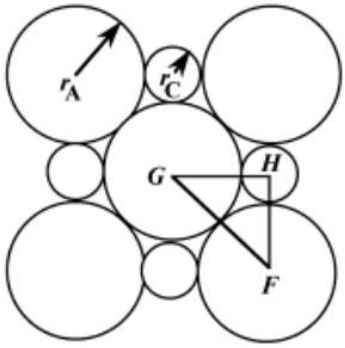
Fundamentals of Materials Science
Homework 10, SS 2017

1. Show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414. [Hint: use the NaCl crystal structure, and assume that anions and cations are just touching along cube edges and across the face diagonals.

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414 (using the rock salt crystal structure). Below is shown one of the faces of the rock salt crystal structure in which anions and cations just touch along the edges, and also the face diagonals.



From triangle *FGH*,

$$\overline{GF} = 2r_A$$

and

$$\overline{FH} = \overline{GH} = r_A + r_C$$

Since *FGH* is a right triangle

$$(\overline{GH})^2 + (\overline{FH})^2 = (\overline{FG})^2$$

or

$$(r_A + r_C)^2 + (r_A + r_C)^2 = (2r_A)^2$$

which leads to

$$r_A + r_C = \frac{2r_A}{\sqrt{2}}$$

Or, solving for r_C/r_A

$$\frac{r_C}{r_A} = \left(\frac{2}{\sqrt{2}} - 1\right) = 0.414$$

2. On the basis of ionic charge and ionic radii given in the Table in your textbook or lecture note, predict crystal structures for the following materials:
(a) CaO, (b) MnS, (c) KBr, and (d) CsBr.
Justify your selections.

Solution

Known numbers

	Ca^{2+}	$O2^{-}$	Mn^{2+}	S^{2-}	K^{+}	Br^{-}	Cs^{+}
ionic radii/nm	0.100	0.140	0.067	0.184	0.138	0.196	0.170

	r_+/r_-	r_+/r_- range	Shape	Structure
CaO	0.714	0.414-0.732	Octahedral	Sodium Chloride
MnS	0.364	0.225-0.414	Tetrahedral	Zinc Blende
KBr	0.334	0.225-0.414	Tetrahedral	Zinc Blende
CsBr	0.867	0.732-1.0	Cubic	Cesium Chloride

3. The unit cell for Al_2O_3 has hexagonal symmetry with lattice parameters a = 0.4759 nm and c =1.2989 nm. If the density of this material is 3.99 g/cm^3, calculate its atomic packing factor.

Solution

Known numbers

Ionic radii of aluminum: 0.053nm

Ionic radii of oxygen: 0.140nm

The volume of unit cell is ,

$$V=S_{basal}\times c=3S_{para}\times c=3a\times\frac{\sqrt{3}}{2}a\times c$$

$$=3\times 0.4759nm\times\frac{\sqrt{3}}{2}\times 0.4759nm\times 1.2989nm$$

$$=0.764nm^3$$

According to the equation,

$$n=\frac{\rho VN_A}{A_{Al_2O_3}}=\frac{3.99g/cm^3\times(0.764\times10^{-21}cm^3)\times(6.022\times10^{23}atoms/mol)}{26.98g/mol\times2+16.00g/mol\times3}=18atoms$$

Thus, the atomic packing factor is,

$$APF=\frac{volume\ of\ atoms\ in\ a\ unit\ cell}{total\ unit\ cell\ volume}=\frac{(18formula\ units/unit\ cell)\times\frac{4}{3}\pi[(0.053nm)^3+(0.140nm)^3]}{(0.764nm^3/unit\ cell)^3}=0.84$$

4. Iron oxide (FeO) has the rock salt crystal structure and a density of 5.70 g/cm^3.
(a) Determine the unit cell edge length.
(b) How does this result compare with the edge length as determined from the radii in Table 4.4, assuming that the Fe^{2+} and O^{2-} ions just touch each other along the edges?

Solution

Known numbers

Ionic radii of iron: R_+=0.077nm

Ionic radii of oxygen: R_-=0.140nm

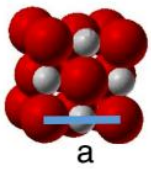
Atomic weight of iron: A_+=55.85g/mol

Atomic weight of oxygen: A_-=16.00g/mol

(a) According to the density equation,

$$V_C=\frac{n(\Sigma A_+ + \Sigma A_-)}{\rho N_A}=\frac{4\times(55.85g/mol+16.00g/mol)}{5.70g/cm^3\times(6.022\times10^{23}atoms/mol)}=8.37\times10^{-23}cm^3==0.0837nm^3$$

$$a=\sqrt[3]{V}=\sqrt[3]{0.0837nm^3}=0.437nm$$



Thus, the unit cell edge length is 0.437nm.

