

## 9. BASIC STRUCTURAL FEATURES

by Fischer (1976), it is very probable that no homogeneous sphere packings with lower density exist; those discussed by Melmore (1942*a,b*) with  $\rho = 0.042$  and  $\rho = 0.045$  are heterogeneous ones. Recently, Koch & Fischer (1995) proved that the Heesch–Laves packing is the least dense homogeneous sphere packing with three contacts per sphere.

The least dense sphere packings with contact number 4 derived so far are described as type 23. All sphere packings of this type are similar in the geometrical sense and are not stable. In contrast, the sphere packings of type 22 are stable. Sphere packings of type 21 (Heesch & Laves, 1933), which have been supposed to be the most open stable ones (*cf.* Hilbert & Cohn-Vossen, 1932, 1952), have a slightly higher density.

On the basis of the material known at that time, Slack (1983) tried to develop empirical formulae for the minimal and the maximal density of circle packings and sphere packings depending on the contact number. A paper by O’Keeffe (1991) on four-connected nets pays special attention to the densest and the least dense sphere packings with four contacts per sphere.

## 9.1.1.4. Applications

Sphere packings have been used for the description of inorganic crystal structures in different ways and by several authors (*e.g.* Brunner, 1971; Figueiredo & Lima-de-Faria, 1978; Frank & Kasper, 1958; Hellner, 1965; Hellner, Koch & Reinhardt, 1981; Koch, 1984, 1985; Laves, 1930, 1932; Lima-de-Faria, 1965; Lima-de-Faria & Figueiredo, 1969*a,b*; Loeb, 1958; Morris & Loeb, 1960; Niggli, 1927; Smirnova, 1956*a,b*, 1958*a,b*, 1959*a,b,c*, 1964; Sowa, 1988, 1997).

In the simplest case, the structure of an element may be described as a sphere packing if all atoms are interrelated by equal or almost equal shortest distances. This does not imply that the atoms really have to be considered as hard spheres of that size. Often such sphere packings are homogeneous ones with a high contact number  $k$  (*e.g.* Cu, Mg with  $k = 12$ ; Pa with  $k = 10$ ; W with  $k = 8$ ). Low values of  $k$  (*e.g.* diamond with  $k = 4$ , white tin with  $k = 6$ ) and heterogeneous sphere packings (La with  $k = 12$ ) have also been observed for structures of elements.

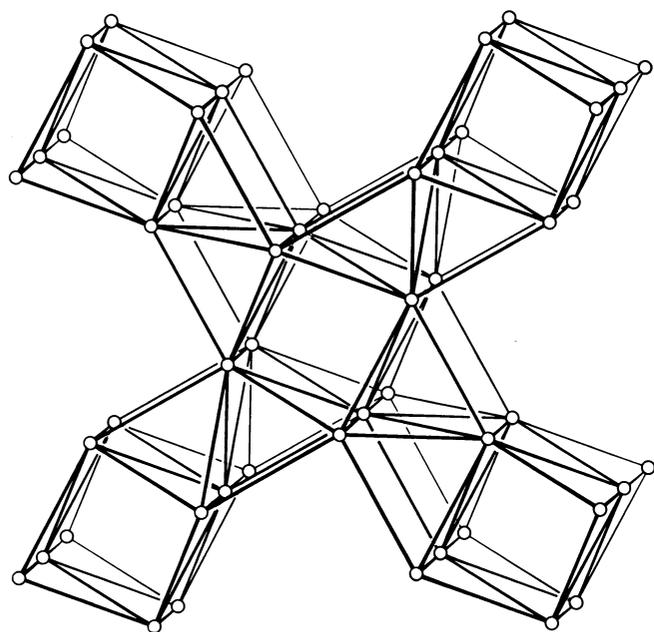


Fig. 9.1.1.6. Sphere packing of type 19 (Table 9.1.1.2) represented by a graph:  $k = 10$ ,  $I4/m$ ,  $8(h)$ ,  $xy0$ .

Crystal structures consisting of different atoms may be related to sphere packings in different ways:

(1) The structure as a whole may be considered as a heterogeneous sphere packing. In that case, contacts at least between different spheres are present (*e.g.* CsCl, NaCl, CaF<sub>2</sub>). In addition, contacts between equal atoms may exist (I—I contacts in CsI) or may even be necessary (CdI<sub>2</sub>). In general, a type of heterogeneous sphere packing is compatible with a certain range of radius ratios (*cf.* alkali halides). In special cases, a heterogeneous sphere packing may be derived from a homogeneous one by subgroup degradation (*e.g.* NaCl, CsCl, PtCu).

