3.1

A&M Chapter 4 Problem 1

(a) Base-centered cubic: is a Bravais lattice, with a set of three primitive vectors that can be chosen as

$$\mathbf{a_1} = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}}), \qquad \mathbf{a_2} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}), \qquad \mathbf{a_3} = a\hat{\mathbf{z}},$$

where a is the length of the side of the cube. Other choices of the primitive vectors include, e.g.,

$$\mathbf{a_1} = a\hat{\mathbf{x}}, \qquad \mathbf{a_2} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}), \qquad \mathbf{a_3} = a\hat{\mathbf{z}}.$$

(b) Side-centered cubic: is NOT a Bravais lattice, since it contains $\frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$ and $\frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$, but not the sum $\frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + 2\hat{\mathbf{z}})$. One representation of this structure with the smallest basis is a simple cubic (Bravais) lattice of side a with a three-point basis

$$\mathbf{0}, \qquad \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}), \qquad \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

(c) Edge-centered cubic: is NOT a Bravais lattice, since it contains $\frac{a}{2}\hat{\mathbf{x}}$ and $\frac{a}{2}\hat{\mathbf{y}}$, but not the sum $\frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$. This structure can be described by a simple cubic lattice of side a with a four-point basis

$$\mathbf{0}, \qquad \frac{a}{2}\hat{\mathbf{x}}, \qquad \frac{a}{2}\hat{\mathbf{y}}, \qquad \frac{a}{2}\hat{\mathbf{z}}.$$

A&M Chapter 4 Problem 3

See Fig. 4.18 in A&M for a picture of the diamond structure. Look at the triangle formed by the three points located at $\mathbf{p}_1 = \mathbf{0}$, $\mathbf{p}_2 = \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, and $\mathbf{p}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$. The angle between the two vectors $(\mathbf{p}_1 - \mathbf{p}_2)$ and $(\mathbf{p}_3 - \mathbf{p}_2)$ is

$$\cos\theta = \frac{(\mathbf{p}_1 - \mathbf{p}_2) \cdot (\mathbf{p}_3 - \mathbf{p}_2)}{|(\mathbf{p}_1 - \mathbf{p}_2)| \, |(\mathbf{p}_3 - \mathbf{p}_2)|} = \frac{(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}) \cdot (\frac{1}{4}, \frac{1}{4}, -\frac{1}{4})}{|(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})| \, |(\frac{1}{4}, \frac{1}{4}, -\frac{1}{4})|} = \frac{-\frac{1}{4}\frac{1}{4} - \frac{1}{4}\frac{1}{4} + \frac{1}{4}\frac{1}{4}}{\frac{\sqrt{3}}{4} \frac{\sqrt{3}}{4}} = \frac{-\frac{1}{16}}{\frac{3}{16}} = \frac{-1}{3},$$

$$\theta = 109.47° = 109°28'.$$

A&M Chapter 4 Problem 6

FCC Lattice Looking at a face diagonal, the radius of the spheres r and the lattice constant a satisfy $r + 2r + r = \sqrt{2}a$, so $r = \frac{a}{2\sqrt{2}}$. There are four complete close-packing spheres in a conventional cubic cell ($8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$). So the total volume of the sphere is $4 \times \frac{4}{3}\pi r^3$. The volume of the conventional cubic cell is a^3, so the packing fraction is

$$\frac{4 \times \frac{4}{3}\pi r^3}{a^3} = \frac{(4)\frac{4}{3}\pi \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = \frac{\sqrt{2}\pi}{6} = 0.74.$$

