Massachusetts Institute of Technology
Department of Materials Science and Engineering
77 Massachusetts Avenue, Cambridge MA 02139-4307

3.012 Fundamentals of Materials Science and Engineering – Fall 2003

Problem Set One Solutions

Problem 1

If we take the ratio of the cation radius to the anion we get:

$$\frac{R_A}{R_B} = \frac{0.6}{1.40} = 0.429$$

Using the lecture handouts we can find what coordination is expected for the radius ratio. For AB_2 compounds, the coordination will be 6:3 for a radius ration of 0.429. This works out in terms of charge balance. There are 6 O^{-2} around every Ti^{+4} and 3 Ti^{+4} around each O^{-2}. The total charge is therefore balanced.

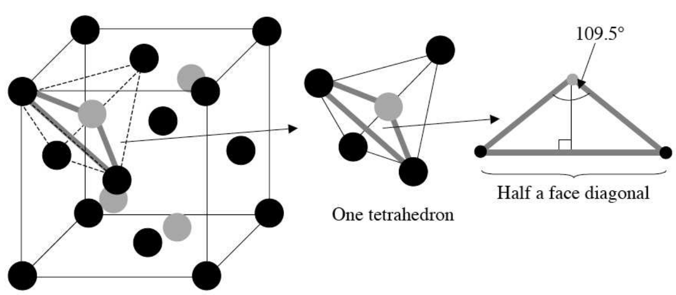
Problem 2

(a)

To find the lattice constant for ZnS we must use the information we know (the radii) and a bit of geometry to find the lattice constant (the length of the cell edge). We know that the Zn^{+2} are 4-fold coordinated with the $S^{-}2$ ions and thus form a tetrahedron. Since the anion and cation are in contact we can find the length of the edge of the tetrahedron as just:

$$r_{Zn^{+2}} + r_{S^{-2}} = 0.60 + 1.84 = 2.44\mathring{A}$$

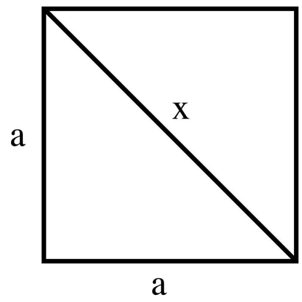
Now this is where a little trig will come in handy.



We can find half of the face diagonal, let's call it x, using the information we know about the ionic radii and the angle of the tetrahedron.

$$\sin\frac{109.8}{2} = \frac{\frac{x}{2}}{r_{Zn^{+2}} + r_{S^{-2}}} = \frac{x}{2 * 2.44}$$

Solving for x we get $x = 3.985$ or the whole face diagonal is $7.970\mathring{A}$ long. Thus with a little more trig, we can get the cell edge in terms of the face diagonal.



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

Plugging this all in we get:

$$a = 5.635\mathring{A}$$

(b)

To find the size of the largest cation that can be placed at an octahedral site we need to figure out how much room there is at one of the octahedral sites (let's pick one of the the centers of the cell edges). The nearest other ion to the center of a cell edge is located at a cell face. If we take into account the size of the anion already there (radius of $1.84\mathring{A}$) then the available space is:

$$\frac{a}{2} - 1.84 = 0.9775\mathring{A}$$

Problem 3

(a)

We can find the volume of the spheres since there is one sphere per cell for simple cubic packing (8 corner sphere which each count as $\frac{1}{8}$).

$$V_{spheres} = \frac{4}{3}\pi r^3$$

Now we just have to find the volume of the cell in terms of the radius of the sphere. For a simple cubic packing, the spheres are touching along a cell edge. So,

$$2r = a$$

And the volume of the cell is:

$$V_{cell} = a^3 = 8r^3$$

And the fraction of available volume that is occupied by spheres:

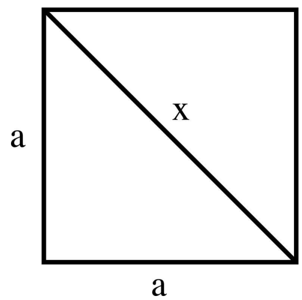
$$\frac{\frac{4}{3}\pi r^3}{8r^3} = 0.524$$

(b)

For face-centered cubic, there are 4 spheres per unit cell (1 from the corner and 3 from the faces). Thus the volume occupied by the spheres is:

$$V_{spheres} = 4 * \frac{4}{3}\pi r^3$$

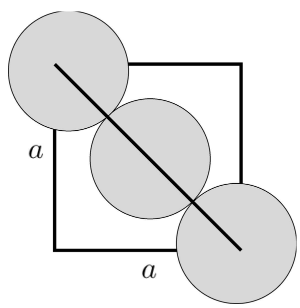
However, unlike the simple cubic case, the spheres now touch along the face diagonal. Thus we have the following geometry:



Where a is the cell edge and x is the length of the face diagonal.

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

But we also know that there are 4 sphere radii along the cell diagonal.



So,

$$\sqrt{2}a = 4r$$
$$a = \frac{4}{\sqrt{2}}r = 2\sqrt{2} * r$$

So the fraction of available volume is:

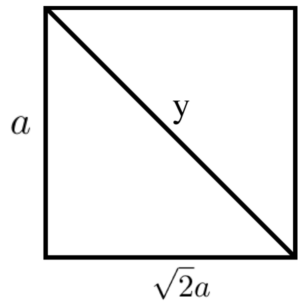
$$\frac{4 * \frac{4}{3}\pi r^3}{a^3} = \frac{4 * \frac{4}{3}\pi r^3}{(2\sqrt{2} * r)^3} = 0.74$$

(c)

For body-centered cubic there are 2 spheres per unit cell (1 from the corners and 1 from the body-centered position).

$$V_{spheres} = 2 * \frac{4}{3}\pi r^3$$

The spheres are now touching along the body diagonal which gives us this geometry:



where y is the body diagonal.

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

$$3a^2 = y^2$$

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

There are again 4 radii touching along the body diagonal so:

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

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

And the fraction of available volume is:

$$\frac{2 * \frac{4}{3}\pi r^3}{a^3} = \frac{2 * \frac{4}{3}\pi r^3}{(\frac{4}{\sqrt{3}}r)^3} = 0.680$$

These results make sense since face-centered is a close-packed structure, meaning it should have the largest fraction of cell volume occupied by spheres. Then body-centered should have slightly less occupied volume and simple cubic should have the least.

	Fraction available volume occupied by spheres
simple cubic	0.524
body-centered	0.680
face-centered	0.740