(b) As shown in the right figure,

$$a=2R_+ + 2R_- = 2\times0.077nm + 2\times0.140nm = 0.434nm$$

Thus, the unit cell edge length is 0.434nm, this compares very favorably with (1) value of 0.437nm.

5. Compute the theoretical density of ZnS, given that the Zn-S distance and bond angle are 0.234 nm and 109.5°, respectively. How does this value compare with the measured density?

Solution

This problem asks that we compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.240 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell volume from the given Zn—S distance. From the previous problem, the unit cell volume V_C is just a^3, a being the unit cell edge length, and

$$V_C = (4y\sin\theta)^3 = \left[(4)(0.240\,\text{nm})(\sin 35.25°)\right]^3$$

$$= 0.17\ \text{nm}^3 = 1.7 \times 10^{-22}\ \text{cm}^3$$

Now we must utilize Equation 4.9 with n' = 4 formula units, and A_{Zn} and A_S being 65.41 and 32.06 g/mol, respectively. Thus

$$\rho = \frac{n'(A_{Zn} + A_S)}{V_C N_A}$$

$$= \frac{(4\ \text{formula units/unit cell})(65.41\ \text{g/mol} + 32.06\ \text{g/mol})}{(1.7\times10^{-22}\ \text{cm}^3/\text{unit cell})(6.022\times10^{23}\ \text{formula units/mol})}$$

$$= 3.80\ \text{g/cm}^3$$

The measured value of the density is 3.80 g/cm^3.

6. The zinc blende crystal structure is one that may be generated from close-packed planes of

anions.

a) Will the stacking sequence for this structure be FCC or HCP? Why?

b) Will cations fill tetrahedral or octahedral positions? Why?

c) What fraction of the positions will be occupied?

Solution

This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions.

(a) The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 4.5).

(b) The cations will fill tetrahedral positions since the coordination number for cations is four (Table 4.5).

(c) Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

7. Magnesium oxide has the rock salt crystal structure and a density of 3.58 g/cm^3.

a) Determine the unit cell edge length.

b) How does this result compare with the edge length as determined from the radii in your textbook or lecture note, assuming that the Mg^{2+} and O^{2-} ions just touch each other along the edges?

Solution

(a) This part of the problem calls for us to determine the unit cell edge length for MgO. The density of MgO is 3.58 g/cm^3 and the crystal structure is rock salt. From Equation 4.2

$$\rho = \frac{n'(A_{Mg} + A_O)}{V_C N_A} = \frac{n'(A_{Mg} + A_O)}{a^3 N_A}$$

Or, solving for a

$$a = \left[\frac{n'(A_{Mg} + A_O)}{\rho N_A} \right]^{1/3}$$

Inasmuch as there are 4 formula units per unit cell for the rock salt crystal structure, and the atomic weights of magnesium and oxygen are 24.31 and 16.00 g/mol, respectively, when we solve for a from the above equation

$$a = \left[\frac{(4 \text{ formula units/unit cell})(24.31 \text{ g/mol} + 16.00 \text{ g/mol})}{(3.58 \text{ g/cm}^3)(6.022 \leftrightarrow 10^{23} \text{ formula units/mol})} \right]^{1/3}$$

$$= 4.21 \times 10^{-8} \text{ cm} = 0.421 \text{ nm}$$

(b) The edge length is determined from the Mg^{2+} and O^{2-} radii for this portion of the problem. Now for the rock salt crystal structure