Diamond Structure See Fig. 4.18 in A&M for a picture of the diamond structure. Looking at a conventional cubic cell of a diamond structure, we see that the twice the radius of the close-packing sphere is equal to one quarter of the body diagonal, i.e. $2r = \frac{\sqrt{3}}{4}a$, or $r = \frac{\sqrt{3}}{8}a$. There are 8 ($= (8)\frac{1}{8} + (6)\frac{1}{2} + (4)(1)$) spheres in one conventional cubic cell. Therefore the packing fraction is

$$\frac{8 \times \frac{4}{3}\pi r^3}{a^3} = \frac{(8)\frac{4}{3}\pi \left(\frac{\sqrt{3}}{8}a\right)^3}{a^3} = \frac{\sqrt{3}\pi}{16} = 0.34.$$

3.5

The NaCl structure is a fcc Bravais lattice with a basis consisting of a sodium ion at $\mathbf{0}$ and a chlorine ion at the center of the conventional cubic cell, $\frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. Each conventional cubic cell contains four Na$^+$ ions and four Cl$^-$ ions. Na atom atomic weight is 22.99 g/mol. Cl atom atomic weight is 35.45 g/mol. Suppose the lattice constant is a, then the density is

$$d = \frac{\frac{(4)(22.99 \times 10^{-3}) + (4)(35.45 \times 10^{-3})}{6.022 \times 10^{23}}}{a^3} = \frac{3.882 \times 10^{-25}}{a^3},$$

$$a = \left(\frac{3.882 \times 10^{-25}}{d}\right)^{\frac{1}{3}} = \left(\frac{3.882 \times 10^{-25}}{2.167 \times 10^3}\right)^{\frac{1}{3}} = 5.637 \times 10^{-10} \text{ m} = 5.637 \text{ Å}.$$

The distance between adjacent atoms is just half of a, i.e. 2.819 Å .

A&M Chapter 4 Problem 5

(b) In the bcc cubic phase, there are two sodium atoms in a conventional cubic cell of a bcc cubic lattice of a lattice constant a_c. Therefore the density is $d_c = \frac{2 \times (\text{mass of a Na atom})}{a_c^3}$. In the hexagonal phase, the density can be found using a parallelepiped spanned by, e.g. $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ in Fig. 4.20 in A&M. The volume of this parallelepiped is $\frac{\sqrt{3}}{2}a^2 c = \frac{\sqrt{3}}{2}a^2\sqrt{\frac{8}{3}}a = \sqrt{2}a^3$, where $\frac{c}{a} = \sqrt{\frac{8}{3}}$ has been used. Each such volume contains two ($= 4 \times \frac{1}{12}$(2 corners along one (face) diagonal; 2 faces)$+ 4 \times \frac{2}{12}$(2 corners along the other diagonal; 2 faces)$+1$(middle)) Na atoms. Therefore the density is $d_h = \frac{2 \times (\text{mass of a Na atom})}{\sqrt{2}a_h^3}$. If $d_c = d_h$, then we have $a_c^3 = \sqrt{2}a_h^3$ or $a_h = \frac{1}{2^{\frac{1}{6}}}a_c = 0.891a_c = (0.891)(4.23) = 3.77$ Å.

