3.091 Fall Term 2009

Homework #7

solution outlines

8. It is valid to describe the structure of a crystalline solid by its unit cell because such a solid displays long-range order generated by repeatedly stacking this smallest unit. The unit cell is selected to be the smallest and simplest representative of the structure that when repeated in three dimensions completely describes the crystal lattice. Its shape must be such that it *tiles*, or fills all space, when stacked together.

15. The three types of cubic unit cell increase in packing efficiency in the order: simple, body-centered, face-centered. There is no difference in packing efficiency between the hexagonal and cubic close-packed structures; they differ only in the layering order of the same close-packed layers.

16. The application of pressure to a substance causes compression, and any rearrangement that allows an increase in density will be favored. The hexagonal close-packed structure has a larger packing efficiency than body-centered cubic, which for the same type of atom is equivalent to a larger density. The hexagonal close-packed structure will, therefore, be favored at high pressure.

21. Terms such as simple cubic, body-centered cubic and face-centered cubic are used to describe the packing of one type of atom or ion. The structures of many ionic binary compounds can be described in terms of how the cations are arranged within a packing of anions in the forms listed above. Neither the Cs^+ or Cl^- ions in the cesium chloride structure is packed in a body-centered cubic arrangement; the Cs^+ ions are found within cubic holes of the simple cubic array of Cl^-. Since all atoms are the same in a unit cell of iron, it is proper to consider it a body-centered cubic packing.

61. To determine the structure of nickel from its bulk density and atomic radius, compare the unit cell densities calculated for some plausible structures with the bulk density. Most metals adopt the body-centered cubic, face-centered cubic, or hexagonal close-packed structures. Simple cubic can be ruled out since it is only adopted by polonium. Additionally, the packing efficiencies of the face-centered cubic and hexagonal close-packed structures are identical, so it is impossible to distinguish these structures by density alone; therefore, only the densities of the bcc and fcc structures need to be examined.

To calculate these densities, the relationships between unit cell volumes and atomic radius must be derived. For fcc, assume that the nickel atoms behave as hard spheres in contact with each other. The length of the face diagonal, x, is equal to four times the atomic radius, r. By trigonometry, x is related to the unit cell edge length, a, by

$$x^2 = a^2 + a^2 \longrightarrow x = \sqrt{2}a$$

and therefore,

$$x = 4r = \sqrt{2}a$$
$$a = 2\sqrt{2}r = (2\sqrt{2})(125\text{ pm}) = 354\text{ pm}$$

The fcc unit cell volume is $V = a^3 = (354\text{ pm})^3 = 4.44 \times 10^{-23}\text{ cm}^3$. Since a fcc unit cell contains four atoms, the calculated density is

$$d_{fcc} = \frac{m}{V} = \frac{(4\text{ atoms})\left(\dfrac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}}\right)(58.69\text{ g/mol})}{4.44 \times 10^{-23}\text{ cm}^3} = 8.78\text{ g/cm}^3$$

For bcc, note that the atoms are in contact along the length of the unit cell body diagonal. The length of the body diagonal, y, is equal to four times the atomic radius, r. By trigonometry, y is related to the unit cell edge length, a, by

$$y^2 = a^2 + (\sqrt{2}a)^2 \longrightarrow y = \sqrt{3}a$$

and therefore,

$$y = 4r = \sqrt{3}a$$
$$a = \frac{4}{\sqrt{3}}r = \left(\frac{4}{\sqrt{3}}\right)(125\text{ pm}) = 289\text{ pm}$$

The bcc unit cell volume is $V = a^3 = (289\text{ pm})^3 = 2.41 \times 10^{-23}\text{ cm}^3$. Since a bcc unit cell contains two atoms, the calculated density is

$$d_{bcc} = \frac{m}{V} = \frac{(2\text{ atoms})\left(\dfrac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}}\right)(58.69\text{ g/mol})}{2.41 \times 10^{-23}\text{ cm}^3} = 8.09\text{ g/cm}^3$$

The calculated density of the fcc cell is closer to the observed value of 8.908 g/cm^3, indicating that nickel is either fcc or hexagonal close-packed; both structures have the same packing efficiency. Nickel is, in fact, face-centered cubic.

*__63.__ To identify the element, calculate its molar mass from the density, d, and the radius, r. Assuming the atoms in the bcc lattice are hard spheres, they will be in contact with each other along the body-diagonal. The length of the body-diagonal, y, is equal to four times the atomic radius, r. By trigonometry, y is related to the unit cell edge length, a, by

$$y^2 = a^2 + (\sqrt{2}a)^2 \longrightarrow y = \sqrt{3}a$$

and therefore,

$$y = 4r = \sqrt{3}a$$

$$a = \frac{4}{\sqrt{3}}r = \left(\frac{4}{\sqrt{3}}\right)(140 \text{ pm}) = 323 \text{ pm}$$

The bcc unit cell volume is $V = a^3 = (323 \text{ pm})^3 = 3.38 \times 10^{-23} \text{ cm}^3$. Since a bcc unit cell contains two atoms, the calculated density is

$$d_{bcc} = \frac{m}{V} = \frac{(2 \text{ atoms})\left(\dfrac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}}\right)(\text{molar mass})}{3.38 \times 10^{-23} \text{ cm}^3} = 10.25 \text{ g/cm}^3$$

Solving for the molar mass gives a value of 104.3 g/mol, which is close to that of rhodium.

