A dense non-crystallographic packing of equal spheres. By A. L. MACKAY, *Birkbeck College Crystallographic Laboratory*, 21, *Torrington Square, London, W. C.* 1. *England*

In a cubic close-packed (c.c.p.) assembly of equal spheres each sphere is surrounded by its first coordination polyhedron which consists of 12 spheres at the vertices of a cuboctahedron. A second layer of spheres packed over the first layer is found to require 42 spheres and in general the nth layer consists of $(10n^2 + 2)$ spheres.
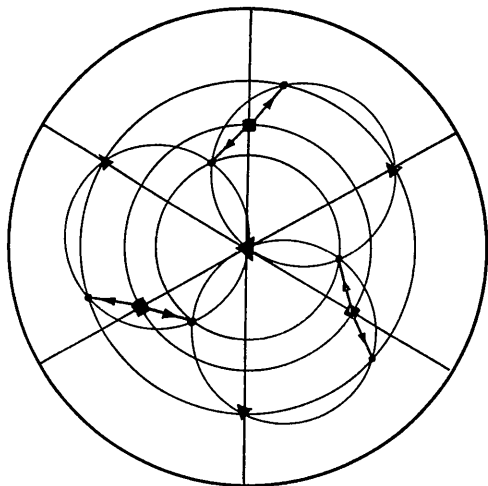

Fig. 1. Stereogram showing the transformation of a cuboctahedron to a regular icosahedron. The square faces (■) become rhombs and split each into two equilateral triangles (●). The triangular faces (▲) remain unchanged. The upper hemisphere only is shown but the remaining faces can be generated by inversion in the centre.
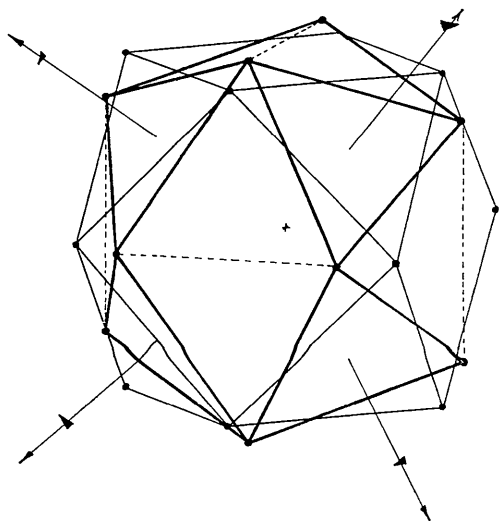

Fig. 2. Illustration of the process by which a cuboctahedron of 12 rigid rods, freely jointed at their ends, (thin lines) can be moved by rotations of its triangular faces about their normals to give a regular icosahedron (thick lines and dotted lines). In the course of the movement each joint moves in towards the centre.

R. Buckminster Fuller (private communication, 1962) has pointed out that a cuboctahedron (a 'vector equilibrium' in his notation), outlined by rigid rods jointed at the 12 vertices, can be distorted into a regular icosahedron (and further into an octahedron) the distances from the vertices to the centre contracting uniformly by 5%. Each of the square faces splits into two equilateral triangles. This process is shown stereographically in Fig. 1 and orthographically in Fig. 2. The same transformation can be performed with a cuboctahedron of 12 spheres, either surrounding a cavity or surrounding a thirteenth sphere; in the latter case no radial contraction takes place.

The coordination polyhedron about each sphere in a hexagonal close-packed (h.c.p.) array can be referred to as a twinned cuboctahedron (*TCO*). It is obtained by halving a cuboctahedron with a plane parallel to a triangular face and rejoining the halves after a rotation of 60°. If the two triangular faces of a *TCO* perpendicular to the triad axis are rotated in their own planes in opposite senses about this triad axis by 60° relative to each other a regular icosahedron is also obtained.

