

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.

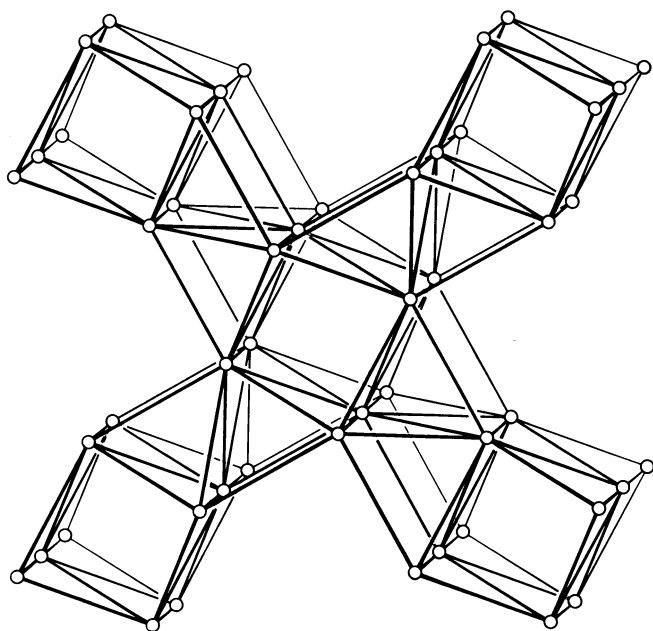


Fig. 9.1.1.6. Sphere packing of type 19 (Table 9.1.1.2) represented by a graph: $k = 10$, $I4/m$, $8(h)$, $xy0$.

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, CaF₂). In addition, contacts between equal atoms may exist (I—I contacts in CsI) or may even be necessary (CdI₂). 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 Li₂O, S in ZnS, O in olivine), but numerous examples for non-closest packings are known in addition (*e.g.* B in CaB₆ with $k = 5$; O in rutile with $k = 11$, type 8 in Table 9.1.1.2; Si in α -ThSi₂ 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

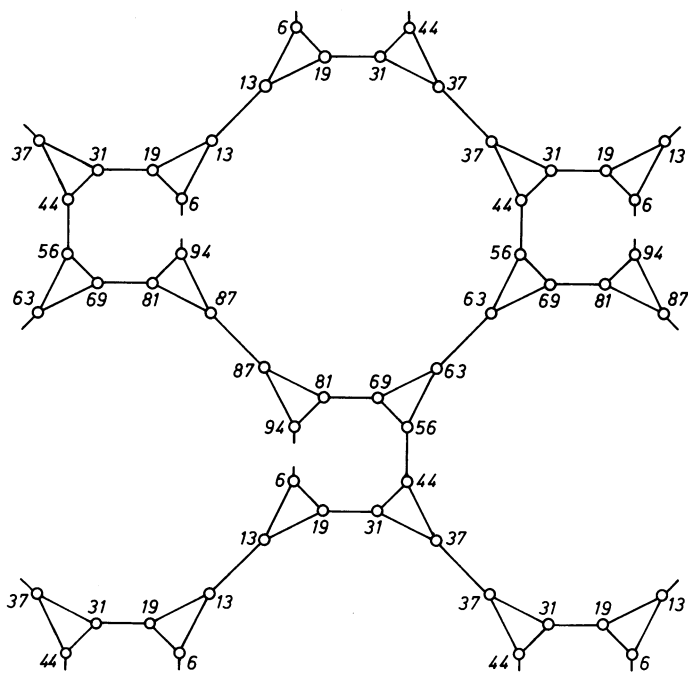


Fig. 9.1.1.7. Least dense sphere packing known so far (type 24 of Table 9.1.1.2) represented by a graph: $k = 3$, $I4_132$, $24(h)$, $\frac{1}{8}, y, \frac{1}{4} - y, z$ coordinates given in multiples of $1/100$.