*__67.__ To calculate the density of lithium, use the following expression using the given edge length and molar mass:

$$d_{bcc} = \frac{m}{V} = \frac{(2 \text{ atoms})\left(\dfrac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}}\right)(6.941 \text{ g/mol})}{\left[(3.509 \text{ Å})\left(\dfrac{1 \text{cm}}{10^8 \text{ Å}}\right)\right]^3} = 0.5335 \text{ g/cm}^3$$

Assuming the atoms in the bcc lattice are hard spheres, they will be in contact with each other along the body-diagonal. The length of the body-diagonal, y, is equal to four times the atomic radius, r. By trigonometry, y is related to the unit cell edge length, a, by

$$y^2 = a^2 + (\sqrt{2}a)^2 \longrightarrow y = \sqrt{3}a$$

and therefore,

$$y = 4r = \sqrt{3}a$$

$$r = \frac{\sqrt{3}}{4}a = \left(\frac{\sqrt{3}}{4}\right)(3.509 \text{ Å}) = 1.519 \text{ Å} = 151.9 \text{ pm}$$

***69.** (a) Since the simple cubic unit cell only contains one atom, the total volume occupied by atoms in the unit cell is

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(100\text{ pm})^3 = 4.19 \times 10^6\text{ pm}^3$$

(b) Since the atoms centered on the corners of the unit cell are in contact along the length of the edge, the edge length a is equal to twice their radius, $a = 2r = 200$ pm.

(c) The volume of the cubic unit cell is $a^3 = (200\text{ pm})^3 = 8.00 \times 10^6\text{ pm}^3$.

(d) The packing efficiency of the cell is equal to the volume occupied by the atoms divided by the total volume of the cell, $(4.19 \times 10^6\text{ pm}^3) \div (8.00 \times 10^6\text{ pm}^3) = 52.4\%$. More precisely, the packing efficiency can be calculated in terms of r, which cancels out:

$$\textit{packing efficiency} = \frac{V_{atoms}}{V_{cell}} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} \cong 52.36\ \%$$

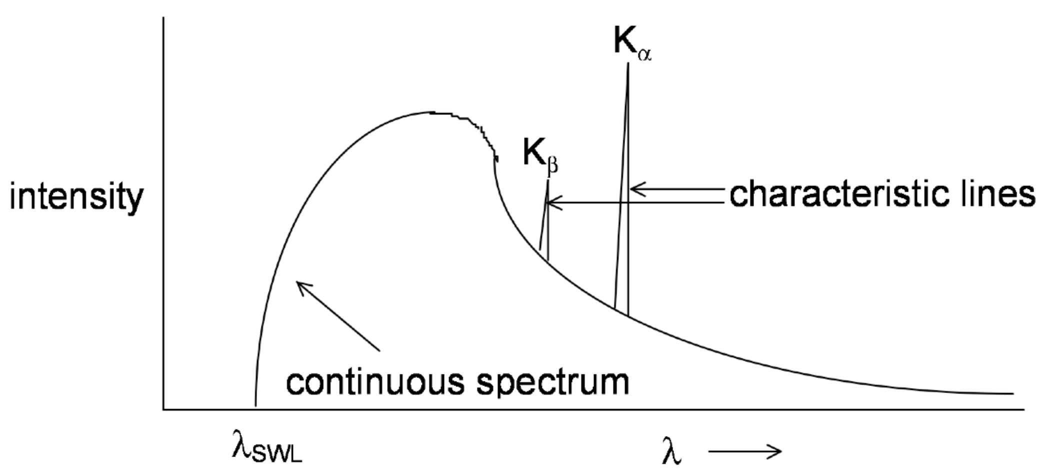
1. A characteristic x-ray spectrum of Cr will show λ_{SWL}, K_β, K_α and the continuous spectrum or *Bremsstrahlung*. We may quantify λ_{K_α} and λ_{SWL}.

$_{24}$Cr: $\bar{\nu}_{K_\alpha} = \frac{3}{4} R(Z-1)^2 = \frac{3}{4} \times 1.097 \times 10^7 (23)^2 = 4.35 \square 10^9\ \text{m}^{-1}$

$\lambda_{K_\alpha} = 2.3 \square 10^{-10}$ m

$\square_{SWL} = \frac{hc}{eV} = \frac{1.24\times10^{-6}\text{m}}{V} = \frac{1.24\times10^{-6}\text{m}}{6\times10^4}$

$= 2.07 \square 10^{-11}$ m



2. (a) $\lambda_{SWL} = \dfrac{12400}{v} = \dfrac{12400}{66\times10^3} = 0.188\ \text{Å}$

(b) see sketch above in answer to problem 9. L_α and L_β line will appear to the right of the analogous K lines (at higher values of λ), the L_α to the right of the L_β.

(c) - incident electrons are deflected by negative charge if the electrons of the target

- change in velocity (speed or direction or both) is an acceleration.

- accelerating charge emits radiation.

- extent of acceleration is NOT QUANTIZED.

- spectrum is continuous.