Suppose an icosahedron of 12 spheres about a central sphere is surrounded by a second icosahedral shell
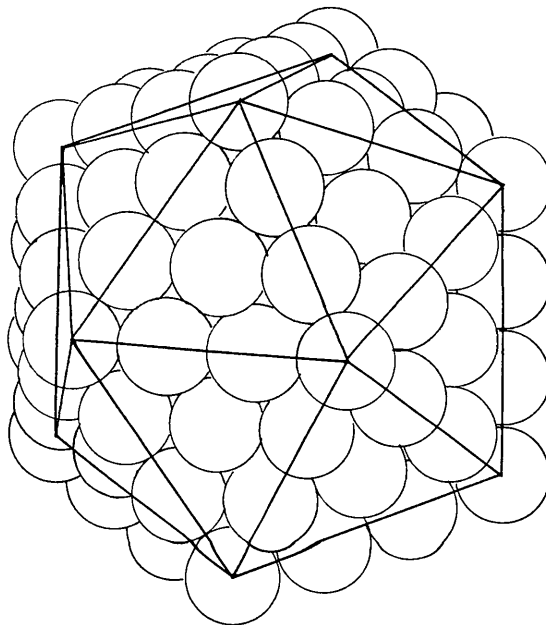

Fig. 3. The icosahedral packing of equal spheres. The third layer ($n=3$) is shown. On each triangular face the layers of spheres succeed each other in cubic close-packing sequence. Each sphere (not on an edge or vertex) touches only 6 neighbours, 3 above and 3 below and is separated by a distance of 5% of its radius from its 6 neighbours in the plane of the face of the icosahedron. The whole assembly of spheres can be distorted by the movement described in Figs. 1 and 2 to cubic close packing in the form of a cuboctahedron.

exactly twice the size of the first. This shell will contain 42 spheres and will lie over the first so that spheres will be in contact along the five-fold axes. As the vertex-centre-vertex angle in an icosahedron is approximately $63° 26'$ the spheres will not be close-packed in the faces of the icosahedron but will be spaced out at intervals of 1.05146 times their diameters. Further layers can be added in the same fashion there being $(10n^2 + 2)$ spheres in the nth shell as for the cuboctahedron (Fig. 3). The whole assembly can be transformed to cubic close-packing from this icosahedral shell packing (i.s.p.) by the same rotation mechanism as that which transforms the icosahedron to the cuboctahedron and vice versa. The packing density of the i.s.p. must therefore be close to that of the c.c.p. (0.74048) and, in view of the non-crystallographic nature of the i.s.p. packing, it is of interest to calculate it.
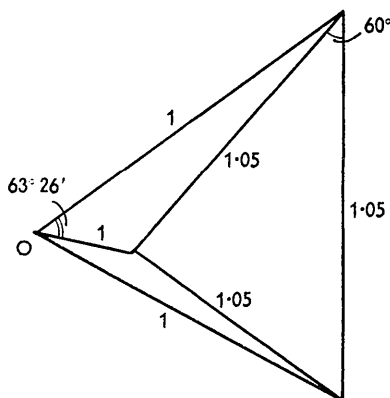

Fig. 4. The distorted tetrahedron, 20 of which make up an icosahedron. The vertex 0 is at its centre.

The unit which occurs repeatedly in the structure is a distorted tetrahedron which is one twentieth of an icosahedron (Fig. 4). The three edges meeting at the icosahedron centre are of unit length and the other three are extended to 1.05146. If a unit sphere is placed at each vertex the fraction of the distorted tetrahedron filled is 0.72585 (as compared with 0.7797 for a regular tetrahedron). The hope of attaining a packing density of 0.74048 with such units (interspersed with octahedral interstices which are still more open) is therefore vain.

