

Rod Packings and Crystal Chemistry

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Some crystallographic packings of identical infinite cylinders are described. It is shown how certain crystal structures are related to these packings when the cylinders are replaced by rods of atoms or groups of atoms (coordination polyhedra). Emphasis is placed on the densest cubic rod packing and structures based on this principle, which include garnet, Th_3P_4 , $\beta\text{-Mn}$, Ag_4RbI_5 and bixbyite.

Introduction

One of the oldest, and most fruitful, ideas in crystal chemistry is to consider crystal structures as derived from sphere packings. Many simple crystal structures can be described as having one or more sets of ions arranged as in hexagonal or cubic closest sphere packing. More complex structures do not lend themselves to description in this way so alternative descriptions, e.g. in terms of connected coordination polyhedra, are invoked.

In our search for unifying principles that simplify the description of crystal structures and the relationships between them (Hyde, Bagshaw, Andersson & O'Keeffe, 1974) we have found that many crystal structures, including some common ones that have resisted simple description before, are naturally and simply described in terms of what we call rod packings. In its simplest form a rod packing is a crystallographic (in the sense of having the symmetry properties of one of the crystallographic space groups) packing of uniform cylinders. In this paper we describe some of the simpler of these packings and illustrate their utility in describing crystal structure by application to some common structure types. References are given only for crystal structures not to be found in the compilations of Wyckoff (1963–1968) and Schubert (1964). In the application to real crystals the uniform cylinder is of course replaced by a generalized rod, *i.e.* any figure with a singular axis but without singular points or planes (Shubnikov & Koptsik, 1974); thus it may be a linear or zigzag chain of atoms or a rod of connected polyhedra (with or without other atoms at their centres).

Rod packings

We describe below some crystallographic packings of uniform cylinders. We restrict ourselves to those packings in which every cylinder is related to every other one by one or more of the operations of a crystallographic space group. In addition to the sym-

metry we record the density, defined as the fraction of space occupied by the cylinders. The position and orientation of the cylinders are defined by the equations of the cylinder axis conveniently given in parametric form. For example, an axis parallel to $[001]$ and passing through the point $0,0,0$ may be expressed by the equations $x=0$, $y=0$, $z=u$ or more simply written $0,0,u$. The positions of a set of rods in a packing will be expressed by a set of parametric equations of

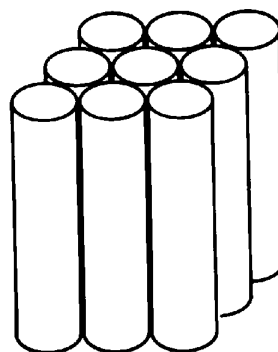


Fig. 1. Hexagonal (honeycomb) packing of parallel cylinders.

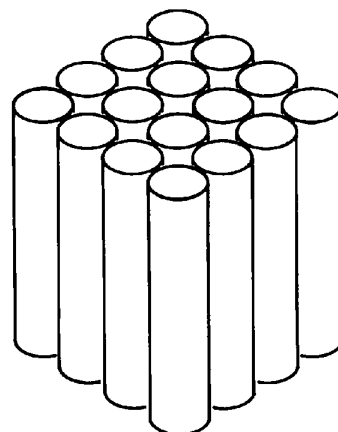


Fig. 2. Tetragonal packing of parallel cylinders.

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this sort involving one parameter and thus may conveniently be considered as derived from one of the univariant sets of equivalent positions (lattice complexes) of the space groups. These also are given in the notation of *International Tables for X-ray Crystallography* (1965). Not all univariant lattice complexes correspond in this way to a set of cylinder axes; in most instances they correspond instead to a set of intersecting lines whereas cylinder axes must of course be non-intersecting.

Packings of cylindrical rods with parallel axes is formally the same problem as that of circle coverings in a plane and as such has been discussed (Niggli, 1926, 1928). We describe just the two simplest packings here.

(i) Fig. 1. The densest packing of cylindrical rods is the familiar honeycomb packing. Not surprisingly it is of frequent occurrence in crystal structures, a few examples of which are given later. The symmetry is $P6/mmm$ with one rod, equations $0,0,u$ corresponding to positions $2(e)$, in the unit cell. The density is 0.9069.

(ii) Fig. 2. This corresponds to a simple square packing of rods and again occurs in many crystal

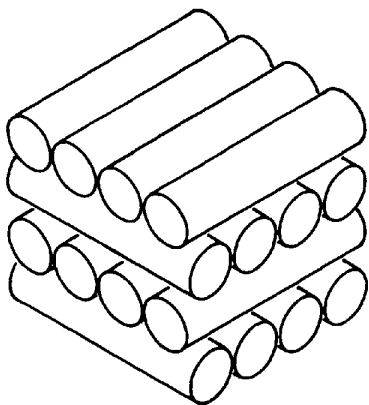


Fig. 3. Tetragonal layer packing of cylinders.

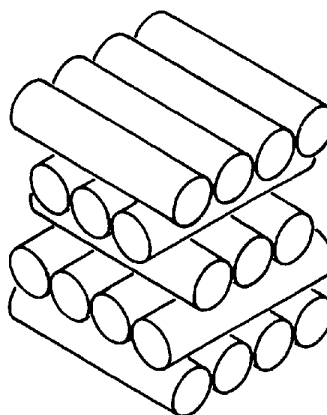


Fig. 5. Body-centred tetragonal layer packing of cylinders.

structures. The symmetry is $P4/mmm$ with one rod, equations $0,0,u$ corresponding to positions $2(g)$, in the unit cell. The packing density is 0.7854.

An example of this packing is the structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which contains strings of Cu atoms along $[001]$ with approximately square $(\text{H}_2\text{O})_2\text{Cl}_2$ groups normal to the strings (compare the Pt oxides discussed below).

In the next set of rod packings, not all rod axes are parallel but they lie in parallel planes. The densities of all these packings of uniform cylinders will be the same (0.7854) as for the packing of Fig. 2.

(iii) Fig. 3. The simplest two-layer packing. The symmetry is $P4_2/mmc$. There are two rods in the unit cell with equations $0,u,0$ and $u,0,\frac{1}{2}$ corresponding to positions $4(l)$. It is not common in crystal structures but an example is PtO (Fig. 4). The structures of many Pt compounds are characterized by strings of Pt atoms with a square arrangement of ligands normal to the rod axis and many compounds (including one-dimensional metallic conductors) are known with the rod axes parallel (Krogman, 1969). In PtO two such sets of rods at right angles may be seen. CaPt_2O_4 (Cahen,

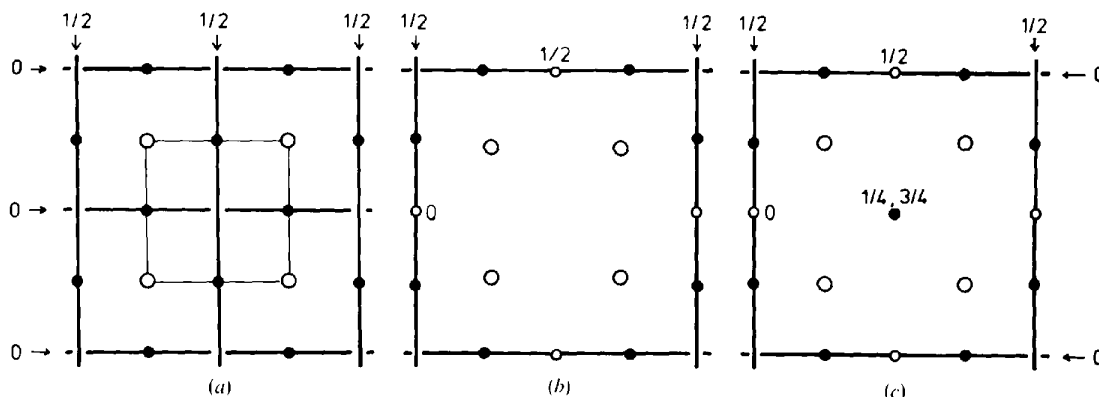


Fig. 4. (a) The structure of PtO projected on (001); (b) the structure of CaPt_2O_4 projected on (001): Ca atoms are the smaller open circles; (c) the structure of $\text{Na}_2\text{Pt}_3\text{O}_4$ projected on (001): smaller open circles are Na positions. In (a), (b) and (c) the larger open circles are O at $\frac{1}{2}, \frac{1}{2}$ and the filled circles are Pt.

