CH445/545 Winter 2008

Assignment # 1 - due 01/18/08

60 total points

SHOW ALL WORKING FOR FULL CREDIT, ANSWERS WITHOUT WORKING WILL BE PENALIZED!

1. Text Ch. 1 # 2 "Calculate the size of the largest sphere that can occupy the octahedral and tetrahedrally coordinated interstices in fcc and hcp structures composed of atoms of radius r." (5 pts each - 10 pts total). Express your answers as a function of the sphere radius r. The results are the same for fcc and hcp. Work out fcc and then explain the physical reason why hcp has to be the same (hcp is much harder to calculate than fcc).

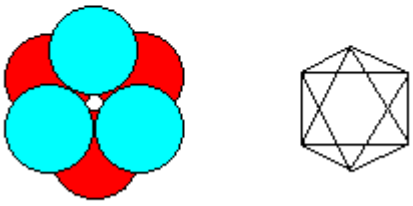
SOLUTION

The problem is to find the maximum radius of a sphere that will occupy the Td and Oh interstices of a close-packed structure of spheres radius r.

Let's start from a close-packed layer. If a triangular void in a close-packed layer has a sphere directly above it, we get a T_d interstice. If a triangular void pointing up in one close-packed layer is covered by another triangular void in a close-packed layer that is pointing down, we obtain an O_h interstice.

Td void

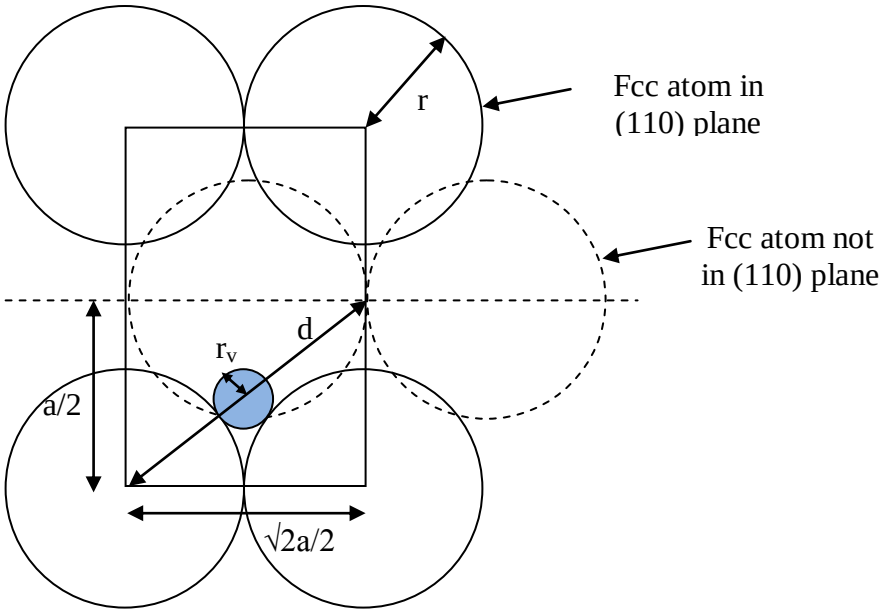
A typical fcc T_d void is located at (¼, ¼, ¼)



Oh void

A typical fcc O_d void is located at (½, ½, ½)

For the fcc T_d void, a good way to proceed is to use a plane on which the center of the void is located, such as the (110) plane:



Fcc T_d void

In the fcc unit cell, the body half-diagonal distance is

$d = \sqrt{3}^{1/2}\ a / 2 = 2(r_v + r)$

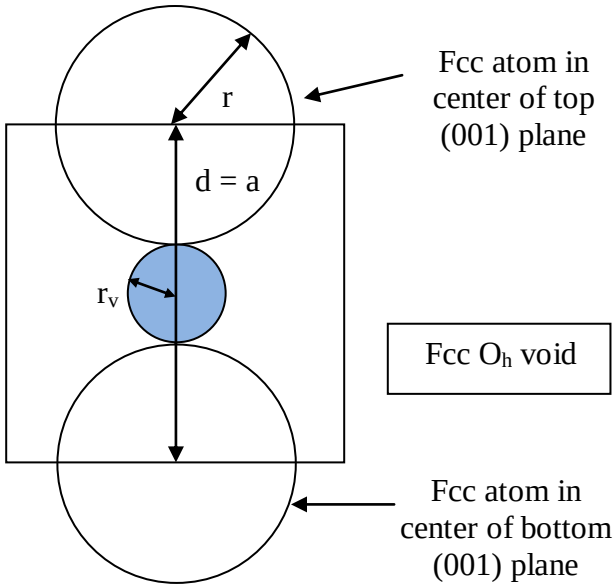
Also we know that face diagonal distance in fcc is