In i.s.p. there are three kinds of positions; spheres may lie on vertices, on edges or in the faces of the icosahedral shells. In the nth shell there are 12 spheres of the first kind, $30(n-1)$ of the second kind and $10(n^2 - 3n + 2)$ of the third. All spheres are 12 coordinated, those at vertices in pentagonal prisms terminated by pyramids (pentagonal pyramidal prisms), those on edges in TCO and those on faces in cuboctahedra. These figures are not exactly regular. From the central sphere outwards the ratio of the numbers of octahedral to tetrahedral cavities increases from 0 towards 1/2. To count the number of spheres in an icosahedron of a given size the spheres in its surface must be divided between the inside and the outside. Using a simple counting system those at the vertices might be counted as 5/20 inside, those on edges as 2/5 inside and those on faces as 1/2 inside, but if the actual solid angles are calculated accurately, the corresponding correct values are 0.20965, 0.38386 and $1/2$ respectively. Thus an assembly of n icosahedral shells

about a central sphere contains $(10/3n^3 + 5n^2 + 11/3n + 1)$ spheres of which $C_n = 10/3n^3 + 0.15183n$ are within the icosahedron having a vertex-to-centre distance of n. The packing densities of spheres in assemblies of increasing size are given in Table 1. The packing density P_n is given by $P_n = \pi C_n/(6 \times n^3 \times 2.53615) = 0.68818 + 0.03767n^{-2}$. The densities have also been calculated for assemblies with the central cavity empty and these, of course, tend to the same limit but more slowly, there being a term in n^{-1}.

Table 1. *The packing densities of icosahedral packings with increasing numbers of shells*

P_n is the density with a central sphere and P_n' without such a sphere

$$P_n = C_n/n^3 \times 6 \times 2.53615$$
$$P_n' = (C_n - 1)/(n - 0.04894)^3 \times 6 \times 2.53615.$$

Shell number	Number of spheres in shell	Contents C_n	P_n (density)	P_n'
0	1	—	—	—
1	12	3.5158	0.72585	0.60378
2	42	27.032	0.69760	0.72362
3	92	90.547	0.69237	0.71935
4	162	214.063	0.69053	0.71317
5	252	417.579	0.68969	0.70864
6	362	721.095	0.68923	0.70539
7	492	1144.611	0.68895	0.70299
8	642	1708.126	0.68877	0.70116
9	812	2431.642	0.68865	0.69971
10	1002	3335.158	0.68856	0.69856
∞	—	—	0.68818	0.68818

It will be seen from Table 1 that the density of i.s.p. tends to a value of 0.68818 which is higher than that for body-centred cubic packing (0.68017) but lower than that for c.c.p. (0.74048) or body-centred tetragonal packing (0.69813) (*International Tables* II, p. 343). The limiting density can be found directly as follows: for large values of n the significance of edges and vertices will be small and the spheres in c.p. layers parallel to the faces will preponderate. These layers are dilated by a factor of $d = 1.05146$ in the planes of the faces which enlarges the interstices. This enables adjacent layers to fit more closely together, the interplanar spacing being reduced by $(3 - d^2)^{1/2}2^{-1/2}$. This leads to a multiplier of 0.92937 which must be applied to the c.c.p. density of 0.74048 to give the resulting density of 0.68818 as before.

What has been described is an assembly of spheres which has the symmetry of the icosahedral point group. It has a unique centre which could be located from any point in the assembly by following a suitable algorithm. The assembly is not a lattice (although it has lattice-like properties) as the spheres do not all have identical environments, but coordinates could be given for every sphere by a general rule. At large distances from the centre the assembly approximates to a c.c.p. structure uniaxially dilated in directions in a (111) plane which has undergone twinning by reflexion on the other {111} planes which are no longer perpendicular to three-fold axes.

The possibility of the natural occurrence of icosahedral shell packing might be considered but there are several reasons which make it unlikely that large numbers of atoms might be found arranged in this way:

(a) The density is less than that of c.c.p. and the possibility of a transition to the latter structure is thus likely as the simplicity of the transition mechanism has been demonstrated above. Each sphere (in a face) makes only 6 contacts with the 12 neighbours in its first co-ordination sphere and the spread of a displacement is facilitated.

(b) As n increases the ratio of pentagonal pyramidal prism to cuboctahedron coordination decreases. The chemical properties of the assembly would thus also have to change with n.

(c) The layers parallel to icosahedron faces are in a cubic stacking sequence. The energy for hexagonally stacked additions might be almost identical and any such stacking fault would prevent the icosahedral packing from continuing. It is possible that the inclusion of a small atom with a decided preference for icosahedral coordination might stabilize a nucleus from which a normally cubic material might grow.

