

Structure of Crystals

W1.1 Crystal Structures Based on Icosahedral Bonding Units

While the $A-A_{12}(\text{cub})$ and $A-A_{12}(\text{hex})$ bonding units appear in the FCC and HCP crystal structures, respectively, the crystal structures that include $A-A_{12}(\text{icos})$ and $A-B_{12}(\text{icos})$ *icosahedral* units are generally much more complicated. An example of a crystal structure based in part on the $A-B_{12}(\text{icos})$ unit, see Fig. 1.11 of the textbook,[†] is the β -tungsten (β -W) crystal structure, an interesting example of which is the intermetallic compound Nb_3Sn . This compound is of the *Frank–Kasper* tetrahedrally close-packed type, with each Sn atom surrounded icosahedrally by 12 Nb atoms at an interatomic distance of 0.296 nm and with each Nb atom at the center of a coordination number CN 14 polyhedron surrounded by four Sn atoms at 0.296 nm, two Nb atoms at 0.264 nm, and eight other Nb atoms at 0.324 nm. Frank–Kasper phases with CN 15 and CN 16 coordination polyhedra also exist (e.g., Fe_7W_6 with CN 12, CN 14, CN 15, and CN 16 coordination polyhedra). In general, larger atoms occupy the CN 15 and CN 16 central sites and smaller atoms occupy the CN 12 and CN 14 central sites.

Another family of close-packed structures based on both icosahedral units and polyhedral units with more than 12 NN is known as the *Laves phases*, the prototype of which is the intermetallic compound MgCu_2 . In this structure each Mg atom is at the center of a CN 16 polyhedron with 12 Cu atoms at 0.292 nm and four Mg atoms at 0.305 nm, while each Cu atom is surrounded icosahedrally by six Mg atoms at 0.305 nm and six Cu atoms at 0.249 nm.

W1.2 Packing Fractions of BCC and CsCl Crystal Structures

The BCC crystal structure results when an identical atom is placed in the body-centered interstitial site of the SC crystal structure. Now $N(\text{atom}) = 2$ and, as can be seen in Fig. W1.2b,[†] three atoms are in contact along the body diagonal (of length $\sqrt{3}a$) of the unit cell in the [111] direction. The atoms along the cube edge are no longer in contact with each other. It follows that $\sqrt{3}a = r + 2r + r = 4r$, and therefore $V(\text{atom}) = \sqrt{3}\pi a^3/16$. Finally,

$$\text{PF(BCC)} = \frac{(2)(\sqrt{3}\pi a^3/16)}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68. \quad (\text{W1.1})$$

[†] The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a “W”; cross-references to material in the textbook appear without the “W.”

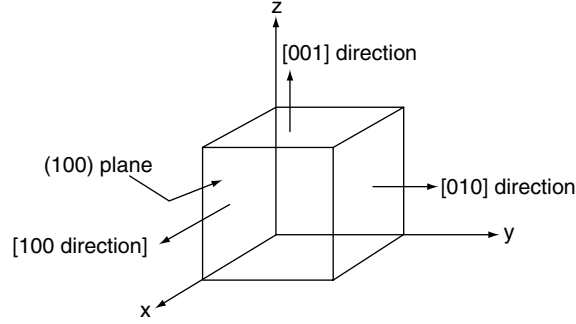


Figure W1.1. Directions in a lattice.

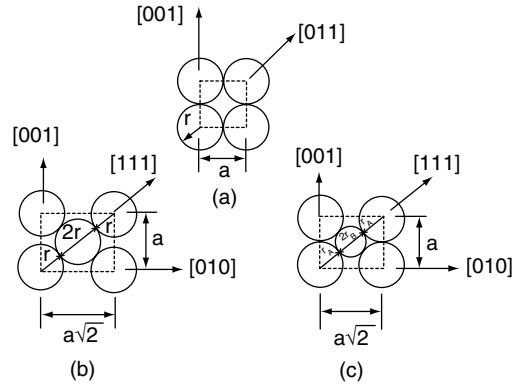


Figure W1.2. Diagrams used in the calculations of packing fractions for the following crystal structures: (a) simple cubic (SC), with the atoms lying in a (100) plane; (b) body-centered cubic (BCC), with the atoms lying in a $(\bar{1}10)$ plane; (c) cesium chloride (CsCl), with the atoms shown in a $(\bar{1}10)$ plane.

The CsCl crystal structure results when a smaller B atom is placed at the body-centered interstitial site of the SC crystal structure, so that it makes contact with the eight larger A atoms surrounding it. For the special case where $r_A = a/2$ and $r_B/r_A = (\sqrt{3} - 1)$, the two A atoms remain in contact along a cube edge, as shown in Fig. W1.2c. It follows, therefore, that $\sqrt{3}a = 2r_A + 2r_B$ along the cube body diagonal. The atom volumes are given by $V(\text{atom A}) = \pi a^3/6$ and $V(\text{atom B}) = (\sqrt{3} - 1)^3 \pi a^3/6$. With one A and one B atom per unit cell, the packing fraction is therefore

$$\begin{aligned} \text{PF} &= \frac{(1)(\pi a^3/6)}{a^3} + \frac{(1)(\sqrt{3} - 1)^3(\pi a^3/6)}{a^3} \\ &= 0.52 + 0.21 = 0.76. \end{aligned} \quad (\text{W1.2})$$

This is the largest possible value for the packing fraction of two spherical atoms of different radii in the CsCl crystal structure and is higher than the value of $\text{PF} = 0.74$ for the FCC and HCP crystal structures.

W1.3 Density of CsCl

To illustrate the use of Eqs. (1.7) and (1.8) of the textbook, consider the case of CsCl where the lattice constant is $a = 0.411$ nm and the atomic masses are $m(\text{Cs}) = 2.207 \times 10^{-25}$ kg and $m(\text{Cl}) = 0.5887 \times 10^{-25}$ kg. Therefore,

$$n(\text{atom}) = \frac{2 \text{ atoms}}{(0.411 \times 10^{-9} \text{ m})^3} = 2.88 \times 10^{28} \text{ atoms/m}^3, \quad (\text{W1.3})$$

$$\begin{aligned} \rho &= \frac{(1)(2.207 \times 10^{-25} \text{ kg})}{(0.411 \times 10^{-9} \text{ m})^3} + \frac{(1)(0.5887 \times 10^{-25} \text{ kg})}{(0.411 \times 10^{-9} \text{ m})^3} \\ &= 4027 \text{ kg/m}^3. \end{aligned} \quad (\text{W1.4})$$

PROBLEM

W1.1 Explain why icosahedral clusters of 13 atoms, corresponding to $A-A_{12}(\text{icos})$, are more stable (i.e., have a lower energy) than FCC or HCP clusters of 13 atoms [i.e., $A-A_{12}(\text{cub})$ and $A-A_{12}(\text{hex})$]. [*Hint*: Count the number of “bonds” formed in each cluster between pairs of atoms that are in contact or, in the case of $A-A_{12}(\text{icos})$, nearly in contact with each other.]