CHAPTER 3

FUNDAMENTALS OF CRYSTALLOGRAPHY

PROBLEM SOLUTIONS

3.5   List the point coordinates of the titanium, barium, and oxygen ions for a unit cell of the perovskite crystal structure (Figure 4.9).

<u>Solution</u>

In Figure 4.9, the barium ions are situated at all corner positions. The point coordinates for these ions are as follows: 000, 100, 110, 010, 001, 101, 111, and 011.

The oxygen ions are located at all face-centered positions; therefore, their coordinates are $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}1$, $1\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}1\frac{1}{2}$.
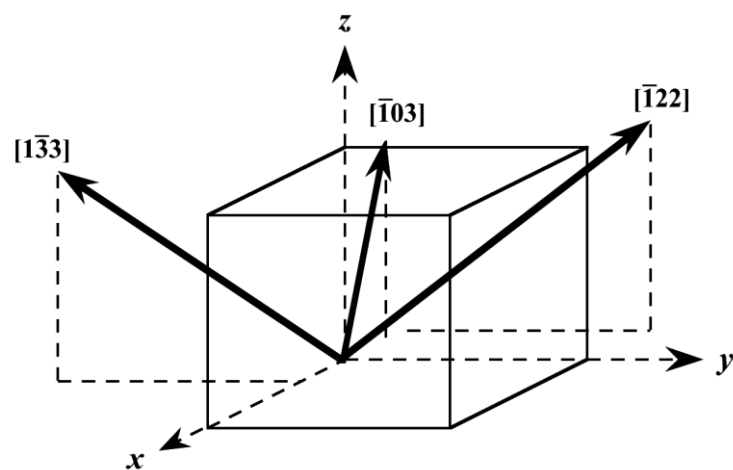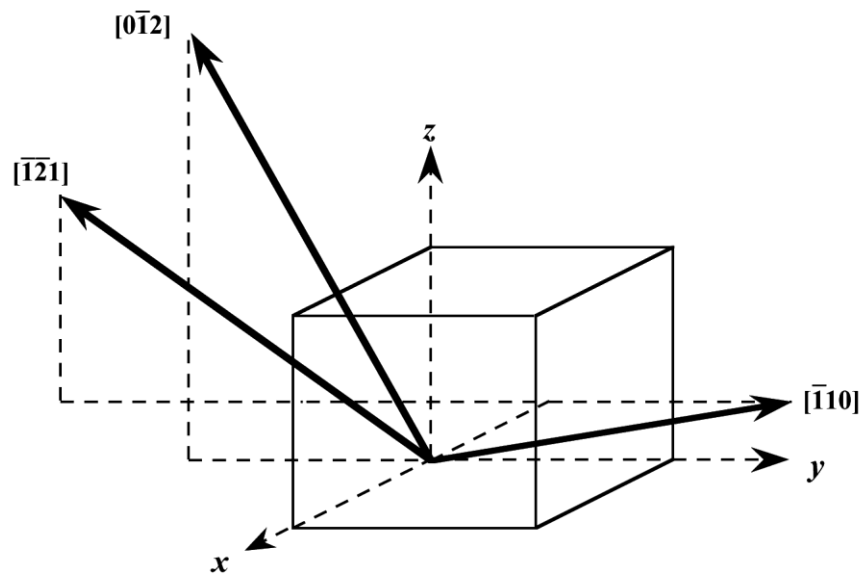
And, finally, the titanium ion resides at the center of the cubic unit cell, with coordinates $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

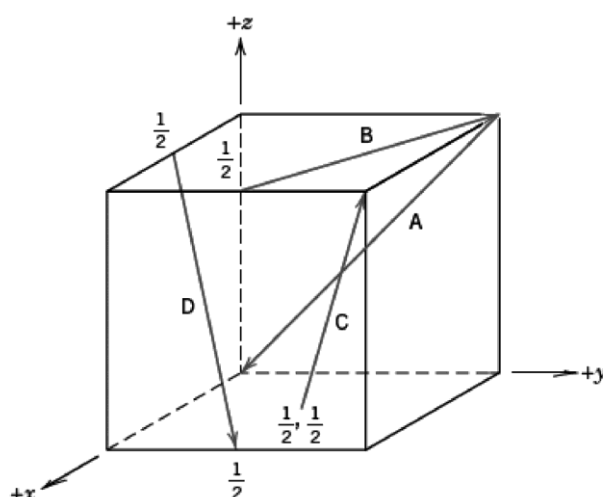3.12 Within a cubic unit cell, sketch the following directions:

    (a) $[\bar{1}10]$,   (e) $[\bar{1}\bar{1}1]$,

    (b) $[\bar{1}\bar{2}1]$,   (f) $[\bar{1}22]$,

    (c) $[0\bar{1}2]$,   (g) $[1\bar{2}\bar{3}]$,

    (d) $[1\bar{3}3]$,   (h) $[\bar{1}03]$.

