



Crystallographic Directions and Plains

Atomic Radius versus Lattice Parameter: Directions in the unit cell along which atoms are in continuous contact are close-packed directions. In simple structures, particularly those with only one atom per lattice point, we use these directions to calculate the relationship between the apparent size of the atom and the size of the unit cell. Geometrically determining the length of the direction relative to the lattice parameters, and then adding the number of atomic radii along this direction, we can determine the desired relationship. Example 2 illustrates how the relationships between lattice parameters and atomic radius are determined.

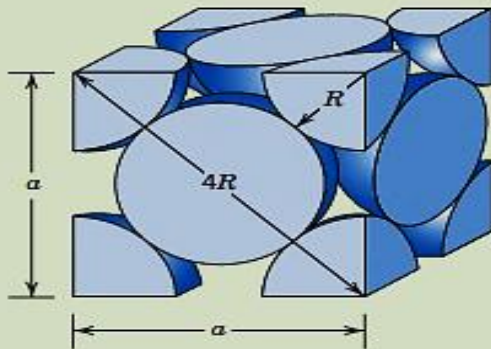
EXAMPLE.1

Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R .

Solution

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Since the unit cell is a cube, its volume is a^3 , where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2$$

or, solving for a ,

$$a = 2R\sqrt{2}$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2}$$

Coordination Number: The coordination number is the number of atoms touching a particular atom, or the number of nearest neighbors for that particular atom. This is one indication of how tightly and efficiently atoms are packed together. For ionic solids, the coordination number of cations is defined as the number of nearest anions. The coordination number of anions is the number of nearest cations. In cubic structures containing only one atom per lattice point, atoms have a coordination number related to the lattice structure. By inspecting the unit cells in figure 3, we see that each atom in the **SC** structure has a coordination number of **six**, while each atom in the **BCC** structure has **eight** nearest neighbors. Later, we will show that each atom in the **FCC** structure has a coordination number of **12**, which is the maximum.

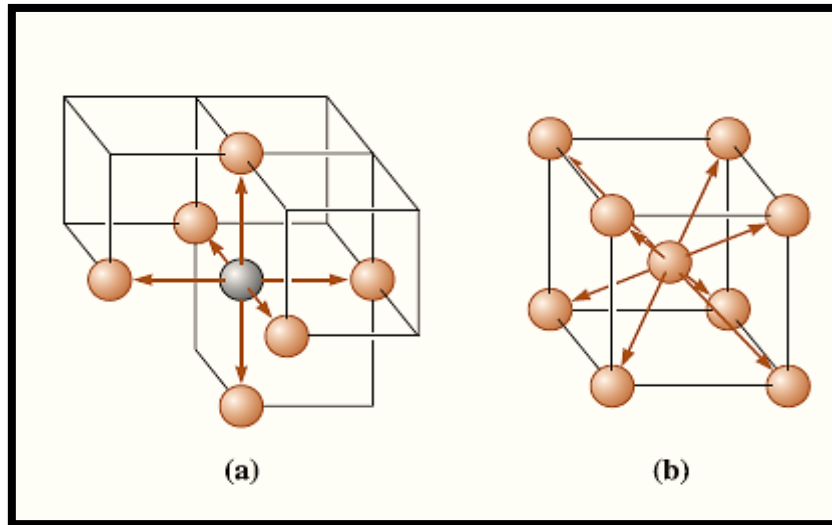


Figure 1. Illustration of coordinations in (a) SC and (b) BCC unit cells. Six atoms touch each atom in SC, while eight atoms touch each atom in the BCC unit cell.

Atomic Packing Factor (APF): The packing factor is the fraction of space occupied by atoms, assuming that atoms are hard spheres sized so that they touch their closest neighbor. The general expression for the packing factor is:

$$\text{APF} = \frac{(\text{number of atoms/unit cell}) \cdot (\text{volume of each atom})}{\text{volume of unit cell}}$$

EXAMPLE.2 Calculating the Packing Factor for the FCC cell.

