Sample Exercise 12.1 Calculating Packing Efficiency

It is not possible to pack spheres together without leaving some void spaces between the spheres. *Packing efficiency* is the fraction of space in a crystal that is actually occupied by atoms. Determine the packing efficiency of a face-centered cubic metal.

Solution

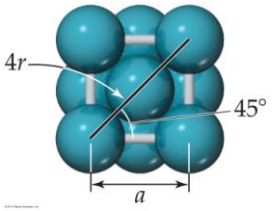
Analyze We must determine the volume taken up by the atoms that reside in the unit cell and divide this number by the volume of the unit cell.

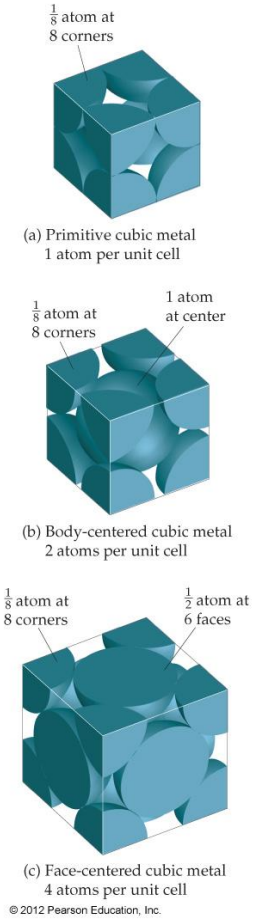
Plan We can calculate the volume taken up by atoms by multiplying the number of atoms per unit cell by the volume of a sphere, $4\pi r^3/3$. To determine the volume of the unit cell, we must first identify the direction along which the atoms touch each other. We can then use geometry to express the length of the cubic unit cell edge, a, in terms of the radius of the atoms. Once we know the edge length, the cell volume is simply a^3.

Solve As shown in Figure 12.12, a face-centered cubic metal has four atoms per unit cell. Therefore, the volume occupied by the atoms is

$$\text{Occupied volume} = 4 \times \left(\frac{4\pi r^3}{3}\right) = \frac{16\pi r^3}{3}$$

For a face-centered cubic metal the atoms touch along the diagonal of a face of the unit cell:





Sample Exercise 12.1 Calculating Packing Efficiency

Continued

Therefore, a diagonal across a face of the unit cell is equal to 4 times the atomic radius, r. Using simple trigonometry, and the identity cos (45°) = $\sqrt{2}/2$, we can show that

$$a = 4r\cos(45°) = 4r\left(\sqrt{2}/2\right) = (2\sqrt{2})r$$

Finally, we calculate the packing efficiency by dividing the volume occupied by atoms by the volume of the cubic unit cell, a^3:

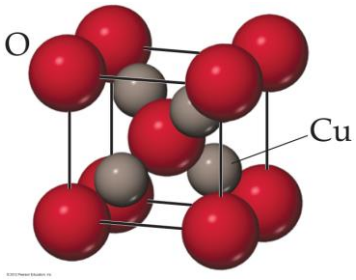
$$\text{Packing efficiency} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{\left(\frac{16}{3}\right)\pi r^3}{(2\sqrt{2})^3 r^3} = 0.74 \text{ or } 74\%$$

Practice Exercise

Determine the packing efficiency by calculating the fraction of space occupied by atoms in a body-centered cubic metal.

Answer: 0.68 or 68%

Sample Exercise 12.2 Calculating the Empirical Formula and Density of an Ionic Solid



The unit cell of a binary compound of copper and oxygen is shown here. Given this image and the ionic radii $r_{Cu}^{+} = 0.74$ Å and $r_{O}^{2-} = 1.26$ Å, **(a)** determine the empirical formula of this compound, **(b)** determine the coordination numbers of copper and oxygen, **(c)** estimate the length of the edge of the cubic unit cell, and **(d)** estimate the density of the compound.

Solution

Analyze and Plan There are four parts to this problem.

(a) To determine the empirical formula we need to determine how many of each type of ion there are per unit cell.