Solution

The directions asked for are indicated in the cubic unit cells shown below.

3.13   Determine the indices for the directions shown in the following cubic unit cell:

Solution

Direction A is a $[0\bar{1}\bar{1}]$ direction. To solve this problem, we first take note of the vector tail and head coordinates, then take the point coordinate differences. We then use Equation 3.2 selecting a value of n that will produce integer values of u, v, and w. In this case select $n = 1$ as there are no fractions in the differences. Finally, the values of u, v, and w are enclosed in brackets to give the direction designation. This is summarized as follows:

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Head coordinates (x_2, y_2, z_2)	$0a$	$0b$	$0c$
Tail coordinates (x_1, y_1, z_1)	$0a$	b	c
Coordinate differences	$0a$	$-b$	$-c$
Calculated values of u, v, and w	$u = 0$	$v = -1$	$w = -1$
Enclosure		$[0\bar{1}\bar{1}]$	

Direction B is a $[\bar{2}10]$ direction as indicated in the summary below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Head coordinates (x_2, y_2, z_2)	$0a$	b	c
Tail coordinates (x_1, y_1, z_1)	a	$b/2$	c
Coordinate differences	$-a$	$b/2$	0
Calculated values of u, v, and w	$u = -2$	$v = 1$	$w = 0$
Enclosure		$[\bar{2}10]$	

Direction C is a [112] direction as indicated in the summary below.

	x	y	z
Head coordinates (x_2, y_2, z_2)	a	b	c
Tail coordinates (x_1, y_1, z_1)	$a/2$	$b/2$	$0c$
Coordinate differences	$a/2$	$b/2$	c
Calculated values of u, v, and w	$u = 1$	$v = 1$	$w = 2$
Enclosure		[112]	

Direction D is a $[11\bar{2}]$ direction as indicated in the summary below.

	x	y	z
Head coordinates (x_2, y_2, z_2)	a	$b/2$	$0c$
Tail coordinates (x_1, y_1, z_1)	$a/2$	$0b$	c
Coordinate differences	$a/2$	$b/2$	-c
Calculated values of u, v, and w	$u = 1$	$v = 1$	$w = -2$
Enclosure		$[11\bar{2}]$	