Computation of the Atomic Packing Factor for FCC

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R . The volume for a sphere is $\frac{4}{3}\pi R^3$, and because there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

From Example Problem 3.1, the total unit cell volume is

$$V_C = 16R^3\sqrt{2}$$

Therefore, the atomic packing factor is

$$\text{APF} = \frac{V_S}{V_C} = \frac{(\frac{16}{3})\pi R^3}{16R^3\sqrt{2}} = 0.74$$



The FCC arrangement represents a close-packed structure (CP) (i.e., the packing fraction is the highest possible with atoms of one size). The SC and BCC structures are relatively open. We will see later that it is possible to have a hexagonal structure that has the same packing efficiency as the FCC structure. This structure is known as the hexagonal close-packed structure (HCP). Metals with only metallic bonding are packed as efficiently as possible. Metals with mixed bonding, such as iron, may have unit cells with less than the maximum packing factor. No commonly encountered engineering metals or alloys have the SC structure, although this structure is found in ceramic materials.

Density: The theoretical density of a material can be calculated using the properties of the crystal structure. The general formula is:

$$\text{Density } (\rho) = \frac{(\text{number of atoms/unit cell})(\text{atomic mass})}{(\text{volume of unit cell})(\text{Avogadro's number})}$$

If a material is ionic and consists of different types of atoms or ions, this formula will have to be modified to reflect these differences. Example.4 illustrates how to determine the density of BCC iron.

EXAMPLE.3 Determining the Density of BCC Iron

Determine the density of BCC iron, which has a lattice parameter of **0.2866 nm**.

SOLUTION

For a BCC cell,

$$\text{Atoms/cell} = 2$$

$$a_0 = 0.2866 \text{ nm} = 2.866 \times 10^{-8} \text{ cm}$$

$$\text{Atomic mass of iron} = 55.847 \text{ g/mol}$$

$$\text{Volume of unit cell} = a_0^3 = (2.866 \times 10^{-8} \text{ cm})^3 = 23.54 \times 10^{-24} \text{ cm}^3/\text{cell}$$

$$\text{Avogadro's number } N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

$$\text{Density } \rho = \frac{(\text{number of atoms/cell})(\text{atomic mass of iron})}{(\text{volume of unit cell})(\text{Avogadro's number})}$$

$$\rho = \frac{(2)(55.847)}{(23.54 \times 10^{-24})(6.02 \times 10^{23})} = 7.882 \text{ g/cm}^3$$

The measured density is 7.870 g/cm^3 . The slight discrepancy between the theoretical and measured densities is a consequence of defects in the material. As mentioned before, the term “defect” in this context means imperfections with regard to the atomic arrangement.

The Hexagonal Close-Packed Structure: A special form of the hexagonal structure, the hexagonal close-packed structure (HCP), is shown in figure 2. The unit cell is the skewed prism, shown separately. The HCP structure has one lattice point per cell (one from each of the eight corners of the prism) but two atoms are associated with each lattice point. One atom is located at a corner, while the second is located within the unit cell. Thus, the basis is 2.

In metals with an ideal HCP structure, the a_0 and c_0 axes are related by the ratio $c_0 = a_0 = 1.633$. Most HCP metals, however, have c_0 / a_0 ratios that differ slightly from the ideal value because of mixed bonding. Because the HCP structure, like the FCC structure, has the most efficient packing factor of **0.74** and a coordination number of **12**, a number of metals possess this structure. Table (1) summarizes the characteristics of crystal structures of some metals.

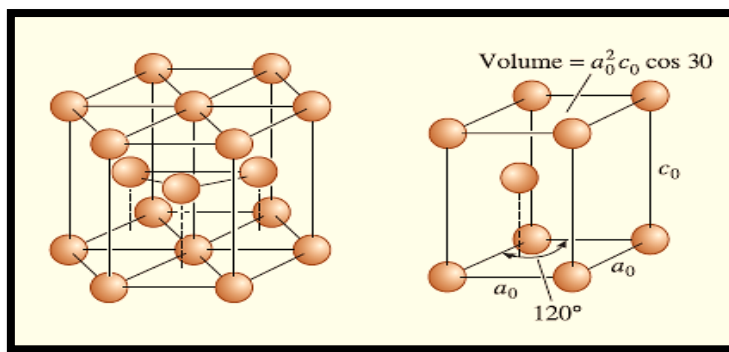


Figure 2. The hexagonal close packed (HCP) structure (left) and its unit cell.

