

## CHAPTER 4

### IMPERFECTIONS IN SOLIDS

#### PROBLEM SOLUTIONS

#### **Vacancies and Self-Interstitials**

4.1 Calculate the fraction of atom sites that are vacant for lead at its melting temperature of 327°C (600 K). Assume an energy for vacancy formation of 0.55 eV/atom.

#### Solution

In order to compute the fraction of atom sites that are vacant in lead at 600 K, we must employ Equation 4.1. As stated in the problem,  $Q_v = 0.55$  eV/atom. Thus,

$$\begin{aligned}\frac{N_v}{N} &= \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.55 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(600 \text{ K})}\right] \\ &= 2.41 \times 10^{-5}\end{aligned}$$

## Impurities in Solids

4.4 Below, atomic radius, crystal structure, electronegativity, and the most common valence are tabulated, for several elements; for those that are nonmetals, only atomic radii are indicated.

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Pt	0.1387	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Which of these elements would you expect to form the following with copper:

- (a) A substitutional solid solution having complete solubility
- (b) A substitutional solid solution of incomplete solubility
- (c) An interstitial solid solution

### Solution

In this problem we are asked to cite which of the elements listed form with Cu the three possible solid solution types. For complete substitutional solubility the following criteria must be met: 1) the difference in atomic radii between Cu and the other element ( $\Delta R\%$ ) must be less than  $\pm 15\%$ , 2) the crystal structures must be the same, 3) the electronegativities must be similar, and 4) the valences should be the same, or nearly the same. Below are tabulated, for the various elements, these criteria.

<u>Element</u>	<u><math>\Delta R\%</math></u>	<u>Crystal Structure</u>	<u><math>\Delta</math>Electro-negativity</u>	<u>Valence</u>
<b>Cu</b>		<b>FCC</b>		<b>2+</b>
C	-44			

H	-64			
O	-53			
Ag	+13	FCC	0	1+
Al	+12	FCC	-0.4	3+
Co	-2	HCP	-0.1	2+
Cr	-2	BCC	-0.3	3+
Fe	-3	BCC	-0.1	2+
Ni	-3	FCC	-0.1	2+
Pd	+8	FCC	+0.3	2+
Pt	+9	FCC	+0.3	2+
Zn	+4	HCP	-0.3	2+

(a) Ni, Pd, and Pt meet all of the criteria and thus form substitutional solid solutions having complete solubility. At elevated temperatures Co and Fe experience allotropic transformations to the FCC crystal structure, and thus display complete solid solubility at these temperatures.

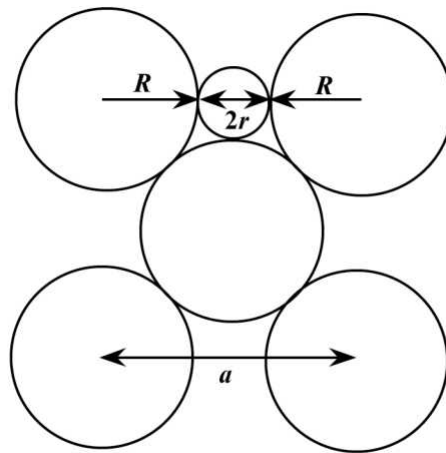
(b) Ag, Al, Co, Cr, Fe, and Zn form substitutional solid solutions of incomplete solubility. All these metals have either BCC or HCP crystal structures, and/or the difference between their atomic radii and that for Cu are greater than  $\pm 15\%$ , and/or have a valence different than 2+.

(c) C, H, and O form interstitial solid solutions. These elements have atomic radii that are significantly smaller than the atomic radius of Cu.

4.5 For both FCC and BCC crystal structures, there are two different types of interstitial sites. In each case, one site is larger than the other, and is normally occupied by impurity atoms. For FCC, this larger one is located at the center of each edge of the unit cell; it is termed an octahedral interstitial site. On the other hand, with BCC the larger site type is found at  $0 \frac{1}{2} \frac{1}{4}$  positions—that is, lying on  $\{100\}$  faces, and situated midway between two unit cell edges on this face and one-quarter of the distance between the other two unit cell edges; it is termed a tetrahedral interstitial site. For both FCC and BCC crystal structures, compute the radius  $r$  of an impurity atom that will just fit into one of these sites in terms of the atomic radius  $R$  of the host atom.

### Solution

In the drawing below is shown an octahedral interstitial site in a face-centered cubic (FCC) unit cell. The site is located at the center of the edge.