3.22   Sketch within a cubic unit cell the following planes:
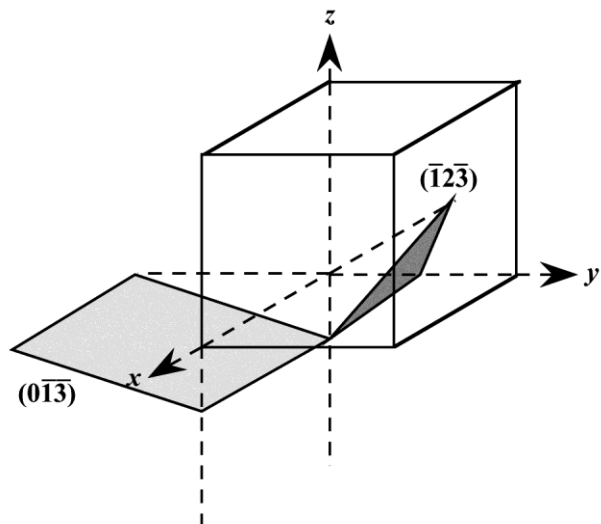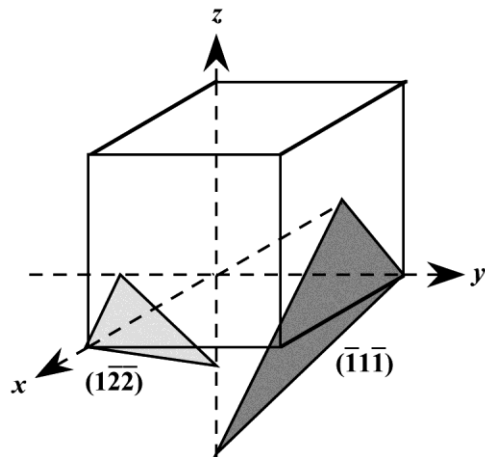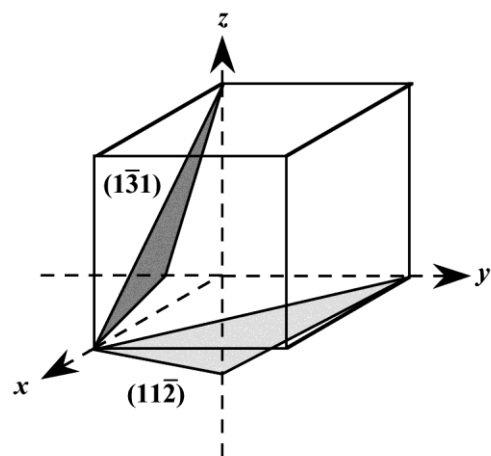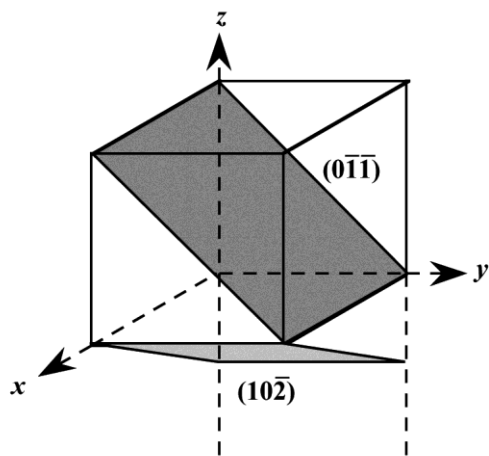(a) $(0\bar{1}\bar{1})$,   (e) $(\bar{1}1\bar{1})$,

(b) $(11\bar{2})$,   (f) $(1\bar{2}\bar{2})$,

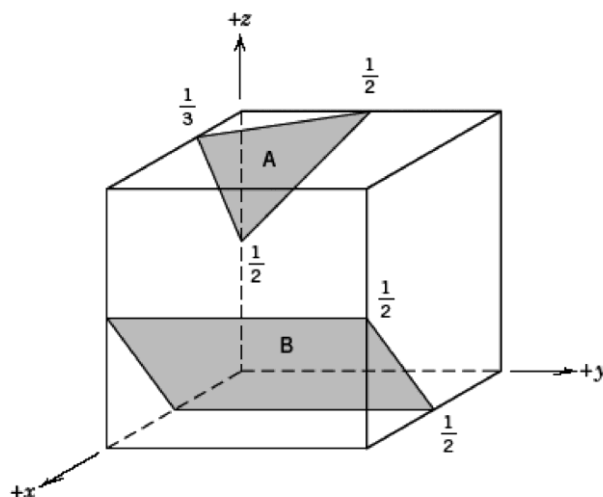(c) $(10\bar{2})$,   (g) $(\bar{1}2\bar{3})$,

(d) $(1\bar{3}1)$,   (h) $(0\bar{1}\bar{3})$

Solution

The planes called for are plotted in the cubic unit cells shown below.

3.24   Determine the Miller indices for the planes shown in the following unit cell:

<u>Solution</u>

For plane A we will move the origin of the coordinate system one unit cell distance to the upward along the z axis; thus, this is a $(32\bar{2})$ plane, as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Intercepts	$\dfrac{a}{3}$	$\dfrac{b}{2}$	$-\dfrac{c}{2}$
Intercepts in terms of a, b, and c	$\dfrac{1}{3}$	$\dfrac{1}{2}$	$-\dfrac{1}{2}$
Reciprocals of intercepts	3	2	-2
Reduction		(not necessary)	
Enclosure		$(32\bar{2})$	

For plane B we will move the original of the coordinate system on unit cell distance along the x axis; thus, this is a $(\bar{1}01)$ plane, as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Intercepts	$-\dfrac{a}{2}$	∞b	$\dfrac{c}{2}$
Intercepts in terms of a, b, and c	$-\dfrac{1}{2}$	∞	$\dfrac{1}{2}$
Reciprocals of intercepts	-2	0	2
Reduction	-1	0	1
Enclosure		$(\bar{1}01)$	