(2) Part of the crystal structure, *e.g.* the anions or the more frequent kind of atoms, may be considered as a sphere packing whereas the other atoms are located within the voids of that sphere packing. For this approach, the atoms corresponding to the sphere packing need not necessarily be in contact (*cf. e.g.* the Cl—Cl distances in NaCl and LiCl). Voids within sphere packings have been discussed in particular in connection with closest packings (*e.g.* Cl in NaCl, O in Li<sub>2</sub>O, S in ZnS, O in olivine), but numerous examples for non-closest packings are known in addition (*e.g.* B in CaB<sub>6</sub> with  $k = 5$ ; O in rutile with  $k = 11$ , type 8 in Table 9.1.1.2; Si in  $\alpha$ -ThSi<sub>2</sub> with  $k = 3$ ). Sphere packings and their voids form the basis for Hellner’s framework concept (*cf. e.g.* Hellner *et al.*, 1981). Voids may be calculated systematically as vertices of Dirichlet domains (*cf.* Hellner *et al.*, 1981; Koch, 1984). The tendency to form regular voids of the appropriate size for the cations may counteract the tendency to form an ideal sphere packing of the anions. Examples are spinel and garnet (*cf.* Hellner, Gerlich, Koch & Fischer, 1979).

(3) Frequently, the cations within a crystal structure are also distributed according to a sphere packing. This is explicable because the repulsion between the cations also favours an arrangement with equal but maximal shortest distances (*cf.* Brunner, 1971). In this sense, many crystal structures may be

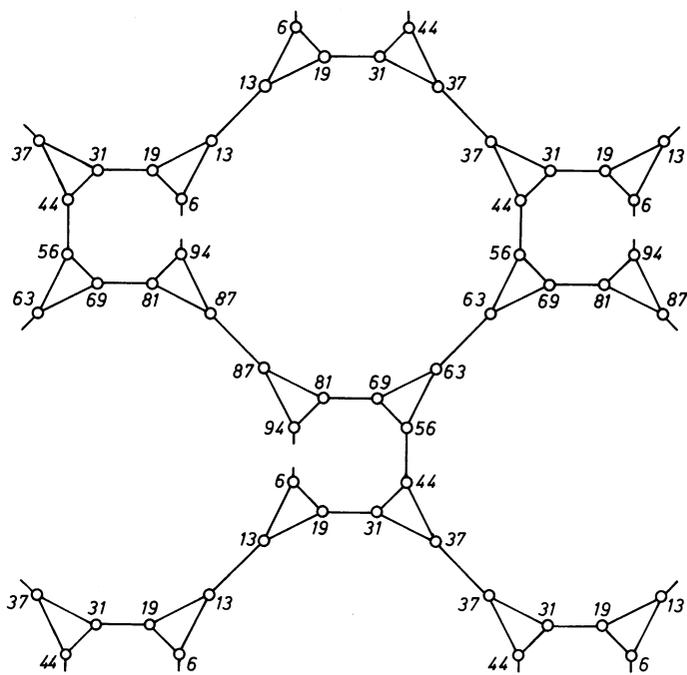


Fig. 9.1.1.7. Least dense sphere packing known so far (type 24 of Table 9.1.1.2) represented by a graph:  $k = 3$ ,  $I4_132$ ,  $24(h)$ ,  $\frac{1}{8}, y, \frac{1}{4} - y, z$  coordinates given in multiples of 1/100.

described as sets of several sphere packings (one for each kind of atom) that are fitted into each other (*e.g.* NaCl, CaF<sub>2</sub>, CaB<sub>6</sub>,  $\alpha$ -ThSi<sub>2</sub>, rutile, Cu<sub>2</sub>O, CaTiO<sub>3</sub>).

Because of their importance for problems in digital communication (error-correcting codes) and in number theory (solving of diophantine equations), densest sphere packings in higher dimensions are of mathematical interest (*cf.* Conway & Sloane, 1988).

#### 9.1.1.5. Interpenetrating sphere packings

Special homogeneous or heterogeneous sets of spheres may be subdivided into a small number  $i$  of subsets such that each subset, regarded by itself, forms a sphere packing and that spheres of different subsets do not have mutual contact. Sets of spheres with these properties are called *interpenetrating sphere packings*.

The cubic Laves phases are a well known example for heterogeneous interpenetrating sphere packings. The Mg atoms in MgCu<sub>2</sub> [ $Fd\bar{3}m$ , 8( $a$ )], for example, correspond to a sphere packing with shortest distances  $d_1 = \sqrt{3}a/4$  and contact number  $k = 4$  whereas the copper atoms [16( $d$ )] refer to another sphere packing with shortest distances  $d_2 = \sqrt{2}a/4$  and  $k = 6$ . The shortest distances between centres of different spheres are  $d_3 = \sqrt{11}a/8 > (d_1 + d_2)/2$ .

The crystal structure of Cu<sub>2</sub>O gives an example of a different kind. If one takes into account the size of the atoms, sphere contacts can only be expected between different spheres. As a consequence, the heterogeneous set of spheres disintegrates into two heterogeneous but congruent subsets with no mutual contact.

