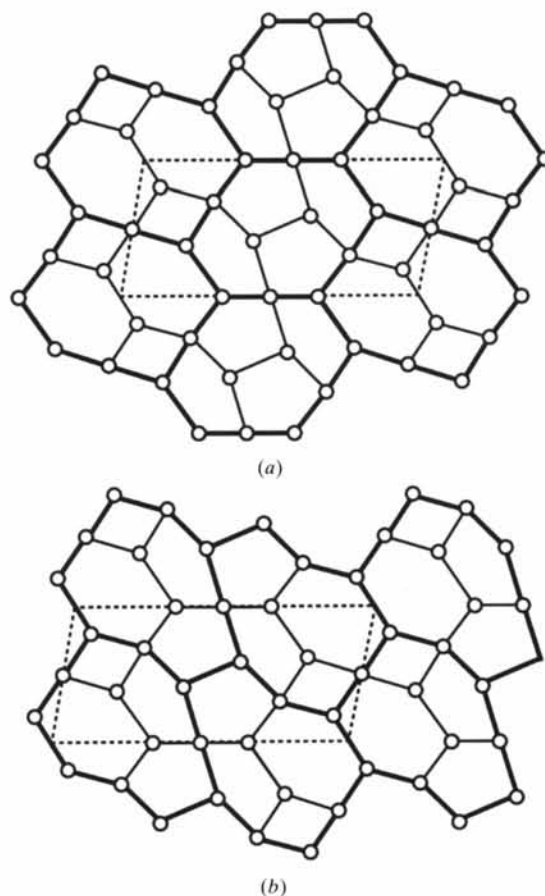

(a)

(b)

Fig. 10. Layers in the $KW_2 + 2O$ structure projected on (010). (a) The $K + W_2$ layer with centers at $y = 0$. (b) The O layer with centers at $y = 1/2$.
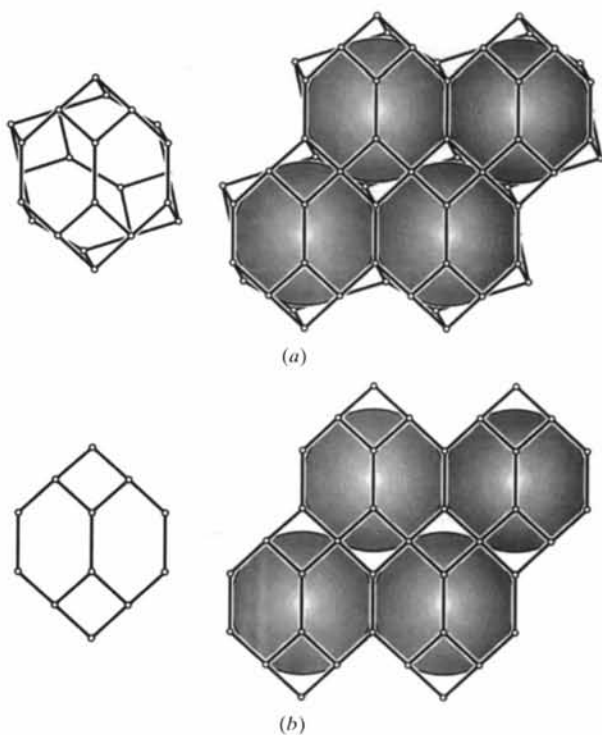

(a)

(b)

Fig. 11. (a) Left: a K' polyhedron; right: part of a (100) layer of the Q structure showing close-packed spheres (large circles) and the encapsulating K' cells. (b) Left: a distorted version of the K polyhedron; right: part of a (100) layer of the I structure showing close-packed spheres (large circles) and the encapsulating K cells.

Table 1. *Shell structure (coordination sequence) of polyhedra in various foams (polyhedron packings)*

n_k is the number of topological neighbors in the kth shell. $\lfloor\ldots\rfloor$ signifies truncation of the fractional part (round down) of a non-integral number. ρ_∞ is the topological density described in the text.