CHAPTER 4

STRUCTUREs OF CRYSTALLINE SOLIDS

PROBLEM SOLUTIONS

4.3   Show that the atomic packing factor for BCC is 0.68.

    Solution

    The atomic packing factor is defined as the ratio of sphere volume to the total unit cell volume, or

$$\text{APF} = \frac{V_S}{V_C}$$

Since there are two spheres associated with each unit cell for BCC

$$V_S = 2(\text{sphere volume}) = 2\left(\frac{4\pi R^3}{3}\right) = \frac{8\pi R^3}{3}$$

Also, the unit cell has cubic symmetry, that is $V_C = a^3$. But a depends on R according to Equation 4.4, and

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64\,R^3}{3\sqrt{3}}$$

Thus,

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi\,R^3/3}{64\,R^3/3\sqrt{3}} = 0.68$$

4.7   Calculate the radius of an iridium atom, given that Ir has an FCC crystal structure, a density of 22.4 g/cm^3, and an atomic weight of 192.2 g/mol.

<u>Solution</u>

We are asked to determine the radius of an iridium atom, given that Ir has an FCC crystal structure. For FCC, $n = 4$ atoms/unit cell, and $V_C = 16R^3\sqrt{2}$ (Equation 4.6). Now,

$$\rho = \frac{nA_{\text{Ir}}}{V_C N_A}$$

$$= \frac{nA_{Ir}}{(16R^3\sqrt{2})N_A}$$

And solving for R from the above expression yields

$$R = \left[\frac{nA_{\text{Ir}}}{16\rho N_A \sqrt{2}}\right]^{1/3}$$

$$= \left[\frac{(4 \text{ atoms/unit cell})(192.2 \text{ g/mol})}{(16)(22.4 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})(\sqrt{2})}\right]^{1/3}$$

$$= 1.36 \times 10^{-8} \text{ cm} = 0.136 \text{ nm}$$

4.13   The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each, determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.

Alloy	Atomic Weight (g/mol)	Density (g/cm³)	Atomic Radius (nm)
A	77.4	8.22	0.125
B	107.6	13.42	0.133
C	127.3	9.23	0.142

Solution

For each of these three alloys we need, by trial and error, to calculate the density using Equation 4.8, and compare it to the value cited in the problem. For SC, BCC, and FCC crystal structures, the respective values of n are 1, 2, and 4, whereas the expressions for a (since $V_C = a^3$) are $2R$, $2R\sqrt{2}$, and $\dfrac{4R}{\sqrt{3}}$.

For alloy A, let us calculate ρ assuming a simple cubic crystal structure.

$$\rho = \frac{nA_A}{V_C N_A}$$

$$= \frac{nA_A}{(2R)^3 N_A}$$

$$= \frac{(1\ \text{atom/unit cell})(77.4\ \text{g/mol})}{\left\{\left[(2)(1.25 \times 10^{-8})\right]^3/\text{(unit cell)}\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 8.22\ \text{g/cm}^3$$

Therefore, its crystal structure is simple cubic.

For alloy B, let us calculate ρ assuming an FCC crystal structure.

$$\rho = \frac{nA_B}{(2R\sqrt{2})^3 N_A}$$

$$= \frac{(4\ \text{atoms/unit cell})(107.6\ \text{g/mol})}{\left\{\left[(2\sqrt{2})(1.33 \times 10^{-8}\ \text{cm})\right]^3/\text{(unit cell)}\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 13.42\ \text{g/cm}^3$$

Therefore, its crystal structure is FCC.

For alloy C, let us calculate ρ assuming a simple cubic crystal structure.

$$= \frac{nA_C}{(2R)^3 N_A}$$

$$= \frac{(1 \text{ atom/unit cell})(127.3 \text{ g/mol})}{\left\{ \left[(2)(1.42 \times 10^{-8} \text{ cm}) \right]^3 /(\text{unit cell}) \right\} (6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 9.23 \text{ g/cm}^3$$

Therefore, its crystal structure is simple cubic.

4.15   Iodine has an orthorhombic unit cell for which the a, b, and c lattice parameters are 0.481, 0.720, and 0.981 nm, respectively.

(a)   If the atomic packing factor and atomic radius are 0.547 and 0.177 nm, respectively, determine the number of atoms in each unit cell.