Ibers & Mueller, 1974) provides another example, also with the same symmetry. As shown in Fig. 4, the Pt–O framework of the structure is derived from that of PtO by removing one half of the Pt rods of the latter.

(iv) Fig. 5. This is a four-layer tetragonal packing more common than the previous one. The symmetry is $I4_1/amd$. There are four rods in the unit cell with equations $0, u, 0$; $u, \frac{3}{4}, \frac{1}{4}$; $\frac{1}{2}, u, \frac{1}{2}$; and $u, \frac{1}{4}, \frac{3}{4}$. These may be considered as derived from positions $16(h)$ ($0, u, z$ etc.) with $z=0$. An example is 'alchemist's gold', $Hg_{2.186}AsF_6$ (Brown *et al.*, 1974), which comprises rods of Hg atoms with this packing. Another example is the structure proposed for laminar (ω_2) sulphur (Tuinstra, 1967); here the rods are helices of S atoms. A third example is Pu_3Zn_{22} , although the rods are considerably separated in the ab plane (Johnson, Wood & Smith, 1968).

It is sometimes convenient to consider the array of octahedral cations and anions in the spinel structure, with stoichiometry MX_2 such as in CTi_2 (Goretzki, 1967) and (distorted) in hydroxychlorides of the atacamite, $Cu_2(OH)_3Cl$, group, as rods of edge-sharing octahedra with this packing. The symmetry of spinel is cubic, but in a derived structure, that of hausmannite (Mn_3O_4) and related compounds such as $CdMn_2O_4$ (Fig. 6), there is a tetragonal distortion (symmetry again $I4_1/amd$) so that the rods are chains of edge-shared squares with this rod packing.

The octahedral framework of the pyrochlore structure (again cubic) can be considered in the same way, but now the rods consist of corner-connected octahedra so that the stoichiometry of the framework is MX_3 . The symmetry of the pyrochlore framework is the same as that of spinel, but ordered occupancy of the cavities in the framework can result in tetragonal symmetry. An example with $I4_1/amd$ symmetry is $SrPb_2I_6 \cdot 7H_2O$ (Ferrari, Braibanti & Lanfredi, 1961) in which $Sr(H_2O)_6$ ions and H_2O occupy cavities in the PbI_3 framework.

(v) Fig. 7. We include this as the simplest layer packing of rods with hexagonal symmetry. The space group is $P6_222$ with three rods in the unit cell. The rod equations are $u, 0, 0$; $u, u, \frac{1}{3}$; $0, u, \frac{2}{3}$ derived from positions 6(g). Examples are high quartz (Fig. 8) in which the rods are zigzag lines of O atoms, and $NaHg_2O_2I$ (Aurivillius, 1960) in which the rods are zigzag lines of $-O-Hg-O-Hg-$ (with Hg atoms on the rod axes).

We turn now to cylinder packings in which the axes are not coplanar. These have cubic symmetry, are less obvious intuitively, but for that reason of greater utility in the description of crystal structures.

(vi) Fig. 9. This is the simplest cubic cylinder packing. The symmetry is $Pm\bar{3}n$ so we call it *primitive cubic rod packing*. The rod equations are $u, 0, \frac{1}{2}$; $\frac{1}{2}, u, 0$; $0, \frac{1}{2}, u$ derived from positions 12(g). The packing density is only 0.5890. An example is the β -W ($A15$) structure which has stoichiometry A_3B and the same symmetry. The A atoms lie in strings along axes with this packing

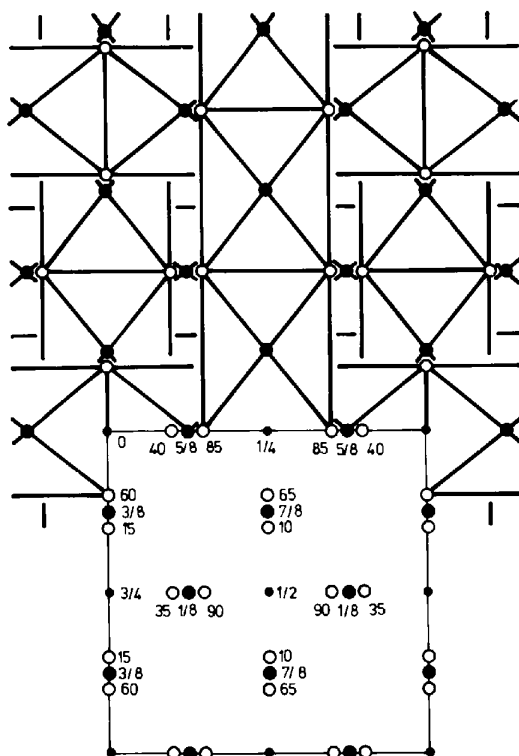


Fig. 6. The structure of $CdMn_2O_4$ projected on (001). Open circles O (heights in $c/100$). Small filled circles Cd, large filled circles Mn.

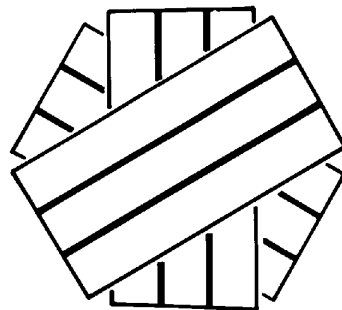


Fig. 7. A three-layer hexagonal cylinder packing.

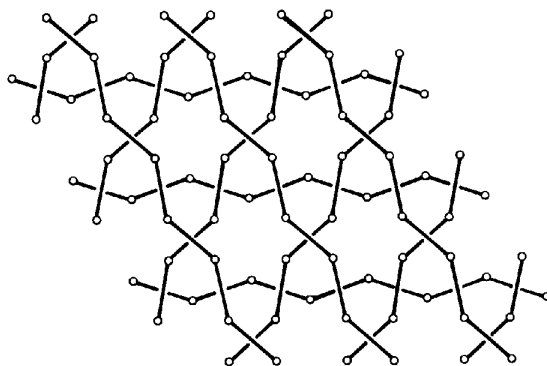


Fig. 8. The oxygen arrangement in high quartz. The zigzag lines lie in planes parallel to (001) and separated by $c/3$.

(Fig. 10a). The occurrence of these strings suggests a simple relationship of this structure to a hypothetical structure derived from ordering atoms on a primitive cubic lattice (Fig. 10b). The two structures can be related by translations of the strings of atoms parallel to their axes. The cubic Pt bronzes $A_2Pt_3O_4$ ($A = Na, Ni$ etc.) have a related structure (Cahen, Ibers & Shannon, 1972) in which the Pt atoms lie on rods with primitive cubic rod packing. The structure of $NaPt_3O_4$ may be derived from that of $CaPt_2O_4$ by insertion of a third rod of Pt atoms while changing Ca to Na (Fig. 4). The structure of Ag_3PO_4 is very similar, with Ag rods in this case, but the symmetry is now lowered to $P43n$ due to displacement of the O atoms to provide tetrahedral coordination for P.

(vii) Fig. 11. This is a second example of primitive cubic packing of identical cylinders. The packing has the same symmetry and density as the previous one. The rod equations are $\frac{1}{8}, \frac{3}{8}, u$; $\frac{1}{8}, \frac{5}{8}, u$; $\frac{7}{8}, \frac{3}{8}, u$; $\frac{7}{8}, \frac{5}{8}, u$; $u, \frac{1}{8}, \frac{3}{8}$; $u, \frac{7}{8}, \frac{5}{8}$; $u, \frac{1}{8}, \frac{5}{8}$; $u, \frac{7}{8}, \frac{3}{8}$; $\frac{3}{8}, u, \frac{1}{8}$; $\frac{3}{8}, u, \frac{7}{8}$; $\frac{5}{8}, u, \frac{1}{8}$ derived from positions 48(l) (x, y, u etc) of $Pm3n$ by setting $x = \frac{1}{8}$, $y = \frac{3}{8}$.