Foam	n_1	n_2	n_3	Equation	Conditions	ρ_∞
K	14	50	110	$12k^2 + 2$	$k > 0$	4.0
K'_D	14	52	114	$\lfloor 25k^2/2\rfloor + 2$	$k > 0$	4.167
K'_{DQ}	14	52	115	$\lfloor 101k^2/8\rfloor + 2$	$k > 0$	4.208
K'_Q	14	52	116	$\lfloor 38k^2/3\rfloor + 2$	$k > 0$	4.222
O	14	52	116	$\lfloor 38k^2/3\rfloor + 2$	$k > 0$	4.222
W_1	14	52	120	$14k^3 - 6$	$k > 2$	4.667
W_2	14	54	124	$14k^2 - 2$	$k > 1$	4.667

it is just the sum of all the n_k's. Coordination sequences for nets and lattices in three dimensions can often be expressed in terms of expressions quadratic in k (O'Keeffe, 1995; O'Keeffe & S. T. Hyde, 1996) and the coordination sequence for the Kelvin structure is the same as for the b.c.c. structure if all (8+6) neighbors are counted. In this case, one has simply $n_k = 12k^2 + 2$. For the structures studied here, coordination sequences were counted (typically for $k \leq 50$) and equations found empirically. In every case, a single expression could be used for every k with the help of the 'round down' function as shown in Table 1. A useful measure of topological density, ρ_∞, is the limit of c_k/k^3 as $k \to \infty$ (O'Keeffe, 1991). This is just $a/3$ where a is the coefficient of the quadratic term in the expression for n_k. For the structures with one kind of bubble described here, ρ_∞ varies from 4 to $14/3 = 4.66\ldots$. Notice that the Kelvin structure is the least dense (has the fewest topological neighbors) and is the only 14-coordinated packing that corresponds to a lattice. A similar situation holds for the 12-coordinated closest packings for which the f.c.c. lattice packing has the lowest topological density (O'Keeffe, 1995; Conway & Sloane, 1997).

Remarkably, the topological density of foams that are duals of the Frank–Kasper phases are significantly higher (Grosse-Kunstleve et al., 1996) even though they have lower coordination numbers. Thus, for the type I clathrate structure (dual of the A15 structure), with average coordination number 13.5, $\rho_\infty = 187/36 = 5.19\ldots$ and for the type II hydrate structure (dual of the C15 structure), with average coordination number 13.33, $\rho_\infty = 2371/432 = 5.48\ldots$. It should be of interest to correlate these topological densities with other properties of foams.

7. Coordinates for nets

Here coordinates are given for nets identified by the space-filling polyhedron as in the text above. The first seven are for structures formed by space fillings of congruent polyhedra and the last is an example of a structure formed by a combination of different polyhedra. Free parameters are determined by fixing all edge lengths equal to unity, and then (approximately)

maximizing the volume subject to this constraint. The origin is always taken at a center of symmetry if present – note, in particular, this is 'origin choice 2' for *Fddd* and *P4₂/ncm* in *International Tables for Crystallography* (Hahn, 1983). The vertices of the 4-connected net are characterized by a vertex symbol (O'Keeffe, 1991) in which the six numbers specify the size of the rings (the number of edges in polyhedron faces in this instance) meeting at the vertex, with pairs of opposite angles appearing sequentially.

K: $Im\bar{3}m$, $a = 2.8284$ Å
$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $12(d)$: $\frac{1}{4}, 0, \frac{1}{2}$ etc.

W_2: $P4_2/mnm$, $a = 2.328$, $c = 3.868$ Å
$5 \cdot 5 \cdot 5 \cdot 5 \cdot 6 \cdot 6$ in $4(d)$: $0, \frac{1}{2}, \frac{1}{4}$ etc.
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 5 \cdot 6$ in $8(j)$: x, x, z etc., $x = 0.1519$, $z = 0.1293$.