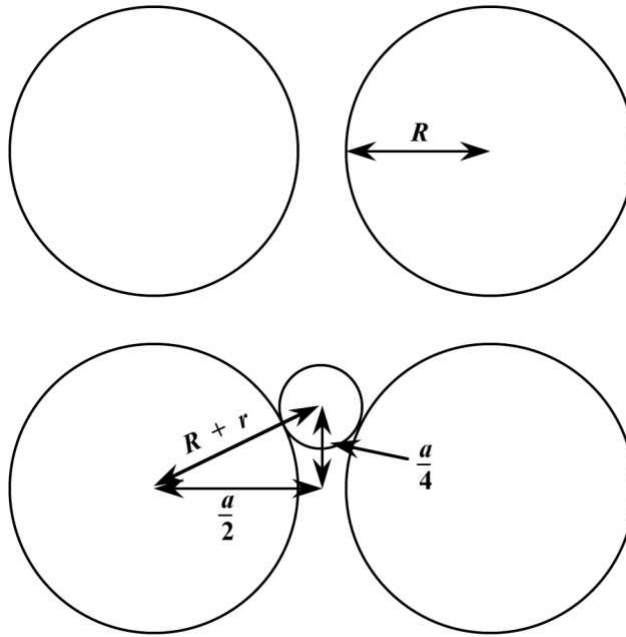
The diameter of an atom that will just fit into this site ( $2r$ ) is just the difference between that unit cell edge length ( $a$ ) and the radii of the two host atoms that are located on either side of the site ( $R$ ); that is

$$2r = a - 2R$$

However, for FCC  $a$  is related to  $R$  according to Equation 3.1 as  $a = 2R\sqrt{2}$ ; therefore, solving for  $r$  from the above equation gives

$$r = \frac{a - 2R}{2} = \frac{2R\sqrt{2} - 2R}{2} = 0.41R$$

A  $\{100\}$  face of a BCC unit cell is shown below.



The interstitial atom that just fits into this interstitial site is shown by the small circle. It is situated in the plane of this (100) face, midway between the two vertical unit cell edges, and one quarter of the distance between the bottom and top cell edges. From the right triangle that is defined by the three arrows we may write

$$\left(\frac{a}{2}\right)^2 + \left(\frac{a}{4}\right)^2 = (R + r)^2$$

However, from Equation 3.3,  $a = \frac{4R}{\sqrt{3}}$ , and, therefore, making this substitution, the above equation takes the form

$$\left(\frac{4R}{2\sqrt{3}}\right)^2 + \left(\frac{4R}{4\sqrt{3}}\right)^2 = R^2 + 2Rr + r^2$$

After rearrangement the following quadratic equation results:

$$r^2 + 2Rr - 0.667 R^2 = 0$$

And upon solving for r:

$$r = \frac{-(2R) \pm \sqrt{(2R)^2 - (4)(1)(-0.667 R^2)}}{2}$$

$$= \frac{-2R \pm 2.582 R}{2}$$

And, finally

$$r(+) = \frac{-2R + 2.582 R}{2} = 0.291 R$$

$$r(-) = \frac{-2R - 2.582 R}{2} = -2.291 R$$

Of course, only the  $r(+)$  root is possible, and, therefore,  $r = 0.291R$ .

Thus, for a host atom of radius  $R$ , the size of an interstitial site for FCC is approximately 1.4 times that for BCC.

4.9 Calculate the composition, in weight percent, of an alloy that contains 218.0 kg titanium, 14.6 kg of aluminum, and 9.7 kg of vanadium.

Solution

The concentration, in weight percent, of an element in an alloy may be computed using a modified form of Equation 4.3. For this alloy, the concentration of titanium ( $C_{Ti}$ ) is just

$$\begin{aligned} C_{Ti} &= \frac{m_{Ti}}{m_{Ti} + m_{Al} + m_V} \times 100 \\ &= \frac{218 \text{ kg}}{218 \text{ kg} + 14.6 \text{ kg} + 9.7 \text{ kg}} \times 100 = 89.97 \text{ wt\%} \end{aligned}$$

Similarly, for aluminum

$$C_{Al} = \frac{14.6 \text{ kg}}{218 \text{ kg} + 14.6 \text{ kg} + 9.7 \text{ kg}} \times 100 = 6.03 \text{ wt\%}$$

And for vanadium

$$C_V = \frac{9.7 \text{ kg}}{218 \text{ kg} + 14.6 \text{ kg} + 9.7 \text{ kg}} \times 100 = 4.00 \text{ wt\%}$$

4.16 Determine the approximate density of a high-leaded brass that has a composition of 64.5 wt% Cu, 33.5 wt% Zn, and 2.0 wt% Pb.