(viii). The final packing we wish to discuss is a cubic packing of cylinders with axes parallel to $\langle 111 \rangle$. It is hard to represent in a drawing so a sketch of the packing (Fig. 12) is supplemented by a photograph of

a model (Fig. 13). It is a denser packing (density = 0.6802) than the primitive cubic rod packing and it is our conjecture that it is the densest cubic packing of equivalent cylinders. The symmetry is $Ia3d$ so we call it *body-centred cubic (b.c.c.) rod packing*. The rod equations u, u, u ; $\frac{1}{2} - u, \frac{1}{2} + u, u$; $u, \frac{1}{2} - u, \frac{1}{2} + u$; $\frac{1}{2} + u, u, \frac{1}{2} - u$ are derived from positions 32(e). A unit cell of this packing of cylinders of unit diameter has a cell edge $a = 2\sqrt{2}$ and contains a total length of cylinder equal to $8\sqrt{6}$.

A striking feature of the symmetry of this packing is that it is the highest-symmetry cubic space group with four non-intersecting threefold axes. This is clearly a requirement for rod packing to be present in crystal structures, so that it will only be found in the cubic subgroups of $Ia3d$; accordingly the hierarchy of these subgroups (Neubüser & Wondratschek, 1969) is displayed in Fig. 14. Not all crystals with the symmetry of one of these groups will be most appropriately described as rod packings however. In particular there is a group of crystals composed of linear molecules without a dipole moment (N_2, CO_2 etc.) in which the centres of the molecules are at the nodes of a face-centred cubic lattice. The lowest quadrupole energy of such an arrangement has been shown (Nagai & Nakamura, 1960) to be that in which the axes of the

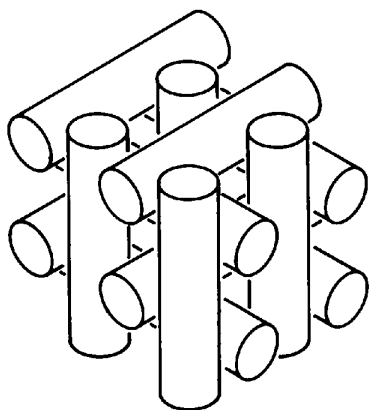


Fig. 9. Primitive cubic cylinder packing.

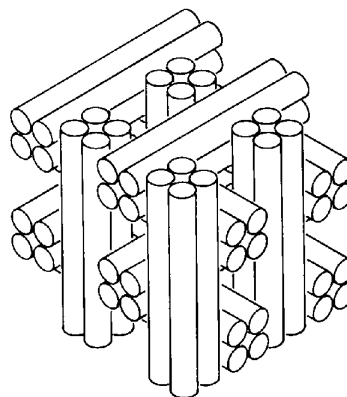


Fig. 11. A second primitive cubic packing of identical cylinders (compare Fig. 9).

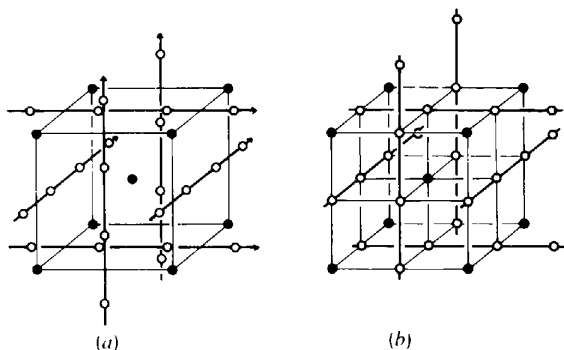


Fig. 10. (a) the $A15$ structure as a rod packing. Displacement of rods in the direction of the arrows produces the structure shown in (b).

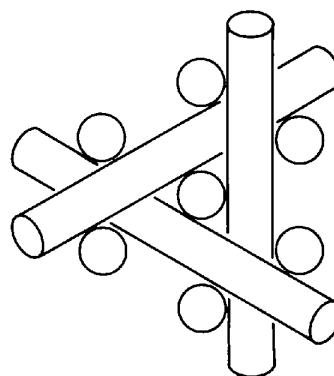


Fig. 12. An element of body-centred cubic rod packing viewed down a trigonal axis.

molecules are aligned along all four $\langle 111 \rangle$ with symmetry $Pa3$. The structure of FeS_2 (pyrite) falls in this category, as does that of ZrP_2O_7 . In the latter the molecule is the $P_2O_7^{4-}$ ion. Crystals of linear molecules with a small dipole moment (e.g. CO) have a related structure with lower symmetry ($P2_13$). With this reservation in mind we have found that most of the cubic crystals with the symmetry of one of the groups of Fig. 14 may be described as body-centred cubic rod packings and in subsequent sections we provide some examples.

Body-centred cubic sphere packing as rod packings and the Th_3P_4 family of structures

It is revealing to describe the b.c.c. sphere packing as a rod packing. The nearest neighbours of a given atom are along the $\langle 111 \rangle$ directions and all the atoms of the structure lie on rods along these directions. There are two ways of dividing the structure into rods. The first is to consider all atoms as lying on the axes of rods parallel to $[111]$, Fig. 15(a). The utility of this description may be illustrated by considering the well-known transition of b.c.c. to the ω -alloy structure. The atomic displacements are simply described as translations of the rods along their axes (Fig. 16) (Andersson, 1960).

The second description of b.c.c. sphere packing in terms of rods concerns us more here. In this case the atoms are on the axes of rods parallel to four different $\langle 111 \rangle$ directions, the rods being packed as in b.c.c. rod packing (Fig. 15b). Fig. 17 shows how a new atomic arrangement is derived from b.c.c. by systematic displacements of rods along their axes. If the atomic displacement is a fraction x of the body diagonal of the 16 atom cell of Fig. 17, the new atom positions will be 16(c) of $I\bar{4}3d$. This is approximately the structure of UCo ($x \approx 0.04$, but note that in UCo ordering of the two kinds of atom lowers the symmetry to $I2_13$).

In the original b.c.c. structure, space is divided into congruent but irregular tetrahedra, of which there are six per atom. In the rod distortion we are now discussing one finds that, as x is initially increased from 0 to $\frac{1}{33}$, one eighth of these tetrahedra (with centres at positions 12(b) of $I\bar{4}3d$: $\frac{7}{8}, 0, \frac{1}{4}$ etc.) are converted to regular tetrahedra. The remaining space consists of 12 bisdisphenoids [with centres at 12(a): $\frac{3}{8}, 0, \frac{1}{4}$ etc.], each of which is derived from seven tetrahedra of the original b.c.c. (Fig. 17). For $x = \frac{1}{32}$ the bisdisphenoids are nearly dodecadeltahedra (all faces equilateral triangles) but in fact there are two edge lengths [with ratio $\sqrt{(25/24)}$]. If x is further increased to $\frac{1}{12}$ one obtains a bisdisphenoid in which the distances from the centre to the eight vertices are all equal. A number of cubic crystal structures can now be derived by filling one or both of these sets of interstices (tetrahedra and bisdisphenoids) with atoms or groups of atoms. We give some examples below.

If an atom, say A , is placed at the centre of the bisdisphenoids of B atoms the stoichiometry is A_3B_4 and one has the well-known Th_3P_4 structure type (for which usually $x \approx \frac{1}{12}$ so that all the shorter $A-B$ distances are equal). The structure of $Hg_3S_2Cl_2$ (and isostructural compounds) is derived from that of Th_3P_4 by replacing P_4 by S_2Cl_2 (arranged as in UCo so that the symmetry is again $I\bar{2}_13$) and replacing Th by Hg off-centre in the bisdisphenoids. The B atoms in the ideal structure ($x = \frac{1}{12}$) have six equidistant A neighbours in an arrangement intermediate between an octahedron (triangular antiprism, triangles rotated by 60° with respect to each other) and a right triangular prism (rotation angle of zero): what might

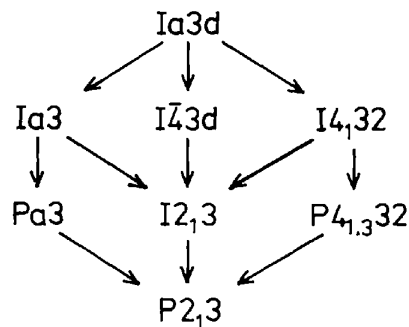


Fig. 14. The cubic subgroups of $Ia3d$. Arrows connect each space group to its cubic maximal subgroups.