W_1 ($\overleftarrow{W_1} \cdot \overrightarrow{W_1}$): $P4_2/ncm$, $a = 2.310$, $c = 7.856$ Å
$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $4(a)$: $\frac{3}{4}, \frac{1}{4}, 0$ etc.
$5 \cdot 5 \cdot 5 \cdot 5 \cdot 6 \cdot 6$ in $4(b)$: $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$ etc.
$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $8(i)$: x, x, z etc., $x = 0.0970$, $z = 0.0614$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 5 \cdot 6$ in $8(i)$: x, x, z etc., $x = 0.0970$, $z = 0.1886$.

O: $Pnma$, $a = 4.680$, $b = 3.707$, $c = 2.468$ Å
$4 \cdot 4 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $8(d)$: x, y, z etc., $x = 0.0577$, $y = 0.1151$, $z = 0.1231$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $8(d)$: x, y, z etc., $x = 0.1928$, $y = 0.1151$, $z = 0.4460$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $8(d)$: x, y, z etc., $x = 0.1315$, $y = 0.0$, $z = 0.7934$.

K'_Q: $P6_422$, $a = 2.462$, $c = 6.083$ Å
$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $3(a)$: $0, 0, 0$ etc.
$4 \cdot 4 \cdot 5 \cdot 5 \cdot 6 \cdot 6$ in $3(c)$: $\frac{1}{2}, 0, 0$ etc.
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $12(k)$: x, y, z; etc., $x = 0.2655$, $y = 0.3828$, $z = 0.4235$.

K'_D: $Fddd$, $a = 2.350$, $b = 4.521$, $c = 8.093$ Å
$4 \cdot 4 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $16(g)$: $\frac{1}{8}, \frac{1}{8}, z$; etc., $z = 0.5071$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $32(h)$: x, y, z; etc., $x = 0.3039$, $y = 0.1849$, $z = 0.3168$.

K'_{DQ}: $Fddd$, $a = 2.464$, $b = 4.259$, $c = 16.252$ Å
$4 \cdot 4 \cdot 5 \cdot 5 \cdot 6 \cdot 6$ in $8(a)$: $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$; etc.
$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $8(b)$: $\frac{1}{8}, \frac{1}{8}, \frac{5}{8}$; etc.
$4 \cdot 4 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $16(g)$: $\frac{1}{8}, \frac{1}{8}, z$; etc., $z = 0.5015$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $32(h)$: x, y, z; etc., $x = 0.125$, $y = 0.0076$, $z = 0.4088$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $32(h)$: x, y, z; etc., $x = 0.2966$, $y = 0.1877$, $z = 0.2163$.

$K + W_2 + 2O$: $P2/m$, $a = 4.800$, $b = 4.044$, $c = 2.197$ Å, $\beta = 99.87°$
$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $2(k)$: $0, \pm y, \frac{1}{2}$, $y = 0.2283$
$5 \cdot 5 \cdot 5 \cdot 5 \cdot 6 \cdot 6$ in $2(j)$: $\frac{1}{2}, \pm y, 0$, $y = 0.2822$
$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $4(o)$: x, y, z; etc., $x = 0.2579$, $y = 0.2627$, $z = 0.3015$

$4 \cdot 4 \cdot 6 \cdot 6 \cdot 6 \cdot 6$ in $4(o)$: x, y, z; etc., $x = 0.0709$, $y = 0.3764$, $z = 0.1955$

$4 \cdot 5 \cdot 5 \cdot 6 \cdot 5 \cdot 6$ in $4(o)$: x, y, z; etc., $x = 0.4115$, $y = 0.3764$, $z = 0.5916$

$4 \cdot 4 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $4(o)$: x, y, z; etc., $x = 0.1901$, $y = 0.1236$, $z = 0.6230$

$4 \cdot 5 \cdot 5 \cdot 6 \cdot 6 \cdot 6$ in $4(o)$: x, y, z; etc., $x = 0.3401$, $y = 0.1236$, $z = 0.0$.