In the case of homogeneous interpenetrating sphere packings, all  $i$  subsets have to be symmetry-equivalent. Then the symmetry of each subset is a subgroup of index  $i$  of the original space group. Homogeneous interpenetrating sphere packings with cubic symmetry have been derived completely by Fischer & Koch (1976). They may be classified into 39 types. For 33 of the 39 types, the number  $i$  of subsets is 2;  $i$  is 3, 4, and 8 for 1, 3, and 2 types, respectively.

Remarkable are those homogeneous interpenetrating sphere packings that are built up from sphere packings of type 24 (Table 9.1.1.2), *i.e.* that type with the least dense sphere packing. Combinations of 2, 4, or 8 such sphere packings result in altogether 8 different types of interpenetrating sphere packings (Fischer, 1976). The P atoms in the crystal structure of Th<sub>3</sub>P<sub>4</sub> give an example for such interpenetrating sphere packings built up from two congruent subsets (Koch, 1984).

Complete results for other crystal systems are not available. With tetragonal symmetry, interpenetrating sphere packings are known, built up from 2, 3, or 5 congruent subsets (Fischer, 1970). Analogous interpenetration patterns are formed by hydrogen bonds within certain molecular structures (Ermer, 1988; Ermer & Eling, 1988).

Interpenetrating sphere packings may be brought in relation to interpenetrating labyrinths as formed by periodic minimal surfaces or by periodic zero-potential surfaces without self-intersection (*cf.* *e.g.* Andersson, Hyde & von Schnering, 1984; Fischer & Koch, 1987, 1996; von Schnering & Nesper, 1987).

#### 9.1.2. Packings of ellipses and ellipsoids

The problem of deriving packings of ellipses in two-dimensional space or of ellipsoids in three-dimensional space may be regarded as a generalization of the problem of deriving circle packings and sphere packings. It is much more complicated, however, because a circle or sphere is fully determined by its centre and its radius, whereas the knowledge of the centre, the lengths of the two semiaxes, and the direction of one of them is needed to construct an ellipse. For an ellipsoid, the knowledge of its centre, the length of its three semiaxes, and the directions of two of them is necessary. Accordingly, the point configuration corresponding to the ellipsoid centres does not define the ellipsoid packing and not even its type.

Nowacki (1948) derived 54 homogeneous 'essentially different packings of ellipses'. In contrast to the definition of types of sphere (circle) packings (Section 9.1.1), Nowacki distinguished between similar packings with different plane-group symmetry, *i.e.* between packings that may differ in the orientation of their ellipses. Under an equivalent classification, Grünbaum & Shephard (1987) derived 57 different cases of ellipse packings, thus correcting and completing Nowacki's list. Each of these 57 cases corresponds uniquely to one of the 11 types of circle packings if one takes into account only the contact relations between ellipses and circles. In eight cases, each ellipse has six contacts. Two of these cases can be derived from the densest packing of circles by affine transformations and, therefore, have the same density, namely  $\rho = 0.9069$ , irrespective of the shape of the ellipses (Matsumoto & Nowacki, 1966). Presumably for the other six cases this density can only be reached (but not exceeded) if the ellipses become circles. A corresponding proof is in progress (Matsumoto, 1968; Tanemura & Matsumoto, 1992; Matsumoto & Tanemura, 1995).

Very little systematic work seems to be carried out on homogeneous or heterogeneous packings of ellipsoids. Matsumoto & Nowacki (1966) derived packings of ellipsoids with contact numbers 12 and high densities by affine deformation of cubic and hexagonal closest packings of spheres. They postulate (without proof) the following: Densest packings of ellipsoids have the same contact number and density as closest packings of spheres and can be derived always from closest sphere packings by affine transformations. If this assumption is true, densest packings of ellipsoids would necessarily consist of parallel ellipsoids only.

Packings of ellipsoids seemed to be useful for the interpretation of the arrangements of organic molecules in crystals. The studies of Kitaigorodsky (1946, 1961, 1973), however, showed that molecular crystals may rather be regarded as dense packings of molecules with irregular shape.

Heterogeneous packings of ellipsoids may possibly be adequate for the geometrical interpretation of some intermetallic compounds like cubic MgCu<sub>2</sub> (*cf.* Subsection 9.1.1.4) or Cr<sub>3</sub>Si. The ellipsoids enable the use of different 'atomic radii' with respect to neighbouring atoms of the same kind or of different kinds. In MgCu<sub>2</sub>, for example, the magnesium atoms have cubic site symmetry  $43m$  [ $Fd\bar{3}m$ , 8( $a$ )] and therefore can only be represented by spheres. The Cu atoms [16( $d$ )] with site symmetry  $\bar{3}m$ , however, may be represented by flattened ellipsoids of revolution.