3.6
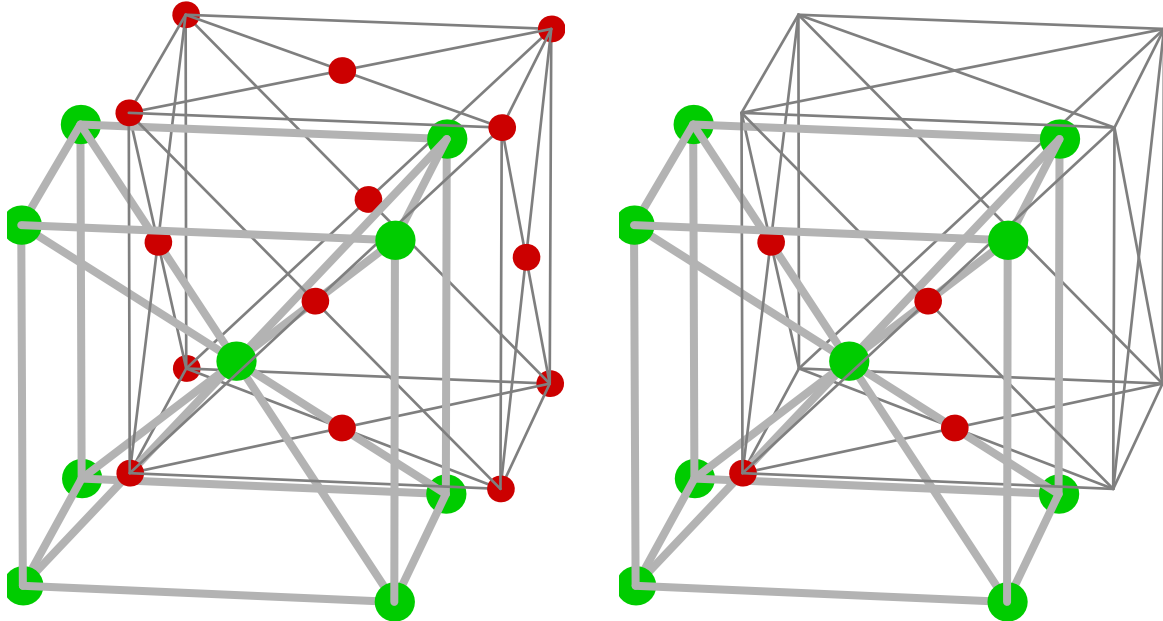
The primitive Bravais lattice of the cuprite structure is the conventional cubic lattice. The cuprite structure can be represented by a conventional cubic lattice with a basis consisting of two O atoms at four Cu atoms, at

$$\text{O}: \mathbf{0}, \qquad\qquad \text{O}: \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}),$$

$$\text{Cu}: \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}), \qquad \text{Cu}: \frac{a}{4}(\hat{\mathbf{x}} + 3\hat{\mathbf{y}} + 3\hat{\mathbf{z}}), \qquad \text{Cu}: \frac{a}{4}(3\hat{\mathbf{x}} + \hat{\mathbf{y}} + 3\hat{\mathbf{z}}), \qquad \text{Cu}: \frac{a}{4}(3\hat{\mathbf{x}} + 3\hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

The other choice of the basis is

$$O : \mathbf{0}, \qquad\qquad O : \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}),$$

$$Cu : \frac{a}{4}(3\hat{\mathbf{x}} + 3\hat{\mathbf{y}} + 3\hat{\mathbf{z}}), \qquad Cu : \frac{a}{4}(3\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}), \qquad Cu : \frac{a}{4}(\hat{\mathbf{x}} + 3\hat{\mathbf{y}} + \hat{\mathbf{z}}), \qquad Cu : \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + 3\hat{\mathbf{z}}).$$

$a = 4.27$ Å . The nearest neighbors for an O atoms are four Cu atoms with a separation of one quarter of a body diagonal of the bcc lattice, i.e. $\frac{\sqrt{3}}{4}a = 1.85$ Å . The nearest neighbors for a Cu atom are two O atoms, also with a separation of $\frac{\sqrt{3}}{4}a = 1.85$ Å .

Cu^+, ionic radius is 0.96 Å from A&M p 391, Table 19.4; see also
`http://www.webelements.com/webelements/elements/text/Cu/radii.html`.
O^{2-}, ionic radius, 1.40 Å from A&M p 386, Table 19.2; see also
`http://www.webelements.com/webelements/elements/text/O/radii.html`. Assuming the Cu^+ and O^{2-} ions are hard spheres touching each other in the body-diagonal direction, then the sum of one Cu^+ ion radius and one O^{2-} ion radius is equal to a quarter of the body diagonal of the conventional cubic lattice, i.e. $0.96 + 1.40 = \frac{\sqrt{3}}{4}a^*$, or $a^* = 5.45$ Å . This estimate is larger than the actual lattice constant, which means this simple estimate is not accurate enough for the cuprite structure in the case of Cu_2O. Comments...

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