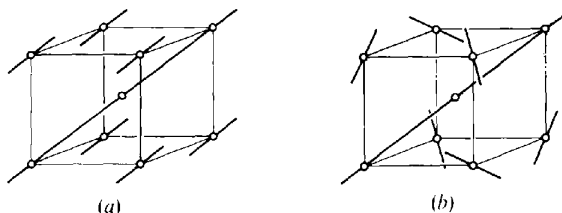


Fig. 15. (a) B.c.c. sphere packing as a hexagonal rod packing, (b) b.c.c. sphere packing as a b.c.c. rod packing.

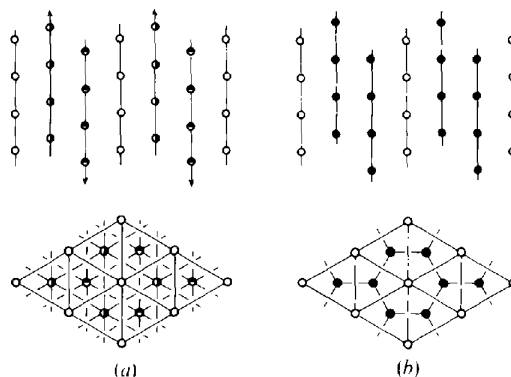


Fig. 16. (a) Top: a (110) section of b.c.c. sphere packing showing the atoms on parallel rods; bottom: a projection along the rod axes $[111]$. Displacement of the rods in the directions shown produces the configuration shown in (b).

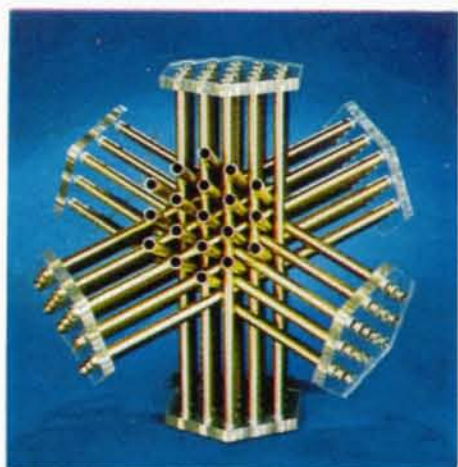


Fig. 13. Photograph of a model of body-centred cubic rod packing. The model comprises four interpenetrating sets of nineteen rods each.

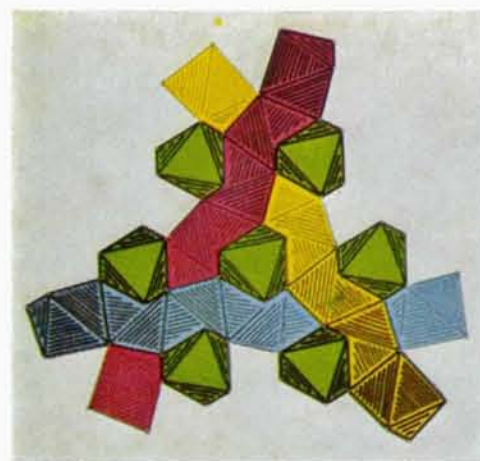


Fig. 18. The rods of Th_6 metaprisms in the Th_3P_4 structure. Rods of different colours are parallel to different $\langle 111 \rangle$. The green rods are viewed down their axes.

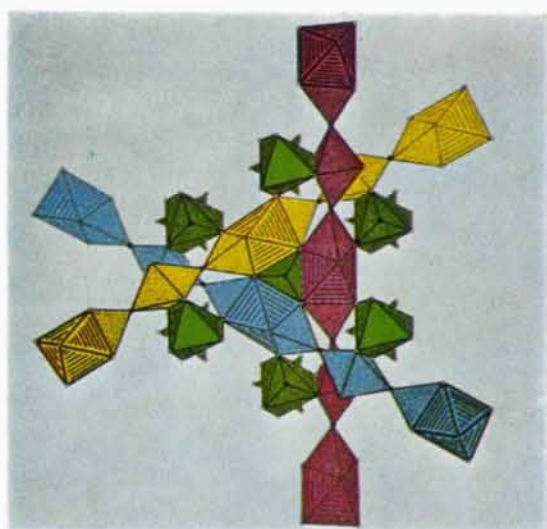


Fig. 21. The rods of tetrahedra and metaprisms comprising the β -Mn structure. The colouring scheme is as in Fig. 18.



Fig. 23. A polyhedral model of the garnet structure. Red octahedra and transparent trigonal prisms form rods packed in b.c.c. rod packing. The rods are joined by green SiO_4 tetrahedra. Some of the large cation sites are shown by grey balls. The small yellow balls represent oxygen atoms.

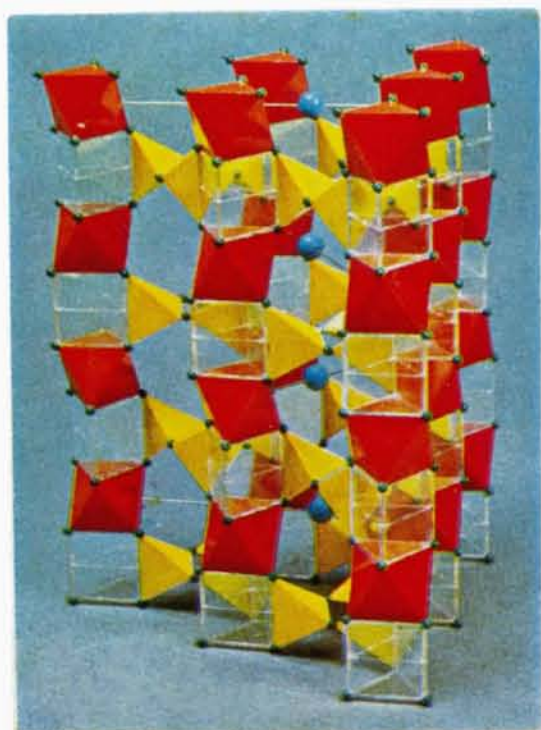


Fig. 26. A polyhedral model of the structure of benitoite, $BaTiSi_3O_9$, showing the parallel rods of empty trigonal prisms (clear) and TiO_6 octahedra (red). Si ions are in the green tetrahedra.

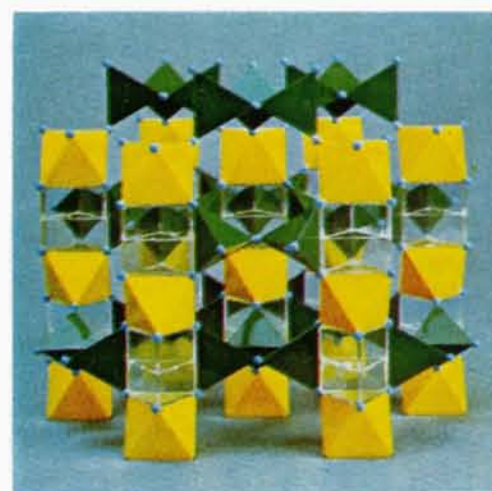


Fig. 27. A polyhedral model of the structure of catapleite, $Na_2ZrSi_3O_9 \cdot 2H_2O$, showing the parallel rods of ZrO_6 octahedra (yellow) and empty trigonal prisms (transparent) joined by SiO_4 tetrahedra (green).

be conveniently termed a *metaprism* [rotation angle $\cos^{-1}(11/14) = 38.2^\circ$]. The structure is now described in terms of a rod packing: rods of BA_6 metaprisms

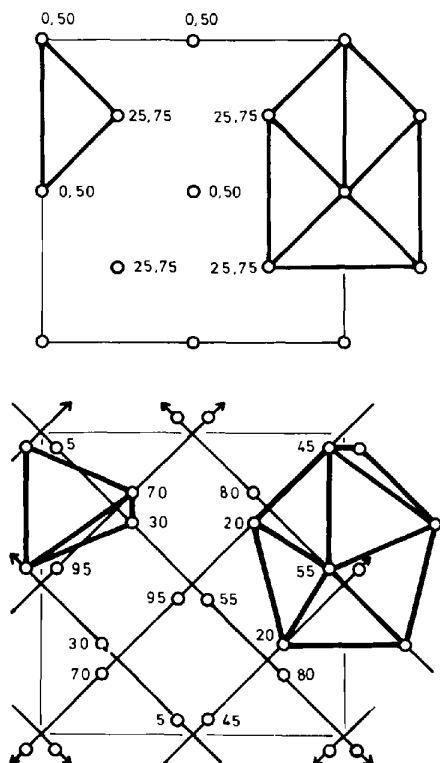


Fig. 17. Top: eight unit cells ($2 \times 2 \times 2$) of b.c.c. Bottom: the atoms of the top figure have been displaced in the directions shown by the arrows along rows by an amount $0.05 \times$ body diagonal.