(b) If we can visually determine the coordination number of one of the ions, we can use Equation 12.1 to determine the coordination number of the other ion.

$$\frac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \frac{\text{anion coordination number}}{\text{cation coordination number}} \quad [12.1]$$

(c) To estimate the length of the unit cell edge we must first determine the direction along which the ions touch. We can then use ionic radii and trigonometry to estimate the size of the unit cell.

(d) Because density is an intensive property, the density of the unit cell is the same as the density of a bulk crystal. To calculate the density we must divide the mass of the atoms per unit cell by the volume of the unit cell.

Sample Exercise 12.2 Calculating the Empirical Formula and Density of an Ionic Solid

Continued

Solve

(a) There are four copper ions and one oxygen ion located completely inside the unit cell. In addition there are eight oxygen ions on the corners of the unit cell. Therefore, the number of oxygen ions per unit cell is $1 + 8(1/8) = 2$. Given the fact that there are four copper ions and two oxygen ions per unit cell the empirical formula is Cu_2O. This is copper(I) oxide.

(b) It is easier to see the coordination environments of atoms within the unit cell because we do not have to visualize the atoms in neighboring unit cells. In this example we see that the oxygen ion at the center of the unit cell is tetrahedrally coordinated by four copper ions. The copper ions appear to have two oxygen neighbors, but we can double check this conclusion using Equation 12.1:

$$\frac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \frac{\text{anion coordination number}}{\text{cation coordination number}} \qquad [12.1]$$

$$\text{Cation coordination number} = \text{anion coordination number}\left(\frac{\text{\# of anions per formula unit}}{\text{\# of cations per formula unit}}\right)$$

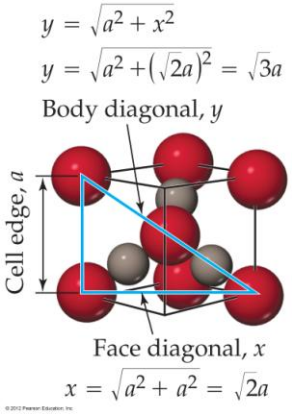
$$\text{Copper coordination number} = 4\left(\frac{1}{2}\right) = 2$$

This result matches our expectations from inspection of the picture.

Sample Exercise 12.2 Calculating the Empirical Formula and Density of an Ionic Solid

Continued

(c) In this structure the ions touch along the body diagonal of the unit cell. This is shown more clearly in the following figure, where the atoms in the front half of the unit cell have been removed for clarity:



Starting in the lower right-hand corner of the unit cell, the distance from the center of the oxygen ion at the corner of the unit cell to the center of the oxygen at the body center of the unit cell is $r(O^{2-}) + 2r(Cu^{+}) + r(O^{2-}) = 2r(O^{2-}) + 2r(Cu^{+})$. Twice this distance is equal to the body diagonal, y.

$$y = 2[2r(Cu^{+}) + 2r(O^{2-})] = 4[r(Cu^{+}) + r(O^{2-})] = 4[0.74\ \text{Å} + 1.26\ \text{Å}] = 8.00\ \text{Å}$$

Using trigonometry and the Pythagorean theorem, it can be shown that the body diagonal of a cube is $\sqrt{3}$ times longer than the edge of the cube, a. We can use this relationship to determine the edge length of the unit cell:

$$a = y/(\sqrt{3}) = (8.00\ \text{Å})/(\sqrt{3}) = 4.62\ \text{Å}$$

Sample Exercise 12.2 Calculating the Empirical Formula and Density of an Ionic Solid

Continued

(d) Because we now know the number of atoms per unit cell and the size of the unit cell, we are in a position to calculate the density from the atomic weights of copper (65.55 amu) and oxygen (16.00 amu) and the appropriate conversions:

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{[4(65.55\ \text{amu}) + 2(16.00\ \text{amu})]\left({}^{1\ \text{g}}/_{6.022\times10^{23}\ \text{amu}}\right)}{\left[(4.62\ \text{Å})\left({}^{1\ \text{cm}}/_{1\times10^{8}\ \text{Å}}\right)\right]^3}$$