$4r = \sqrt{2}a$, so $a = 4r / \sqrt{2}$

and hence,

$r_v = [\ (\sqrt{3} / \sqrt{2}\ ) - 1\ ]\ r = 0.225\ r$

Now consider the O_h void in the center of the cell. It touches four face-centering atoms in a (002) type plane that bisects the cell at the center level and two atoms in the center of the top and bottom faces that all lie in a (200) type plane. Considering the latter:



Here

d = a = 2(r_v + r) and we already know that a = 4r / √2

so, r_v = [(2 / √2) - 1] r = 0.414 r

Because both fcc and hcp structures are built by stacking the same type of close-packed layers, the same voids occur in either fcc or hcp packing.

2. Text Ch. 1 # 3 - "What are the atomic densities of the (100), (110) and (111) planes of the bcc and fcc structures? Areas can be expressed in terms of a_0". (5 pts each - 15 pts total)

SOLUTION

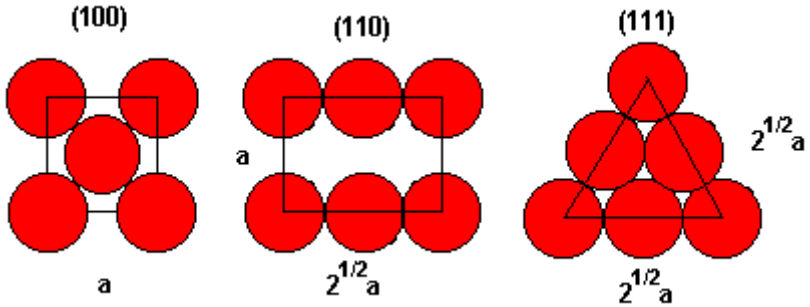
For this problem we find the total 2D cell area either in units of a or r^2. Then we find the number of atoms contained in the 2D cell. This requires a little different method of counting from 3D cells:

Each corner atom is shared with 4 cells.

edge atom is shared with 2 cells etc.

Finally, we divide the area occupied by atoms by the total area of the cell.

For fcc structures :

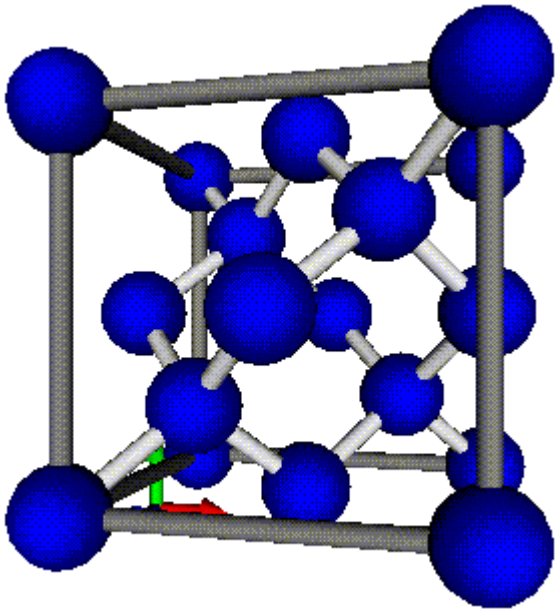


		(100)	(110)	(111)
1	2D cell area in units of a^2	1	$\sqrt{2}$	$\sqrt{3}$ / 2
2	2D cell area in units of r^2	$8r^2$	$8\sqrt{2}\ r^2$	$4\sqrt{3}^{1/2}\ r^2$
3	No. of atoms/2D cell	2	2	2
4	Atom area	$2\pi r^2$	$2\pi r^2$	$2\pi r^2$
5	Atom density / a^2 = 3 / 1	0.5	$\sqrt{2}$	4 / $\sqrt{3}$
6	Atom density (%) = 100 x 4 / 2	78.5	55.5	90.6

3. Text Ch. 1 # 8 - "The unit cell dimension of is 356 pm. Calculate the C-C bond distance." (5 pts) Note that the unit cell dimension of diamond is 356 pm not 89.1 pm as stated in the text.