(b)   The atomic weight of iodine is 126.91 g/mol; compute its theoretical density.

Solution

(a) For iodine, and from the definition of the APF

$$\text{APF} = \frac{V_S}{V_C} = \frac{n\left(\frac{4}{3}\pi R^3\right)}{abc}$$

we may solve for the number of atoms per unit cell, n, as

$$n = \frac{(\text{APF})\,abc}{\frac{4}{3}\pi R^3}$$

Incorporating values of the above parameters provided in the problem state leads to

$$= \frac{(0.547)(4.81 \times 10^{-8} \text{ cm})(7.20 \times 10^{-8} \text{ cm})\left(9.81 \times 10^{-8} \text{ cm}\right)}{\frac{4}{3}\pi\left(1.77 \times 10^{-8} \text{ cm}\right)^3}$$

$$= 8.0 \text{ atoms/unit cell}$$

(b) In order to compute the density, we just employ Equation 4.8 as

$$\rho = \frac{nA_I}{abc\,N_A}$$

$$= \frac{(8 \text{ atoms/unit cell})(126.91 \text{ g/mol})}{\left\{(4.81 \times 10^{-8} \text{ cm})(7.20 \times 10^{-8} \text{ cm})\left(9.81 \times 10^{-8} \text{ cm}\right)/\text{unit cell}\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 4.96 \text{ g/cm}^3$$

4.50 Sketch the atomic packing of (a) the (100) plane for the BCC crystal structure, and (b) the (201) plane for the FCC crystal structure (similar to Figures 4.20*b* and 4.21*b*).
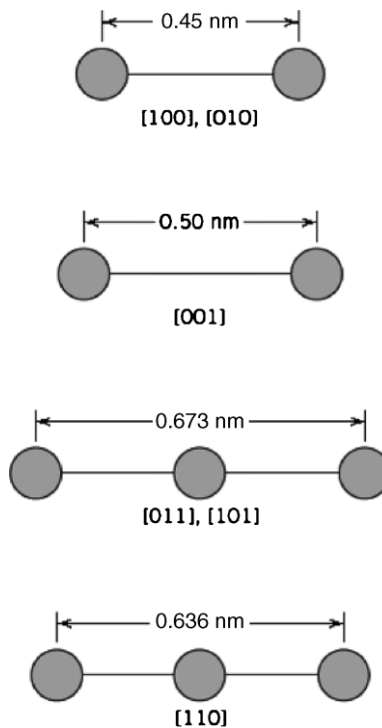
Solution

(a) A BCC unit cell, its (100) plane, and the atomic packing of this plane are indicated below. Corresponding atom positions in the two drawings are indicated by letters W, X, Y, and Z.
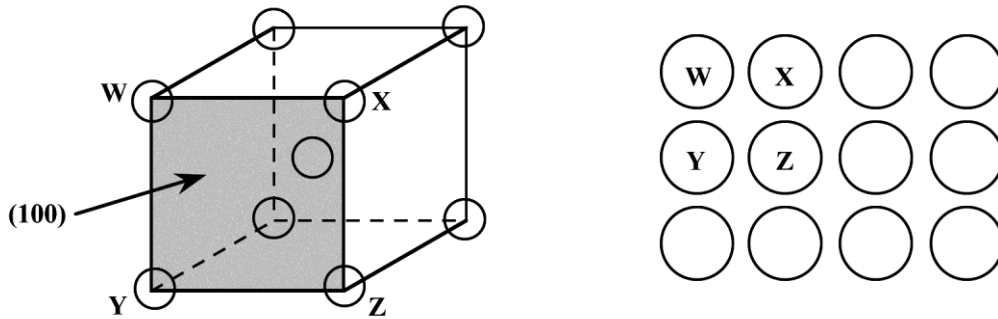
(b) An FCC unit cell, its (201) plane, and the atomic packing of this plane are indicated below. Corresponding atom positions in the two drawing are indicated by the letters A, B, and C.
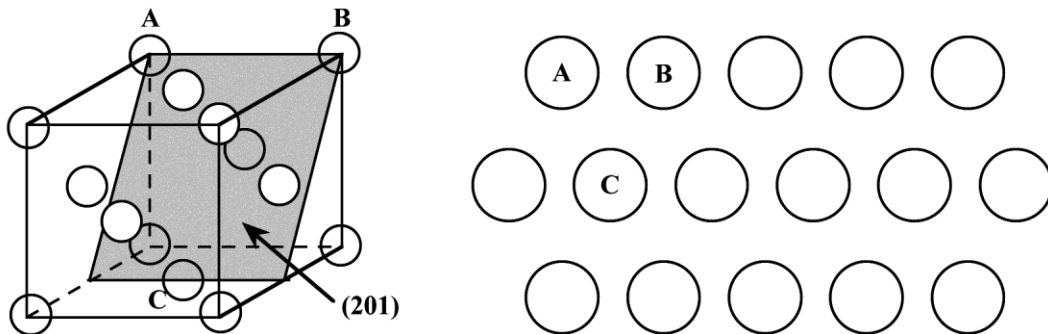
4.52   The accompanying figure shows the atomic packing schemes for several different crystallographic directions for some hypothetical metal. For each direction, the circles represent only those atoms contained within a unit cell; the circles are reduced from their actual size.