Solution

In order to solve this problem, Equation 4.10a is modified to take the following form:

$$\rho_{\text{ave}} = \frac{100}{\frac{C_{\text{Cu}}}{\rho_{\text{Cu}}} + \frac{C_{\text{Zn}}}{\rho_{\text{Zn}}} + \frac{C_{\text{Pb}}}{\rho_{\text{Pb}}}}$$

And, using the density values for Cu, Zn, and Pb—i.e., 8.94 g/cm<sup>3</sup>, 7.13 g/cm<sup>3</sup>, and 11.35 g/cm<sup>3</sup>—(as taken from inside the front cover of the text), the density is computed as follows:

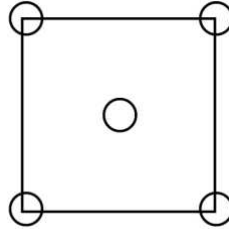
$$\begin{aligned}\rho_{\text{ave}} &= \frac{100}{\frac{64.5 \text{ wt}\%}{8.94 \text{ g/cm}^3} + \frac{33.5 \text{ wt}\%}{7.13 \text{ g/cm}^3} + \frac{2.0 \text{ wt}\%}{11.35 \text{ g/cm}^3}} \\ &= 8.27 \text{ g/cm}^3\end{aligned}$$



- 3.54 (a) Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius  $R$ .  
 (b) Compute and compare planar density values for these same two planes for nickel.

Solution

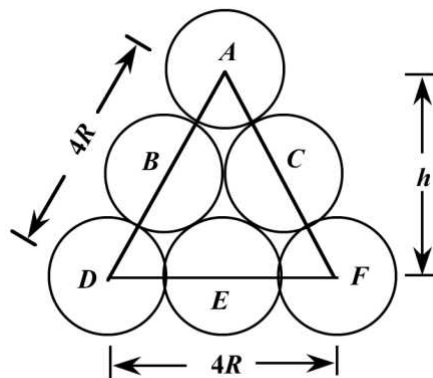
- (a) In the figure below is shown a (100) plane for an FCC unit cell.



For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this FCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length,  $2R\sqrt{2}$ . Hence, the planar density for this (100) plane is just

$$\begin{aligned} PD_{100} &= \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}} \\ &= \frac{2 \text{ atoms}}{8R^2} = \frac{1}{4R^2} \end{aligned}$$

That portion of an FCC (111) plane contained within a unit cell is shown below.



There are six atoms whose centers lie on this plane, which are labeled A through F. One-sixth of each of atoms A, D, and F are associated with this plane (yielding an equivalence of one-half atom), with one-half of each of atoms B, C, and E (or an equivalence of one and one-half atoms) for a total equivalence of two atoms. Now, the area of the triangle shown in the above figure is equal to one-half of the product of the base length and the height,  $h$ . If we consider half of the triangle, then

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

which leads to  $h = 2R\sqrt{3}$ . Thus, the area is equal to

$$\text{Area} = \frac{4R(h)}{2} = \frac{(4R)(2R\sqrt{3})}{2} = 4R^2\sqrt{3}$$

And, thus, the planar density is

$$\begin{aligned} \text{PD}_{111} &= \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}} \\ &= \frac{2 \text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}} \end{aligned}$$

(b) From the table inside the front cover, the atomic radius for nickel is 0.125 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(\text{Ni}) = \frac{1}{4R^2} = \frac{1}{4(0.125 \text{ nm})^2} = 16.00 \text{ nm}^{-2} = 1.600 \times 10^{19} \text{ m}^{-2}$$

While for the (111) plane

$$\text{PD}_{111}(\text{Ni}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}(0.125 \text{ nm})^2} = 18.48 \text{ nm}^{-2} = 1.848 \times 10^{19} \text{ m}^{-2}$$

## Interfacial Defects

4.27 For an FCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (111) plane? Why? (Note: You may want to consult the solution to Problem 3.54 at the end of Chapter 3.)

### Solution

The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.54, planar densities for FCC (100) and (111) planes are  $\frac{1}{4R^2}$  and  $\frac{1}{2R^2\sqrt{3}}$ , respectively—that is  $\frac{0.25}{R^2}$  and  $\frac{0.29}{R^2}$  (where R is the atomic radius). Thus, since the planar density for (111) is greater, it will have the lower surface energy.

4.29 (a) For a given material, would you expect the surface energy to be greater than, the same as, or less than the grain boundary energy? Why?

(b) The grain boundary energy of a small-angle grain boundary is less than for a high-angle one. Why is this so?

Solution

(a) The surface energy will be greater than the grain boundary energy. For grain boundaries, some atoms on one side of a boundary will bond to atoms on the other side; such is not the case for surface atoms. Therefore, there will be fewer unsatisfied bonds along a grain boundary.

(b) The small-angle grain boundary energy is lower than for a high-angle one because more atoms bond across the boundary for the small-angle, and, thus, there are fewer unsatisfied bonds.

4.31 For each of the following stacking sequences found in FCC metals, cite the type of planar defect that exists:

(a) ...ABC ABC BAC BA...

(b) ...ABC ABC BC ABC...

Now, copy the stacking sequences and indicate the position(s) of planar defect(s) with a vertical dashed line.

Solution

(a) The interfacial defect that exists for this stacking sequence is a twin boundary, which occurs at the indicated position.



The stacking sequence on one side of this position is mirrored on the other side.

(b) The interfacial defect that exists within this FCC stacking sequence is a stacking fault, which occurs between the two lines.



Within this region, the stacking sequence is HCP.