1

a

12.28 *Would you expect Frenkel defects for anions to exist in ionic ceramics in relatively large concentrations? Why or why not?*

Solution

Frenkel defects for anions would not exist in appreciable concentrations because the anion is quite large and is highly unlikely to exist as an interstitial.

b

Dislocations—Linear Defects

4.26 *Cite the relative Burgers vector–dislocation line orientations for edge, screw, and mixed dislocations.*

Solution

The Burgers vector and dislocation line are perpendicular for edge dislocations, parallel for screw dislocations, and neither perpendicular nor parallel for mixed dislocations.

c

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.

2

4.3 *Calculate the activation energy for vacancy formation in aluminum, given that the equilibrium number of vacancies at 500°C (773 K) is 7.57×10^{23} m^{-3}. The atomic weight and density (at 500°C) for aluminum are, respectively, 26.98 g/mol and 2.62 g/cm^3.*

Solution

Upon examination of Equation 4.1, all parameters besides Q_v are given except N, the total number of atomic sites. However, N is related to the density, (ρ_{Al}), Avogadro's number (N_A), and the atomic weight (A_{Al}) according to Equation 4.2 as

$$N = \frac{N_A \rho_{Al}}{A_{Al}}$$

$$= \frac{(6.022 \times 10^{23} \ \text{atoms/mol})(2.62 \ \text{g/cm}^3)}{}$$

$$= \frac{(6.022 \times 10^{23} \ \text{atoms/mol})(2.62 \ \text{g/cm}^3)}{26.98 \ \text{g/mol}}$$

$$= 5.85 \times 10^{22} \ \text{atoms/cm}^3 = 5.85 \times 10^{28} \ \text{atoms/m}^3$$

Now, taking natural logarithms of both sides of Equation 4.1,

$$\ln N_v = \ln N - \frac{Q_v}{kT}$$

and, after some algebraic manipulation

$$Q_v = -kT \ln\left(\frac{N_v}{N}\right)$$

$$= -(8.62 \times 10^{-5} \ \text{eV/atom-K})(500°C + 273 \ \text{K}) \ \ln\left|\frac{7.57 \times 10^{23} \ \text{m}^{-3}}{5.85 \times 10^{28} \ \text{m}^{-3}}\right|$$

$$= 0.75 \ \text{eV/atom}$$

3

4.18 *Some hypothetical alloy is composed of 12.5 wt% of metal A and 87.5 wt% of metal B. If the densities of metals A and B are 4.27 and 6.35 g/cm³, respectively, whereas their respective atomic weights are 61.4 and 125.7 g/mol, determine whether the crystal structure for this alloy is simple cubic, face-centered cubic, or body-centered cubic. Assume a unit cell edge length of 0.395 nm.*

Solution

In order to solve this problem it is necessary to employ Equation 3.5; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{ave} = \frac{nA_{ave}}{V_C N_A}$$

Inasmuch as for each of the possible crystal structures, the unit cell is cubic, then $V_C = a^3$, or

$$\rho_{ave} = \frac{nA_{ave}}{a^3 N_A}$$

And, in order to determine the crystal structure it is necessary to solve for n, the number of atoms per unit cell. For $n = 1$, the crystal structure is simple cubic, whereas for n values of 2 and 4, the crystal structure will be either BCC or FCC, respectively. When we solve the above expression for n the result is as follows:

$$n = \frac{\rho_{ave} a^3 N_A}{A_{ave}}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$n = \frac{\left(\dfrac{100}{\dfrac{C_A}{\rho_A} + \dfrac{C_B}{\rho_B}}\right) a^3 N_A}{\left(\dfrac{100}{\dfrac{C_A}{} + \dfrac{C_B}{}}\right)}$$

$$n = \cfrac{100}{\left(\cfrac{C_A}{A_A} + \cfrac{C_B}{A_B}\right)}$$

Substitution of the concentration values (i.e., $C_A = 12.5$ wt% and $C_B = 87.5$ wt%) as well as values for the other parameters given in the problem statement, into 課 第 above equation gives

$$n = \cfrac{\left(\cfrac{100}{\cfrac{12.5 \text{ wt\%}}{4.27 \text{ g/cm}^3} + \cfrac{87.5 \text{ wt\%}}{6.35 \text{ g/cm}^3}}\right)(3.95 \times 10^{-8} \text{ nm})^3 (6.022 \times 10^{23} \text{ atoms/mol})}{\left(\cfrac{100}{\cfrac{12.5 \text{ wt\%}}{61.4 \text{ g/mol}} + \cfrac{87.5 \text{ wt\%}}{125.7 \text{ g/mol}}}\right)}$$

$$= 2.00 \text{ atoms/unit cell}$$

Therefore, on the basis of this value, the crystal structure is *body-centered cubic*.