J. D. Bernal (private communication, 1960) has pointed to the existence of a class of hierarchic structures, indefinitely extended in three dimensions, which are non-lattice packings. The unit of packing is the arrangement of 13 spheres as an icosahedron making a quasi-spherical unit, 13 of which are packed together to make a quasi-sphere of the next order. Tetrahedral units are used to pack the interstices and as all smaller units are available for packing the interstices between larger units it is difficult to give simple rules for this packing. However, there is a clear relationship between the early stages of such a hierarchy and the packing described above. Counting the central sphere as the zeroth layer, the first three layers of Bernal's structure are the same as in the i.s.p. described above. Looking at the packing of the layers parallel to the faces of the core icosahedron the stacking sequence is $ABCA$ (that is, c.c.p.). If the fourth layer were B as in i.s.p. then the coordination about the spheres on the five-fold axes in the layer below (third layer) would be pentagonal pyramidal prisms, but if the fourth layer were C (stacking fault in hexagonal sequence) and spheres were also placed on the five-fold axis as before then 12 icosahedra (each of 13 spheres) would appear round the first icosahedron with a tetrahedron of 4 spheres filling each cavity between 4 icosahedra. The resulting solid of 279 spheres is thus the second-order icosahedral unit described by Bernal. The outside shell is not close packed (i.s.p. would have 309 spheres instead of 279) and, on attempting to pack these large units together, description of the exact position of each atom becomes very difficult. It is improbable that the density can be kept up even to the value of 0·68818.

Crystal data for some 5α-pregnane »ol-ones«.
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Crystal data for seven 5α-pregnane 'ol-ones' have been determined from goniostat-collected reciprocal lattice measurements using Cu Kα radiation. Space groups were deduced from systematic absences and the fact that these compounds are optically active.

The number of molecules per unit cell was calculated in the usual way using floatation density measurements, assuming no solvent of crystallization. That solvent of crystallization (probably alcohol) is sometimes present in crystals of 5α-pregnane compounds, however, is indicated by the discrepancies between the calculated and measured densities.

The crystal data obtained are given in Table 1.

Table 1. *Crystal data*

	1.	2.	3.	4.	5.	6.	7.
Formula	$C_{21}H_{34}O_2$	$C_{21}H_{32}O_3$	$C_{21}H_{32}O_3$	$C_{21}H_{30}O_5$	$C_{21}H_{32}O_5$	$C_{21}H_{34}O_5$	$C_{21}H_{34}O_5$
Molecular wt.	318·48	332·5	332·5	362·45	364·47	366·48	366·48
(g.cm.$^{-3}$, meas.)	1·100	1·208	1·171	1·185	1·154	1·205	1·198
(g.cm.$^{-3}$, calc.)	1·061	1·206	1·173	0·991	1·041	1·278	1·214
Z	4	4	4	2	4	4	8
Space group	$P2_1$	$P2_122$	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)*	13·485	10·667	17·546	16·525	11·545	12·539	14·061
b (Å)*	12·385	23·447	7·502	7·504	25·523	12·830	23·468
c (Å)*	12·114	7·320	14·637	9·820	8·447	11·686	11·995
β	99·88°	—	102·63°	94·50°	110·96°	—	—
V (Å³)	1993	1831	1880	1214	2324	1880	3958
Solvent	ethanol	ethanol	ethanol	ethanol	ethanol	ethanol	toluene

1. 5α—pregnane—3β—ol—20—one
2. 5α—pregnane—11α—ol—3, 20—dione
3. 5α—pregnane—3β—ol—11, 20—dione
4. 5α—pregnane—17α, 21—diol—3, 11, 20—trione
5. 5α—pregnane—3β, 17α, 21—triol—11, 20—dione
6. 5α—pregnane—3α, 11β, 17α, 21—tetrol—20—one
7. 5α—pregnane—3β, 11β, 17α, 21—tetrol—20—one

* ±0·004 Å.