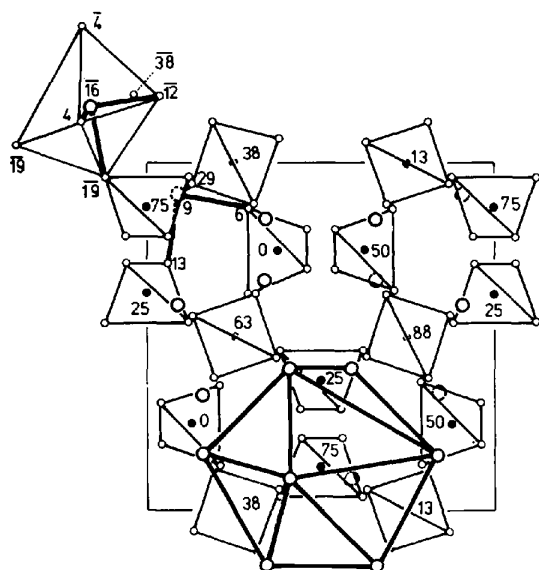


Fig. 19. The SiO_4 groups of eulytine, $Bi_3Si_4O_{12}$ shown in projection on (001). One bisdisphenoid of Bi ions (large open circles) is shown and in the top left corner the 3+3 coordination of Bi by oxygen is shown.

sharing faces are packed as in b.c.c. rod packing (Fig. 18). In this packing each BA_6 polyhedron shares five faces with congruent adjacent polyhedra (Kharitonov, Smirnova & Belov, 1966).

One may see now a simple relationship between the Th_3P_4 structure type and some other phosphide and sulphide structures which contain rods of face-sharing trigonal prisms and/or octahedra. For example in Fe_2P , PFe_6 trigonal prisms form rods by sharing triangular faces; there are two kinds of rod, isolated and edge-sharing. In MoP (with the WC structure type) rods of PMo_6 prisms share all vertical edges. TiP has rods of alternating PTi_6 octahedra and prisms, again joined by edge-sharing. Only a small rotation of the triangular faces normal to the trigonal axis of the TiP rod is required to transform it into a rod of metaprisms such as of PTh_6 found in Th_3P_4 . These rods can now share faces increasing the P/metal ratio to greater than one.

There are other ways of filling the bisdisphenoid sites to produce structures with $I43d$ symmetry. Thus one may put A_2 groups into each bisdisphenoid with the A atoms on the $24(d)$ sites. The stoichiometry is $(A_2)_3B_4$ and one has the well-known structure of Pu_2C_3 , Rb_2O_3 etc.

The next level of complexity is to put suitably oriented tetrahedral A_4 groups into the bisdisphenoids (compare Fig. 19). This can be done with A atoms occupying positions $48(e)$ (with e.g. $x \approx 0.06$, $y \approx 0.13$, $z \approx 0.29$). The stoichiometry is $(A_4)_3B_4$; an example is the mineral domeykite, Cu_3As .

Closely related to the last structure is one obtained by putting A_4 groups in the bisdisphenoids and A' groups in the tetrahedra. The stoichiometry is now $A'_3(A_4)_3B_4$ and known compounds with this structure include $Cu_{15}Si_4$, $Na_{15}Pb_4$ and $H_{15}Th_4$.

Finally, a structure is known with CA_4 tetrahedral groups in the bisdisphenoids. This is the structure of compounds isostructural with eulytine $Bi_4(SiO_4)_3$. A (100) projection is shown in Fig. 19, in which the configuration of the SiO_4 is shown and a bisdisphenoid of Bi atoms around one tetrahedron is sketched in.

In the eulytine structure Bi has only three nearest neighbours in a configuration typical for lone-pair cations and this structure is only found with $B = Bi^{3+}$ or Pb^{2+} . However, there is a related structure derived from that of eulytine by rotation of the tetrahedra about their centres in such a way that the coordination of half of the B ions approximates the shape of a regular octahedron while the other half have a less regular coordination of more distant anions. This is the structure of langbeinite, $K_2Mg_2(SO_4)_3$, and isostructural compounds, for which the configuration of tetrahedral groups is shown in Fig. 20 for comparison with those of eulytine in Fig. 19. The S atoms of langbeinite have almost exactly the same positions in the unit cell as the Si atoms of eulytine; the symmetry is however now reduced to $P2_13$.