References

Aste, T., Boosé, D. & Rivier, N. (1996). *Phys. Rev. E***53**, 6181–6191.

Charvolin, J. & Sadoc, J.-F. (1996). *Philos. Trans. R. Soc. London Ser. A*, **354**, 2173–2192.

Conway, J. H. & Sloane, N. J. A. (1988). *Sphere Packings, Lattices and Groups.* New York: Springer-Verlag.

Conway, J. H. & Sloane, N. J. A. (1994). *J. Number Theory*, **48**, 373–382.

Conway, J. H. & Sloane, N. J. A. (1997). *Proc. R. Soc. London Ser. A*, **53**, 2369–2389.

Dünner, J. & Mewis, A. (1990). *J. Alloys Compds*, **167**, 127–134.

Fischer, W. & Koch, E. (1983). *International Tables for Crystallography*, Vol. A, edited by Th. Hahn, ch. 14. Dordrecht: Kluwer.

Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184–190.

Frank, F. C. & Kasper, J. S. (1959). *Acta Cryst.* **12**, 483–499.

Grosse-Kunstleve, R. W., Brunner, G. O. & Sloane, N. J. A. (1996). *Acta Cryst.* A**52**, 879–889.

Hahn, Th. (1983). Editor. *International Tables for Crystallography*, Vol. A. Dordrecht: Kluwer.

Hellner, E. (1986). *Z. Kristallogr.* **175**, 227–248.

Johrendt, D. & Mewis, A. (1994). *J. Alloys Compds*, **205**, 183–189.

Keimes, V., Johrendt, D. & Mewis, A. (1995). *Z. Anorg. Allg. Chem.* **621**, 925–930.

Koch, E. & Fischer, W. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 654–659. Dordrecht: Kluwer.

Kusner, R. (1992). *Proc. R. Soc. London Ser. A*, **439**, 683–686.

Kusner, R. & Sullivan, J. M. (1996). *Forma*, **11**, 233.

O'Keeffe, M. (1991). *Z. Kristallogr.* **196**, 21–37.

O'Keeffe, M. (1995). *Z. Kristallogr.* **210**, 905–908.

O'Keeffe, M. & Hyde, B. G. (1996). *Crystal Structures I: Patterns and Symmetry.* Washington, DC: Mineralogical Society of America.

O'Keeffe, M. & Hyde, S. T. (1996). *Z. Kristallogr.* **211**, 73–78.

Pearson, W. B. (1972). *The Crystal Chemistry and Physics of Metals and Alloys.* New York: Wiley.

Pearson, W. B. (1985). *J. Solid State Chem.* **56**, 278–287.

Rivier, N. & Aste, T. (1996). *Philos. Trans. R. Soc. London Ser. A*, **354**, 2055–2069.

Sadoc, J.-F. & Mosseri, R. (1996). *Frustration Géométrique.* Paris: Editions Eyrolle.

Shoemaker, D. P. & Shoemaker, C. B. (1986). *Acta Cryst.* B**42**, 3–11.

Sommerville, D. M. Y. (1923). *Proc. Edinburgh Math. Soc.* **41**, 49–57.

Weaire, D. (1997). Editor. *The Kelvin Problem.* London: Taylor and Francis.

Weaire, D. & Phelan, R. (1994a). *Philos. Mag. Lett.* **69**, 107.

Weaire, D. & Phelan, R. (1994b). *Philos. Mag. Lett.* **70**, 345.

Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed. Oxford: Clarendon Press.

Wells, A. F. & Chamberland, B. L. (1987). *J. Solid State Chem.* **66**, 26–39.

Williams, R. E. (1968). *Science*, **161**, 276–277.