(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

Solution

Below is constructed a unit cell using the six crystallographic directions that were provided in the problem.
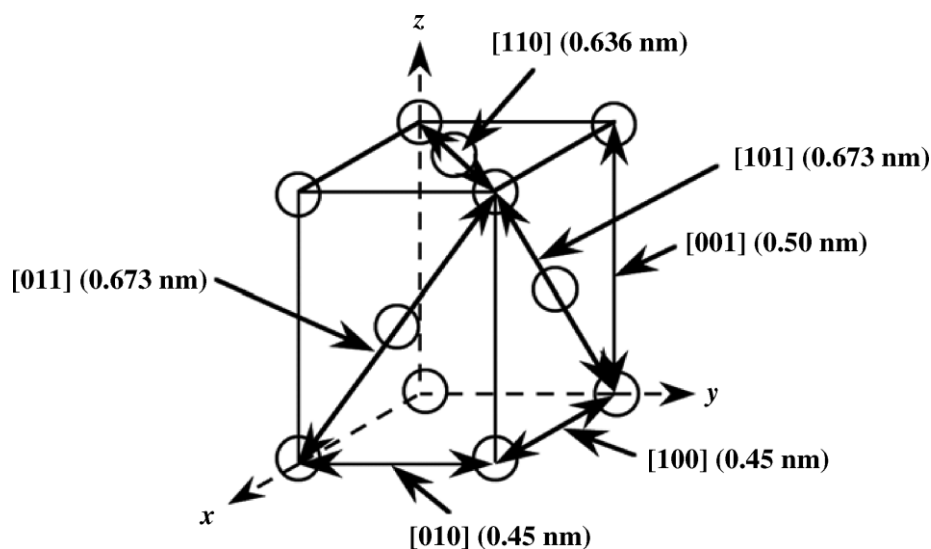
(a) This unit cell belongs to the tetragonal system since $a = b = 0.45$ nm, $c = 0.50$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *face-centered tetragonal* since the unit cell has tetragonal symmetry, and an atom is located at each of the corners, as well as at the centers of all six unit cell faces. In the figure above, atoms are only shown at the centers of three faces; however, atoms would also be situated at opposite faces.

4.57   (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.
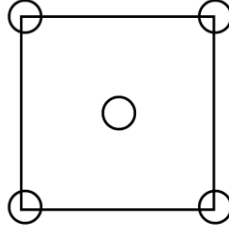
For this (100) plane there is one atom at each of the four cube corners, each of which is shared with
four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the
equivalence of 2 atoms associated with this FCC (100) plane. The planar section represented in the
above figure is a square, wherein the side lengths are equal to the unit cell edge length, $2R\sqrt{2}$
(Equation 4.1); and, thus, the area of this square is just $(2R\sqrt{2})^2 = 8R^2$. Hence, the planar density for
this (100) plane is just

$$PD_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{2 \text{ atoms}}{8R^2} = \frac{1}{4R^2}$$