The langbeinite structure (as indeed all the struc-

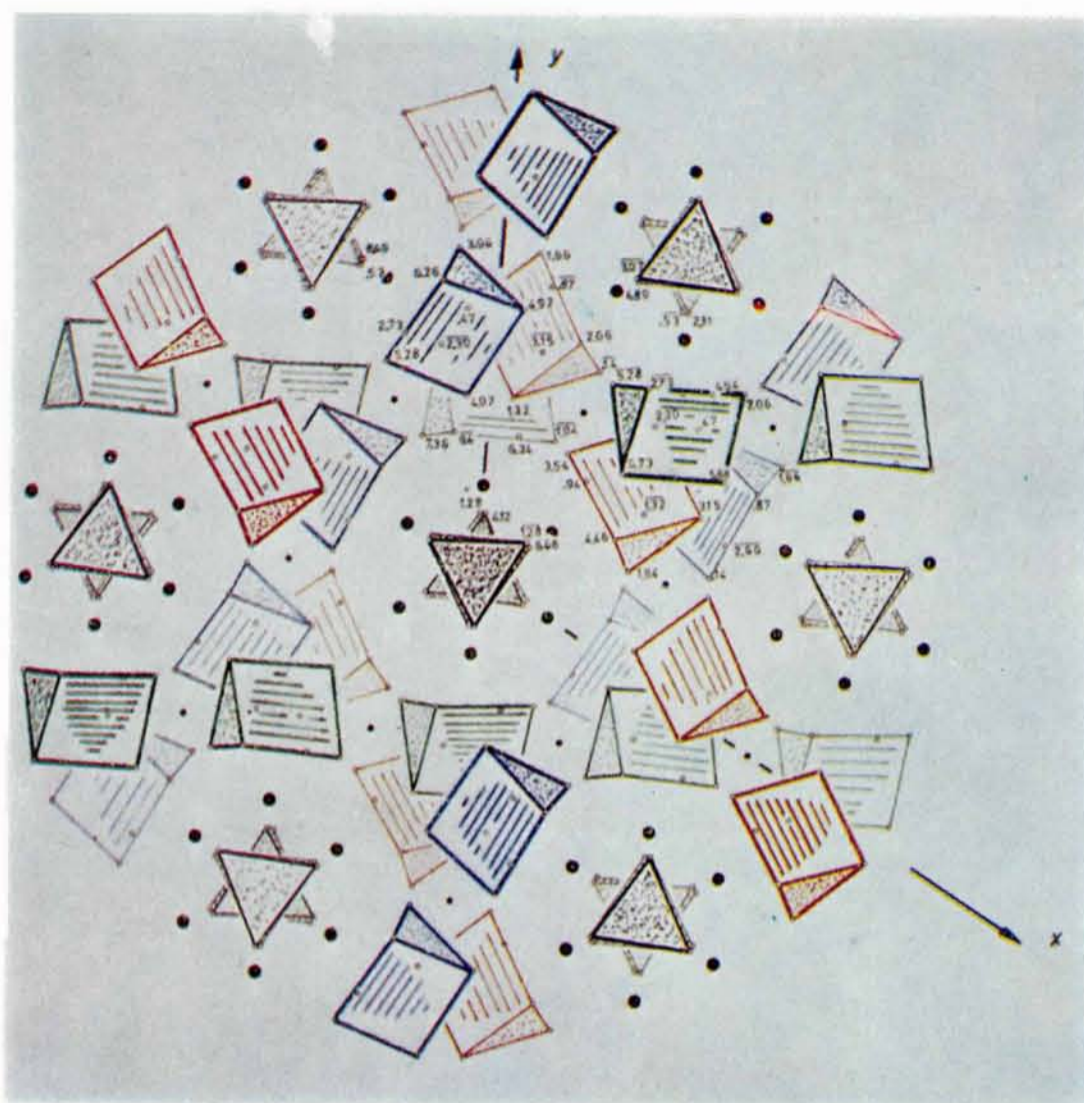


Fig. 24. The structure of $Y_3Fe_5O_{12}$ projected on (111). The empty trigonal prisms are outlined. Prisms of different colours lie on rods parallel to different $\langle 111 \rangle$.

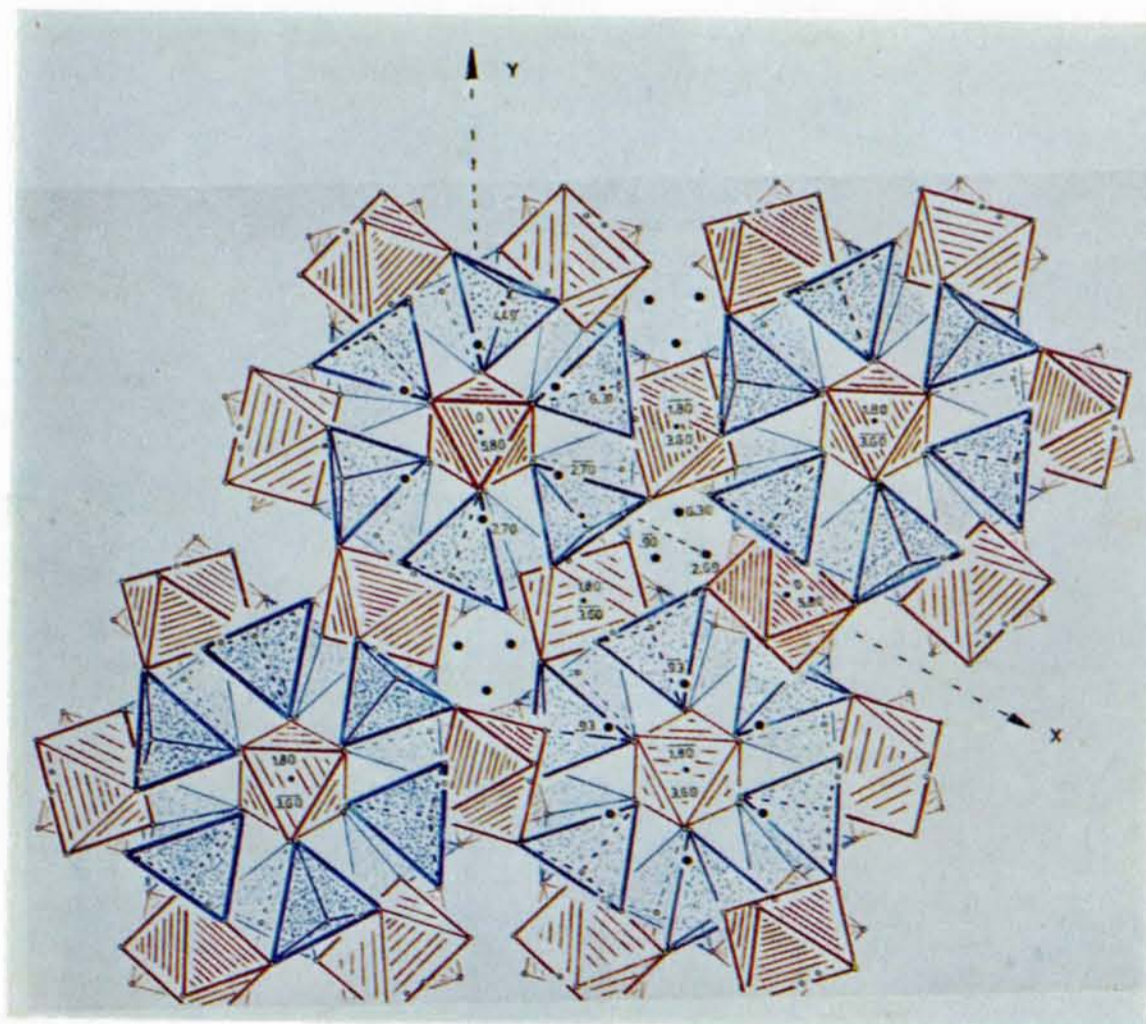


Fig. 25. The network of octahedra and tetrahedra of the structure of $Y_3Fe_5O_{12}$ drawn in the same projection as in Fig. 24.

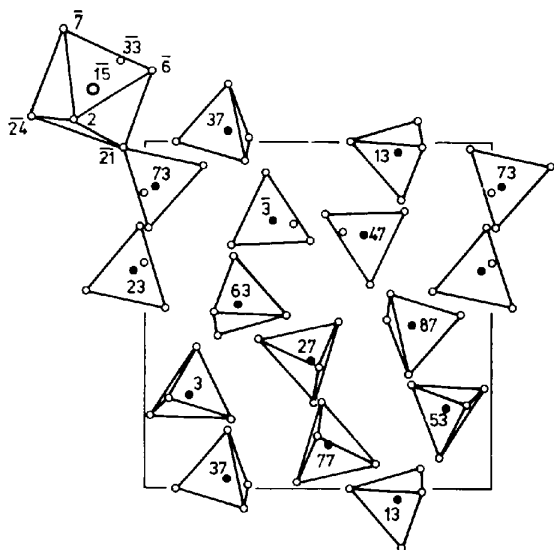


Fig. 20. The SO_4 groups of langbeinite, $\text{K}_2\text{Mg}_2\text{S}_4\text{O}_{12}$ shown in (001) projection for comparison with Fig. 19. In the top right the octahedral coordination of one Mg ion (larger open circle) is shown.

tures described in this section) is conveniently described as a body-centred cubic rod packing. In this instance the rods consist of a repeating sequence $\text{K}, \text{K}, \text{O}_3\text{MgO}_3, \text{O}_3\text{MgO}_3$ (the O_3MgO_3 group approximating a regular octahedron). When packed as in b.c.c. rod packing all the K, Mg and O atoms of the structure are accounted for; the S atoms in tetrahedral coordination hold the rods together (compare garnet, discussed below).

Table 1 summarizes the structural relationships between the compounds of this section.

Table 1. Structures with $I\bar{4}3d$ symmetry derived from b.c.c. sphere packing

Structure	Tetrahedral site		Bisdisphenoid site		
	16(c)	12(b)	12(a)	24(d)	
b.c.c.	$x=0$				
UCo*	U, Co				
Th_3P_4	P		Th		
Pu_2C_3	Pu			C	
Cu_3As	As				Cu
$\text{Cu}_{15}\text{Si}_4$	Si	Cu			Cu
$\text{Bi}_4\text{Si}_3\text{O}_{12}$	Bi		Si		O

* $I2_13$.