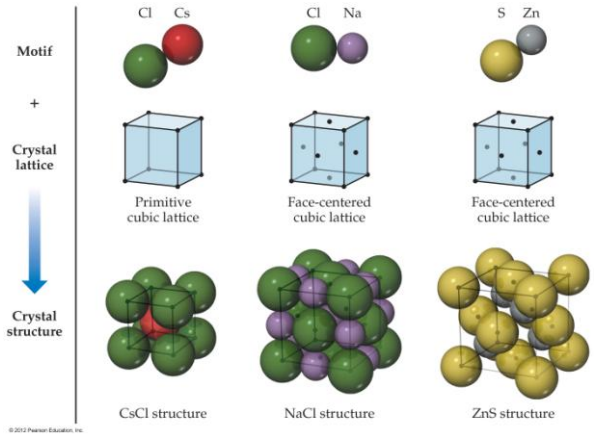
$$\rho = 4.95\ \text{g/cm}^3$$

Check Copper is often found in the +1 oxidation state, so Cu_2O is a realistic empirical formula. The densities of most solids fall between the density of lithium (0.5 g/cm^3) and that of iridium (22.6 g/cm^3), so this value is reasonable.

Practice Exercise

Estimate the length of the cubic unit cell edge and the density of CsCl (Figure 12.26) from the ionic radii of cesium, 1.81 Å, and chloride, 1.67 Å.

Answer: a = 4.02 Å and ρ = 4.31 g/cm^3



Sample Exercise 12.3 Qualitative Comparison of Semiconductor Band Gaps

Will GaP have a larger or smaller band gap than ZnS? Will it have a larger or smaller band gap than GaN?

Solution

Analyze The size of the band gap depends on the vertical and horizontal positions of the elements in the periodic table. The band gap will increase when either of the following conditions is met: (1) The elements are located higher up in the periodic table, where enhanced orbital overlap leads to a larger splitting between bonding and antibonding orbitals, or (2) the horizontal separation between the elements increases, which leads to an increase in the electronegativity difference and bond polarity.

Plan We must look at the periodic table and compare the relative positions of the elements in each case.

Solve Gallium is in the fourth period and group 3A. Phosphorus is in the third period and group 5A. Zinc and sulfur are in the same periods as gallium and phosphorus, respectively. However, zinc, in group 2B, is one element to the left of gallium; sulfur in group 6A is one element to the right of phosphorus. Thus, we would expect the electronegativity difference to be larger for ZnS, which should result in ZnS having a larger band gap than GaP.

For both GaP and GaN the more electropositive element is gallium. So we need only compare the positions of the more electronegative elements, P and N. Nitrogen is located above phosphorus in group 5A. Therefore, based on increased orbital overlap,we would expect GaN to have a larger band gap than GaP.

Check External references show that the band gap of GaP is 2.26 eV, ZnS is 3.6 eV, and GaN is 3.4 eV.

Sample Exercise 12.3 Qualitative Comparison of Semiconductor Band Gaps

Continued

Practice Exercise

Will ZnSe have a larger or smaller band gap than ZnS?

Answer: Because zinc is common to both compounds and selenium is below sulfur in the periodic table, the band gap of ZnSe will be smaller than ZnS.

Sample Exercise 12.4 Identifying Types of Semiconductors

Which of the following elements, if doped into silicon, would yield an n-type semiconductor: Ga, As, or C?

Solution

Analyze An n-type semiconductor means that the dopant atoms must have more valence electrons than the host material. Silicon is the host material in this case.

Plan We must look at the periodic table and determine the number of valence electrons associated with Si, Ga, As, and C. The elements with more valence electrons than silicon are the ones that will produce an n-type material upon doping.

Solve Si is in column 4A, and so has four valence electrons. Ga is in column 3A, and so has three valence electrons. As is in column 5A, and so has five valence electrons; C is in column 4A, and so has four valence electrons. Therefore, As, if doped into silicon, would yield an n-type semiconductor.

Practice Exercise

Suggest an element that could be used to dope silicon to yield a p-type material.

Answer: Because Si is in group 4A, we need to pick an element in group 3A. Boron and aluminum are both good choices—both are in group 3A. In the semiconductor industry boron and aluminum are commonly used dopants for silicon.