Table 1. Crystal structure characteristics of some metals

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α -Mn
Body-centered cubic	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

Structures of ionically bonded materials can be viewed as formed by the packing (cubic or hexagonal) of anions. Cations enter into the interstitial sites or holes that remain after the packing of anions.

Determination of HCP Unit Cell Volume

- Calculate the volume of an HCP unit cell in terms of its a and c lattice parameters.
- Now provide an expression for this volume in terms of the atomic radius, R , and the c lattice parameter.

Solution

- We use the adjacent reduced-sphere HCP unit cell to solve this problem.

Now, the unit cell volume is just the product of the base area times the cell height, c . This base area is just three times the area of the parallelepiped $ACDE$ shown below. (This $ACDE$ parallelepiped is also labeled in the above unit cell.)

The area of $ACDE$ is just the length of \overline{CD} times the height \overline{BC} . But \overline{CD} is just a , and \overline{BC} is equal to

$$\overline{BC} = a \cos(30^\circ) = \frac{a\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(a)\left(\frac{a\sqrt{3}}{2}\right) = \frac{3a^2\sqrt{3}}{2}$$

Again, the unit cell volume V_C is just the product of the AREA and c ; thus,

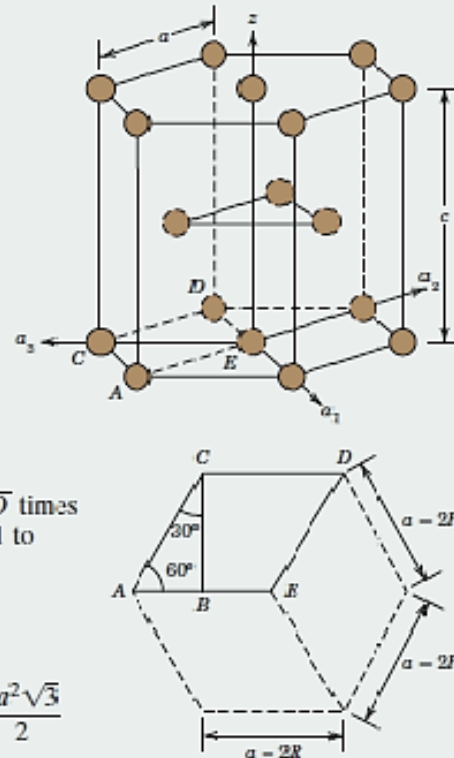
$$\begin{aligned} V_C &= \text{AREA}(c) \\ &= \left(\frac{3a^2\sqrt{3}}{2}\right)(c) \\ &= \frac{3a^2c\sqrt{3}}{2} \end{aligned} \tag{3.7a}$$

- For this portion of the problem, all we need do is realize that the lattice parameter a is related to the atomic radius R as

$$a = 2R$$

Now making this substitution for a in Equation 3.7a gives

$$\begin{aligned} V_C &= \frac{3(2R)^2c\sqrt{3}}{2} \\ &= 6R^2c\sqrt{3} \end{aligned} \tag{3.7b}$$



Allotropic or Polymorphic Transformations

Materials with more than one crystal structure at different temperature are called **allotropic** or **polymorphic**. The term allotropy is normally reserved for this behavior in pure elements, while the term polymorphism is used for compounds. You may have noticed in Table 2 that some metals, such as **iron** and **titanium**, have more than one crystal structure. At low temperatures, iron has the BCC structure, but at higher temperatures, iron transforms to an FCC structure. These transformations result in changes in properties of materials and form the basis for the heat treatment of steels and many other alloys.

Many ceramic materials, such as silica (SiO₂) and zirconia (ZrO₂), also are polymorphic. A volume change may accompany the transformation during heating or cooling; if not properly controlled, this volume change causes the ceramic material to crack and fail.

Polymorphism is also of central importance to several other applications. The properties of some materials can depend quite strongly on the type of polymorph. For example, the dielectric properties of such materials as **PZT** and **BaTiO₃** depend upon the particular polymorphic form.