One of the strongest motivations for recognizing and describing structural relationships is to identify possibilities for intergrowth of structures, and for structural defects and non-stoichiometry (Hyde *et al.*, 1974). In this connection the rod distortions of b.c.c. discussed here are suggestive. The b.c.c. structure is characterized by having a large number (six) of tetrahedral interstitial sites per atom, yet thermodynamic data, for example for hydrogen dissolved in b.c.c. metals (O'Keeffe & Steward, 1972), suggests the avail-

ability of a smaller number (~ 1) of interstitial sites per atom. The rod distortions of b.c.c. described here suggest ways in which the small tetrahedral sites can be combined into larger sites (e.g. seven tetrahedra into a bisdisphenoid) and one is led naturally to consider the possibility of local rod distortions in the neighbourhood of an interstitial atom. The possibility of interstitial atoms stabilizing regions of ω structure has been raised before (Andersson, 1960); equally possible is the occurrence of regions of the Th_3P_4 type of structure in a b.c.c. matrix (the existence of the compound Th_4H_{15} already mentioned enforces this point of view). Conversely the well-known problem of non-stoichiometry in chalcogenides with the Th_3P_4 structure (for example the range of composition of the rare-earth sulphides from Ln_2S_3 to Ln_3S_4 , Flahaut *et al.*, 1965) suggests the possibility that the cation-deficient compounds contain regions in which the anion packing is more closely that of the undistorted b.c.c. parent structure.

Once the possibility of making larger interstices in the b.c.c. structure by local displacements of rows of atoms is recognised, one is led immediately to the recognition of possible diffusion mechanisms for interstitial atoms in a b.c.c. framework involving cooperative motion of b.c.c. atoms along rod fragments coupled with interstitial jumps. Such considerations are relevant to the anomalously high diffusivity of H in b.c.c. metals and of Ag^+ in solid electrolytes such as AgI and Ag_2S (in which the lattice of immobile ions is b.c.c.).

The β -Mn family of structures

The structure of β -Mn has proved difficult to describe but lends itself to a simple description in terms of body-centred cubic rod packing. The symmetry of the structure is $P4_132$ (or $P4_332$). There are two kinds of Mn atom (most examples of this structure occur as binary alloys, e.g. Fe_2Re_3): Mn(1) in $8(c)$ x, x, x etc. with $x \approx 0.06$ and Mn(2) in $12(d)$: $\frac{1}{8}, y, \frac{1}{4} + y$ etc with $y \approx 0.21$. With these parameters it is found that the Mn(2) atoms form a three-dimensional network of corner-connected metaprisms (very similar in shape to the Th_6 metaprisms of Th_3P_4). The Mn(1) atoms lie on threefold symmetry axes between two equilateral triangular faces of the Mn(2) metaprisms thus forming $\text{Mn}(1)\text{Mn}(2)_3$ tetrahedra.

It is easy to derive ideal values for the free parameters. First it is required that the two equilateral faces of the metaprisms be congruent [so that as many as possible of the shorter Mn(2)–Mn(2) distances are equal]. This is the case for

$$y = (9 - \sqrt{33})/16 = 0.2035.$$

Secondly it is required that the six shortest Mn(1)–Mn(2) distances are all equal. This occurs for

$$x = 1/(9 + \sqrt{33}) = 0.0678.$$

With these parameters (which are very close to those found in real structures) the shortest Mn(1)–Mn(2) and Mn(2)–Mn(2) distances are nearly equal (their ratio is 1.055) so that the Mn(1)Mn(2)₃ tetrahedra are nearly regular.

The rods of the structure consist of strings of the two types of polyhedron. Specifically each rod consists of a repeating sequence of Mn(2)₆ metaprisms and four Mn(1)Mn(2)₃ tetrahedra joined as shown in Fig. 21. If the metaprisms are replaced by octahedra the rods would approximate mixed hexagonal and cubic close packing. The rods share Mn(2) atoms so that the Mn(2)₆ metaprisms share corners. The Mn(2) network alone is shown in Fig. 22.

A related structure is that of Mo₃Al₂C and isostructural nitrides and carbides (Jeitschko, Novotny & Benesovsky, 1964). C atoms [in positions 4(a)] centre the metaprisms of Mo. Also related is the structure of RbAg₄I₅ (Geller, 1967a). In this compound the I(2)₃I(1)₂Rb packing is as in Mo₃Al₂C and the Ag ions are disordered over several sets of interstitial sites.

No MX₃ compound [with just the 4(a) and 12(d) sites of P4₁32 filled] appears to be known, but mention might be made of SrSi₂ (Pringle, 1972) with Sr in 4(a) and Si in 8(c). The rods are now strings of Si atoms along the threefold axes arranged such that each Si atom has three nearest neighbours belonging to three adjacent rods.

The garnet and related structures

The garnets, typified by grossularite (Ca₃Al₂Si₃O₁₂), include many compounds of interest in mineralogy and solid state physics and, especially since the discovery of the ferrimagnetic garnets (Bertaut & Forrat, 1956), many new compounds have been made that have the same structure so that today many hundreds of garnets are known (Geller, 1967b). Nevertheless this structure, which has been known for over fifty years (Menzer, 1926, 1928), has resisted all attempts at a simple analytical description.

When a polyhedral model (Fig. 26) was built it was

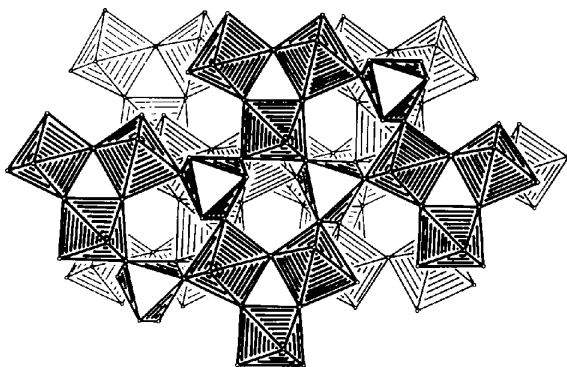


Fig. 22. The network of corner-connected Mn(2)₆ metaprisms in β-Mn projected on (111).

quickly realised that the structure is best described in terms of the b.c.c. rod packing. The rods consist of alternating octahedra and trigonal prisms along the non-intersecting trigonal axes of Ia3d. The trigonal prisms are empty while the octahedra contain cations (e.g. Al) in the special positions 16(a) of the space group. The O atoms at the corners of the octahedra and prisms of the rod are all in the set 96(h). When such rods are arranged along the trigonal axes all the anions are accounted for and tetrahedral interstices are created. Cations (e.g. Si) in positions 24(d) centre the tetrahedra and similarly the larger cations (e.g. Ca) in 24(c) are interstitially situated in twisted cubes between the polyhedral rods.

Fig. 23 is a photograph of a polyhedral model. The red octahedra are joined to transparent trigonal prisms forming the rods. Green tetrahedra containing the smaller cations share corners with four octahedra, one from each of four rods aligned in different directions. The larger grey balls represent the larger cations in irregular polyhedra in the shape of twisted cubes with two square faces from the empty trigonal prisms. Only a few of these larger cations have been built into the structure model. O atoms are represented by smaller yellow balls.

Fig. 24 shows a projection of the structure along the space diagonal with the coordinates for Y₃Fe₂Fe₃O₁₂ (Batt & Post, 1962). Only the empty trigonal prisms are shown and those of each of the four different rods are shown in a different colour. The black polyhedra in the centre represent trigonal prisms belonging to one rod, the somewhat twisted appearance being due to an alternating clockwise and anticlockwise rotation of octahedra along the rod, a characteristic distortion occurring in the garnet structure and discussed further below. Heights of most of the atoms are given in the upper right-hand part of the drawing in Å. Missing heights may be found in Fig. 25 which is the same projection, but now the octahedra and tetrahedra are shown, emphasising the network of corner-connected polyhedra.

As with the structures of Th₃P₄ and β-Mn, parameters for an ideal structure and the unit-cell edge may be calculated. This is done by requiring the octahedra and trigonal prisms of the rods to be regular. One then finds for the unit-cell edge:

$$a = (4\sqrt{3} + 4\sqrt{2/3})d,$$

where d is the polyhedron edge length (the anion–anion distance). Thus with $d = 2.8$ (appropriate for oxides) $a = 11.7$ Å.

The O parameters for the ideal structure are

$$\begin{aligned} x &= (2\sqrt{3} - 3\sqrt{2} + \sqrt{6} - 2)/8 = -0.0411 \\ y &= (\sqrt{6} - 2)/8 = 0.0562 \\ z &= (3\sqrt{2} - 2\sqrt{3} + \sqrt{6} - 2)/8 = 0.1535. \end{aligned}$$

The cation positions are of course fixed by the symmetry.