SOLUTION

The diamond structure is:



There are 2 C atoms in the diamond lattice at (0,0,0) and (1/4,1/4,1/4). There is more than one way to calculate the C-C distance. One that is very easy is to the distance formula in 3D:

$d = a\,[(x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2]^{1/2}$

$= 356\ (pm) \times \sqrt{(3/16)} = 154\ pm$ or 1.54 angstroms

4. Text Ch. 1 # 10 - "Calculate the fractional volume of space filled by equidimensional spheres that have a point of tangency with all of their nearest neighbors and are in (b) BCC and (c) FCC configurations." Do parts b and c only (5 pts each part - 10 pts total) - show working!

SOLUTION

The fractional volume occupied by tangential spheres is given by :

V_f = volume of spheres in unit cell / total volume unit cell (V)

If there are Z = # atoms/unit cell and each one has a volume $4/3\ \pi\ r^3$, then

$V_f = Z\ (4/3\ \pi\ r^3) / V$

a) primitive cubic: Z = 1, $V = (2r)^3\ (= a^3)$

$V_f = (4/3\ \pi\ r^3) / (2r)^3 = 0.524$

b) body-centered cubic: Z = 2, $V = (4r/\sqrt{3})^3\ (= a^3)$

$V_f = 2\ (4/3\ \pi\ r^3) / (4r/\sqrt{3})^3 = 0.680$

c) face-centered cubic: Z = 4, $V = (4r/\sqrt{2})^3\ \ (= a^3)$

$V_f = 4\ (4/3\ \pi\ r^3) / (4r/\sqrt{2})^3 = 0.740$

5. (20 pts total) The mineral cuprite is an oxide of copper with lattice dimensions a = b = c = 427 pm and $a = \beta = \gamma = 90°$. The basis is :

Cu : (1/4, 1/4, 1/4), (3/4, 3/4, 1/4), (3/4, 1/4, 3/4), (1/4, 3/4, 3/4)

O : (0, 0, 0), (1/2, 1/2, 1/2)

a) draw a perspective view of the structure (8 pts)

b) what is the formula of the compound? (2 pts)

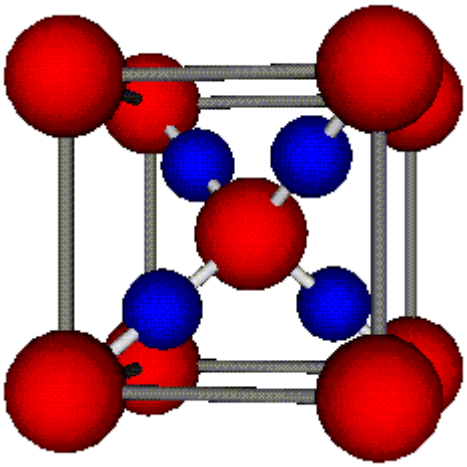
c) what is the number of formula units per unit cell? (2 pts)

d) calculate the shortest Cu-O distance (4 pts)

e) what is the density of cuprite in g/ml ? (4 pts)

SOLUTION

a) The cuprite structure is :



Red = O

Blue = Cu

Notice that there are O atoms at the cell vertices that are symmetrically equivalent to (0,0,0).

b) In the unit cell we can identify

1/8 x 8 = 1 O^{2-} at the cell vertices

1 O^{2-} at the cell center

4 Cu^{2+} ions in the cell

So we have Cu_2O

c) the number of formula units/cell = 2

d) the cell diagonal length is $\sqrt{3}$ a

The shortest Cu-O distance = 1/4 of this distance so

d(Cu-O) = $\sqrt{3}$ a / 4 = 1.85A

e) Volume of unit cell = $(4.27A)^3$ = 77.85 A^3

Volume of N_A unit cells = 6.02 x 10^{23} x 77.85 A^3

= 4.687 x 10^{25} A^3 = 46.87 cm^3

N_A unit cells contain ($2N_A$) formula units which weight

2(2 x 63.55 + 16.0) = 286.2 g

So the density of cuprite is 286.2 / 46.87 = 6.11 g/cm^3