       That portion of an FCC (111) plane contained within a unit cell is shown below.
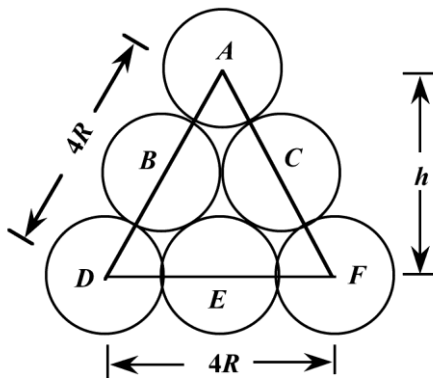
There are six atoms whose centers lie on this plane, which are labeled A through F. One-sixth of each of atoms A, D, and F are associated with this plane (yielding an equivalence of one-half atom), with one-half of each of atoms B, C, and E (or an equivalence of one and one-half atoms) for a total equivalence 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

$$PD_{111} = \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}}$$

$$= \frac{2 \text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(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

$$PD_{100}(\text{Ni}) = \frac{1}{4R^2} = \frac{1}{4(0.125 \text{ nm})^2} = 16.00 \text{ nm}^{-2} = 1.600 \times 10^{19} \text{ m}^{-2}$$
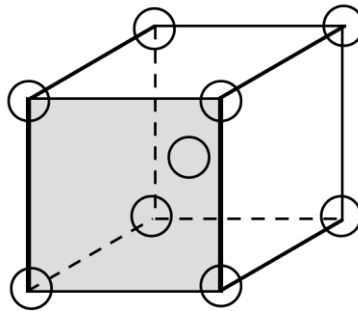
While for the (111) plane

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

4.58 (a) Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius R.

(b) Compute and compare planar density values for these same two planes for vanadium.

Solution

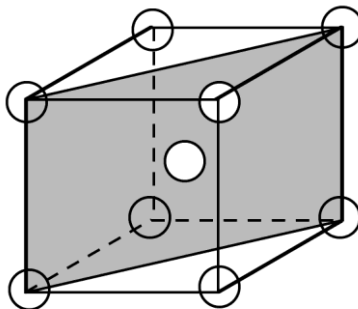(a) A BCC unit cell within which is drawn a (100) plane is shown below.

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. Thus, there is the equivalence of 1 atom associated with this BCC (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, $\dfrac{4R}{\sqrt{3}}$ (Equation 4.4); and, thus, the area of this square is just $\left(\dfrac{4R}{\sqrt{3}}\right)^2 = \dfrac{16R^2}{3}$.

Hence, the planar density for this (100) plane is just

$$\text{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{\dfrac{16\,R^2}{3}} = \frac{3}{16\,R^2}$$

A BCC unit cell within which is drawn a (110) plane is shown below.

For this (110) plane there is one atom at each of the four cube corners through which it passes, 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 BCC (110) plane. The planar section represented in the above figure is a rectangle, as noted in the figure below.
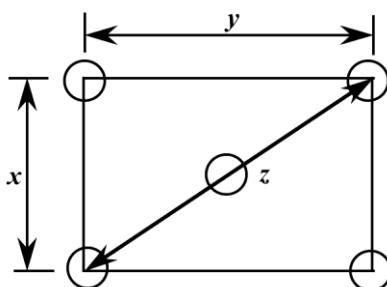
From this figure, the area of the rectangle is the product of x and y. The length x is just the unit cell edge length, which for BCC (Equation 4.4) is $\dfrac{4R}{\sqrt{3}}$. Now, the diagonal length z is equal to $4R$. For the triangle bounded by the lengths x, y, and z

$$y = \sqrt{z^2 - x^2}$$

or

$$y = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Thus, in terms of R, the area of this (110) plane is just

$$\text{Area}(110) = xy = \left(\frac{4R}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right) = \frac{16R^2\sqrt{2}}{3}$$

And, finally, the planar density for this (110) plane is just

$$PD_{110} = \frac{\text{number of atoms centered on (110) plane}}{\text{area of (110) plane}}$$

$$= \frac{2 \text{ atoms}}{\dfrac{16R^2\sqrt{2}}{3}} = \frac{3}{8R^2\sqrt{2}}$$

(b) From the table inside the front cover, the atomic radius for vanadium is 0.132 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(V) = \frac{3}{16R^2} = \frac{3}{16(0.132 \text{ nm})^2} = 10.76 \text{ nm}^{-2} = 1.076 \times 10^{19} \text{ m}^{-2}$$

While for the (110) plane

$$\text{PD}_{110}(V) = \frac{3}{8R^2\sqrt{2}} = \frac{3}{8(0.132 \text{ nm})^2\sqrt{2}} = 15.22 \text{ nm}^{-2} = 1.522 \times 10^{19} \text{ m}^{-2}$$