4

4.25 *Silver and palladium both have the FCC crystal structure, and Pd forms a substitutional solid solution for all concentrations at room temperature. Compute the unit cell edge length for a 75 wt% Ag–25 wt% Pd alloy. The room-temperature density of Pd is 12.02 g/cm³, and its atomic weight and atomic radius are 106.4 g/mol and 0.138 nm, respectively.*

<u>Solution</u>

First of all, the atomic radii for Ag (using the table inside the front cover) and Pd are 0.144 and 0.138 nm, respectively. Also, using Equation 3.5 it is possible to compute the unit cell volume, and inasmuch as the unit cell is cubic, the unit cell edge length is just the cube root of the volume. However, it is first necessary to calculate the density and average atomic weight of this alloy using Equations 4.10a and 4.11a. Inasmuch as the densities of silver and palladium are 10.49 g/cm³ (as taken from inside the front cover) and 12.02 g/cm³, respectively, the average density is just

$$\rho_{ave} = \frac{100}{\dfrac{C_{Ag}}{\rho_{Ag}} + \dfrac{C_{Pd}}{\rho_{Pd}}}$$

$$= \frac{100}{\dfrac{75 \ wt\%}{10.49 \ g/cm^3} + \dfrac{25 \ wt\%}{12.02 \ g/cm^3}}$$

$$= 10.83 \ g/cm^3$$

And for the average atomic weight

$$A_{ave} = \frac{100}{\dfrac{C_{Ag}}{A_{Ag}} + \dfrac{C_{Pd}}{A_{Pd}}}$$

$$= \frac{100}{\dfrac{75 \ wt\%}{107.9 \ g/mol} + \dfrac{25 \ wt\%}{106.4 \ g/mol}}$$

$$= 107.5 \ g/mol$$

Now, V_C is determined from Equation 3.5 as

$$V_C = \frac{nA_{ave}}{\rho_{ave}N_A}$$

$$= \frac{(4 \text{ atoms/unit cell})(107.5 \text{ g/mol})}{(10.83 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 6.59 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

And, finally

$$a = (V_C)^{1/3}$$

$$= (6.59 \times 10^{-23} \text{ cm}^3/\text{unit cell})^{1/3}$$

$$= 4.04 \times 10^{-8} \text{ cm} = 0.404 \text{ nm}$$

5

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 the atoms on the (100) face of an FCC unit cell; the interstitial site is at the center of the edge.

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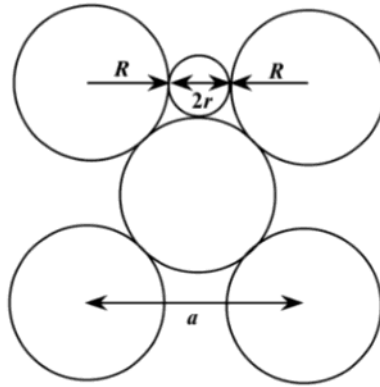

The diameter of an atom that will just fit into this site (2r) is just the difference between that unit cell edge length (a) and the radii of the two host atoms that are located on either side of the site (R); that is

$$2r = a - 2R$$

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

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

A (100) face of a BCC unit cell is shown below.
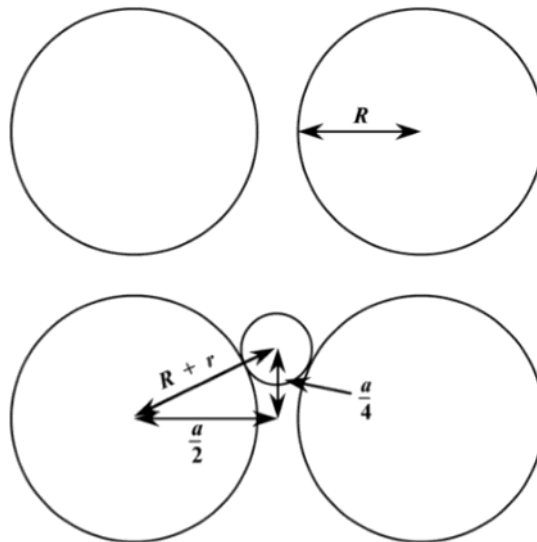
The interstitial atom that just fits into this interstitial site is shown by the small circle. It is situated in the plane of this (100) face, midway between the two vertical unit cell edges, and one quarter of the distance between the bottom and top cell edges. From the right triangle that is defined 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, $a = \dfrac{4R}{\sqrt{3}}$, 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:

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

And upon solving for r:

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

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

And, finally

$$r(+) = \frac{-2R + 2.582R}{2} = 0.291R$$
$$r(-) = \frac{-2R - 2.582R}{2} = -2.291R$$

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.