EXAMPLE.4 Calculating Volume Changes in Polymorphs of Zirconia (ZrO₂)

Calculate the percent volume change as zirconia (ZrO₂) transforms from a tetragonal to a monoclinic structure. The lattice constants for the monoclinic unit cells are: [(**a = 5.156**), (**b = 5.191**), and (**c = 5.304**)] Å°, respectively. The angle **b** for the monoclinic unit cell is (**98.9°**). The lattice constants for the tetragonal unit cell are [(**a = 5.094**) and (**c = 5.304**)] Å°, respectively. Does the zirconia expand or contract during this transformation? What is the implication of this transformation on the mechanical properties of zirconia ceramics ?

SOLUTION

The volume of a tetragonal unit cell is given by $V = a^2c = (5.094)^2(5.304) = 134.33 \text{ \AA}^3$.

The volume of a monoclinic unit cell is given by $V = abc \sin \beta = (5.156)(5.191)(5.304) \sin(98.9) = 140.25 \text{ \AA}^3$.

Thus, there is an expansion of the unit cell as ZrO₂ transforms from a tetragonal to monoclinic form.

The percent change in volume = (final volume – initial volume)/(initial volume) * 100 = $(140.25 - 134.33 \text{ \AA}^3)/134.33 \text{ \AA}^3 * 100 = 4.42\%$.

Points, Directions, and Planes in the Unit Cell

Coordinates of Points: We can locate certain points, such as atom positions, in the lattice or unit cell by constructing the right-handed coordinate system in figure 3. Distance is measured in terms of the number of lattice parameters we must move in each of the x, y, and z coordinates to get from the origin to the point in question. The coordinates are written as the three distances, with commas separating the numbers.

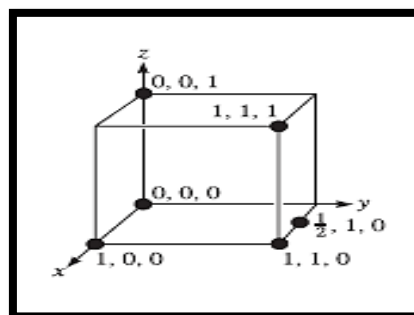


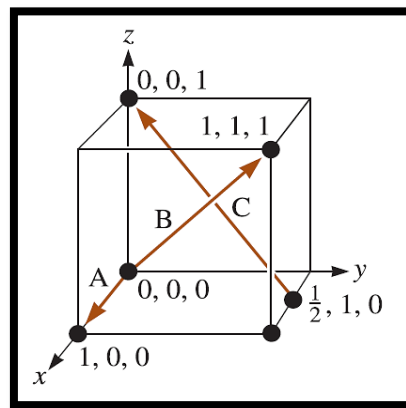
Figure 3. Coordinates of selected points in the unit cell. The number refers to the distance from the origin in terms of lattice parameters.

Directions in the Unit Cell: Certain directions in the unit cell are of particular importance. Miller indices for directions are the shorthand notation used to describe these directions. The procedure for finding the Miller indices for directions is as follows:

1. Using a right-handed coordinate system, determine the coordinates of two points that lie on the direction (**Intercept**).
2. Subtract the coordinates of the “tail” point from the coordinates of the “head” point to obtain the number of lattice parameters traveled in the direction of each axis of the coordinate system (**Reciprocals**).
3. Clear fractions and/or reduce the results obtained from the subtraction to lowest integers (**Reduction**).
4. Enclose the numbers in square brackets []. If a negative sign is produced, represent the negative sign with a bar over the number (**Enclosure**).

EXAMPLE.5 Determining Miller Indices of Directions

Determine the Miller indices of directions A, B, and C in figure below.



SOLUTION

Direction A

1. Two points are 1, 0, 0, and 0, 0, 0
2. $1, 0, 0 - 0, 0, 0 = 1, 0, 0$
3. No fractions to clear or integers to reduce
4. [100]

Direction B

1. Two points are 1, 1, 1 and 0, 0, 0
2. $1, 1, 1 - 0, 0, 0 = 1, 1, 1$
3. No fractions to clear or integers to reduce
4. [111]

Direction C

1. Two points are 0, 0, 1 and $\frac{1}{2}, 1, 0$
2. $0, 0, 1 - \frac{1}{2}, 1, 0 = -\frac{1}{2}, -1, 1$
3. $2(-\frac{1}{2}, -1, 1) = -1, -2, 2$
4. $[\bar{1}\bar{2}2]$