The experimentally observed garnet parameters are in general remarkably close to these ideal values, encouraging us to believe that we have identified the correct building unit (the rods) to describe the structure, a belief that is reinforced by the observation that the same rods may be identified in many other mineral structures (see below).

In order to analyse more closely the deviations of real structures from the ideal, it is convenient to work with a hexagonal cell appropriate to the [111] projection. The ideal parameters for the transformed coordinates are:

$$x_0 = y_0 = -(3\sqrt{2} - 2\sqrt{3})/8 = -0.0973$$

$$z_0 = (\sqrt{6} - 2)/8 = 0.0562.$$

We recognise three different kinds of distortion which may occur, depending on the nature of the cations that are in the structure, and which provide an explanation for the remarkably flexible nature of the structure; $Ia3d$ symmetry is retained for a wide variety of combinations of cations of different sizes (Novak & Gibbs, 1971). The distortions are:

- (a) Compression or expansion of the octahedra along the trigonal axis. In the hexagonal coordinate system this is measured by the z parameter:

$$\% \text{ expansion} = 100(z - z_0)/z_0.$$

- (b) Umbrella distortion in which O atoms move in the plane perpendicular to the trigonal axis.

$$\% \text{ distortion} = 100[(x_0 - x) + (y_0 - y)]/(x_0 + y_0).$$

- (c) Rotation of the octahedra, alternately clockwise and anticlockwise, along the trigonal axis from the ideal position by an angle θ . For small angles

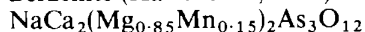
$$\theta \simeq 60^\circ - \sin^{-1}[\sqrt{3}x/(x + y)].$$

The significance of these distortions is as follows. The ideal structure obtained with rods of regular polyhedra of edge d results in irregular tetrahedra with slightly shorter edges ($0.968d$ and $0.938d$). The tetrahedron may be made regular by a 6.8% compression of the octahedra (with *cubic* parameters $x = -0.0449$, $y = 0.0524$, $z = 0.1497$).

Rotation alone makes the tetrahedra less regular, while negative umbrella distortion results in larger tetrahedra. We give below three examples of garnet structures that have been refined to illustrate the extent of these distortions in real structures.

- (i) Grossularite (Abrahams & Geller, 1958)
 $a = 11.855 \text{ \AA}$
 $x = -0.0382$, $y = 0.0457$, $z = 0.1512$ (cubic)
 expansion = 3.0%, umbrella distortion = -3.8%,
 rotation = 3.6°.
- (ii) $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (Batt & Post, 1962)
 $a = 12.376 \text{ \AA}$
 $x = -0.0269$, $y = 0.0581$, $z = 0.1495$ (cubic)
 $x = -0.0871$, $y = -0.0893$, $z = 0.0602$ (hexagonal)
 expansion = 7.1%, umbrella distortion = -9.4%,
 rotation = 1.2°.

- (iii) Berzeliite (Hawthorne, 1976):



$$a = 12.355 \text{ \AA}$$

$$x = -0.0391, y = 0.0522, z = 0.1568 \text{ (cubic)}$$

$$x = -0.0857, y = -0.1002, z = 0.0566 \text{ (hexagonal)}$$

$$\text{expansion} = 0.7\%, \text{ umbrella distortion} = 0.7\%,$$

$$\text{rotation} = 2.2^\circ.$$

It may be seen that berzeliite provides an example of a garnet with a structure very close to our ideal one.

The garnet rod structure also is known in an alloy, RhBi_4 (Zhuravlev & Zhdanov, 1955). Here the Bi polyhedra of the rods are all empty, as are the tetrahedral sites. Rh fills the larger interstitial positions, 24(c), occupied by the large cations in the oxide garnets.

In our description of the garnet structure we have emphasised the rods of alternating octahedra (filled with *e.g.* Al) and trigonal prisms (empty) with three large cations (*e.g.* Ca) opposite each of the three square faces of the trigonal prisms. In the garnet structure each Ca is shared between two rods, so that the composition of the rods is $(\text{Ca}_{1/2})_3\text{AlO}_6$; on the other hand the composition of isolated rods would be Ca_3AlO_6 . Related structural units are of common occurrence in crystals. An example with rods in hexagonal packing is $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$ (in which Cl replaces Ca and H_2O replace O). Crystals of compounds isostructural with rinneite, $\text{K}_3\text{NaFeCl}_6$, have the anti-structure of $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$, with Na centring the trigonal prisms and K^+ replacing Cl^- (*i.e.* K_3FeCl_6 replacing Ca_3AlO_6).

In a related group of structures we again find isolated garnet rods but in a hydrated form. Thus if in the Ca_3AlO_6 rod the eightfold coordination of each Ca is completed by adding four water molecules and the O is replaced by OH, the rod composition becomes $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{3+}$. Just such rods (which might be expected to occur in aqueous solution) with the same repeat distance as those in grossularite are found in hexagonal packing. Examples of such structures, which differ only in the details of the positioning of the compensating anions are those of $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{CrO}_4)_3$ (Feitknecht & Buser, 1949), ettringite, $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $x \simeq 1.5$ (Moore & Taylor, 1970) and jouravskite, $[\text{Ca}_3\text{Mn}^{\text{IV}}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]\text{SO}_4\text{CO}_3$ (Granger & Protas, 1969).

The trigonal prism-filled octahedron rod is a common structural unit in many other structures also, so that these may be seen to be related to garnet too. We show polyhedral models emphasising the rods in the structures of benitoite, $\text{BaTiSi}_3\text{O}_9$ (Fig. 26) and (in Fig. 27) catapleite, $\text{Na}_2\text{ZrSi}_3\text{O}_9$ or wadeite, $\text{K}_2\text{ZrSi}_3\text{O}_9$ (Shumyatskaya *et al.*, 1973), the $\text{ZrSi}_3\text{O}_9^{2-}$ framework in these last two structure types being topologically identical. Structural relations between these and many other compounds are readily recognized and described in terms of packings of one or more of a few different kinds of rod. We propose to discuss some of these in a subsequent publication.

Other b.c.c. rod packings

We have analysed in detail the structures of three groups of crystals that are most simple described as b.c.c. rod packings. We could readily extend the discussion to other structures such as $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (space group $I\bar{4}3d$, $a=11.97$ Å, Buessom & Eitel, 1936), $\text{Ca}_3\text{Al}_2\text{O}_6$ (space group $Pa3$, $a=15.266$ Å, Mondal & Jeffery, 1975) and AlP_3O_9 (space group $I\bar{4}3d$, $a=13.66$). There are other crystals with symmetry $Ia3d$ or one of its cubic subgroups whose structures are not yet fully elucidated; their resolution should be simplified by a decomposition of the structure into rods.

Mention might also be made of crystal structures in which there are hollow rods. An example is provided by the analcime-pollucite group of minerals (e.g. high leucite, KAlSi_2O_6 , symmetry $Ia3d$, $a=13.43$ Å). In this structure the network of corner-connected tetrahedra has empty channels along $\langle 111 \rangle$ that can accommodate, for example, water molecules. The empty channels are packed as in b.c.c. rod packing and thus not intersecting. An analogous example with body-centred tetragonal rod packing is the zeolite Na-P1 ($\text{Na}_3\text{Al}_3\text{Si}_5\text{O}_{16} \cdot 6\text{H}_2\text{O}$). The symmetry is $I4_1/amd$ and the structure (Baerlocher & Meier, 1972) again contains non-intersecting channels.

A last example of a cubic structure that has a simple description in terms of b.c.c. rod packing is bixbyte, Mn_2O_3 (space group $Ia3$, $a=9.40$ Å). The structure is often described as derived from that of fluorite, CaF_2 (in which the anions are on a simple cubic array), by ordered omission of one quarter of the anions. The description is greatly simplified when it is noted that the omitted anions are those lying on strings along $\langle 111 \rangle$ (Hyde & Eyring, 1965) the strings now being packed as in b.c.c. rod packing.

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