$$a = 2r_{Mg^{2+}} + 2r_{O^{2-}}$$

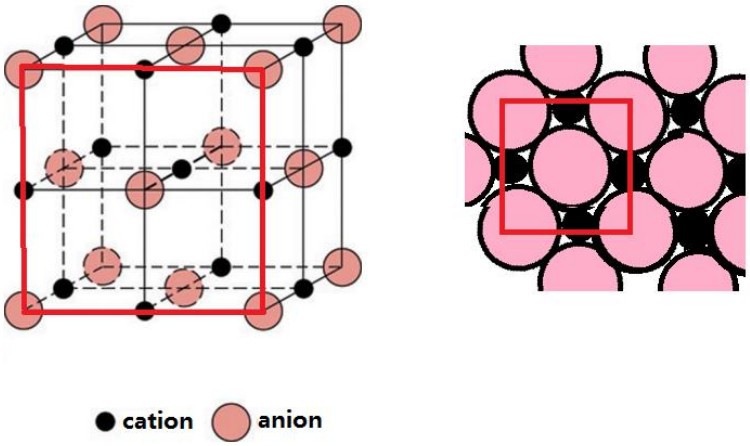
From Table 4.4

$$a = 2(0.072 \text{ nm}) + 2(0.140 \text{ nm}) = 0.424 \text{ nm}$$

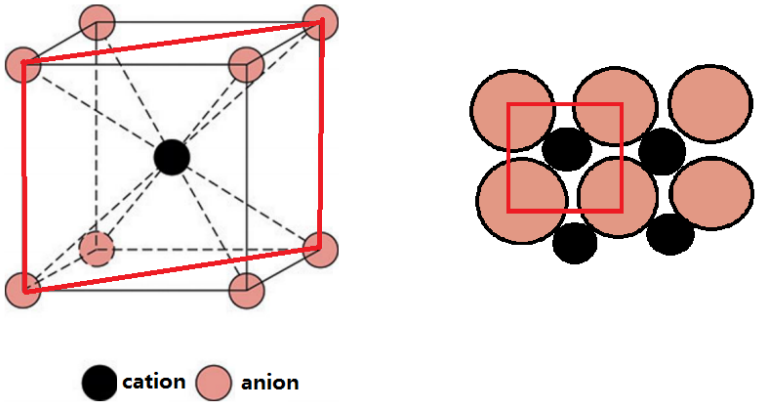
8. For each of the following crystal structures, represent the indicated plane in the manner of Figure 4.20 and 4.21, showing both anions and cations:
   a) (100) plane for the rock salt crystal structure,
   b) (110) plane for the cesium chloride crystal structure.

Solution

(a)



(b)



9. Nanowires are high aspect-ratio metal or semiconducting wires with diameters on the order of 1 to 100 nanometers and typical lengths of 1 to 100 microns. Nanowires likely will be used in the future to create high-density electronic circuits.

   Nanowires can be fabricated from ZnO. ZnO has the wurtzite structure. The wurtzite structure is a hexagonal lattice with four atoms per lattice point at Zn (0, 0, 0), Zn (2/3, 1/3, 1/2), O (0, 0, 3/8), and O (2/3, 1/3, 7/8).

   a) How many atoms are there in the conventional unit cell?
   b) If the atoms were located instead at Zn (0, 0, 0), Zn (1/3, 2/3, 1/2), O (0, 0, 3/8), and O (1/3, 2/3, 7/8), would the structure be different? Please explain.
   c) For ZnO, the unit cell parameters are a=3.24 Å and c=5.19 Å. (Note: this is not the ideal HCP c/a ratio.) A typical ZnO nanowire is 20 nm in diameter and 5 μm long. Assume that the nanowires are cylindrical. Approximately how many atoms are there in a single ZnO nanowire?

On average, these are the contributions from each type of site:

Zn (0, 0, 0): 8 corner sites per cell × 1/8 atom per site = 1 atom

Zn (2/3, 1/3, 1/2): 1 site per cell × 1 atom per site = 1 atom

O (0, 0, 3/8): 4 edge sites per cell × 1/4 atom per site = 1 atom

O (2/3, 1/3, 7/8): 1 site per cell × 1 atom per site = 1 atom

Thus, there are 4 atoms per unit cell. Alternatively, there is one lattice point per unit cell and four atoms per lattice point, again giving a total of 4 atoms per unit cell.

No, the structure would not be different. The (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2) sites and (1/3, 2/3, 7/8) and (2/3, 1/3, 7/8) sites are equivalent.

The total volume of the nanowire, V_{total}, is given by

$$V_{\text{total}} = \pi R^2 L$$

Where R is the radius and L the length of the nanowire.

$$V_{\text{total}} = (\pi)\left(\frac{20 \times 10^{-9}}{2}\ \text{m}\right)^2 (5 \times 10^{-6}\ \text{m})$$

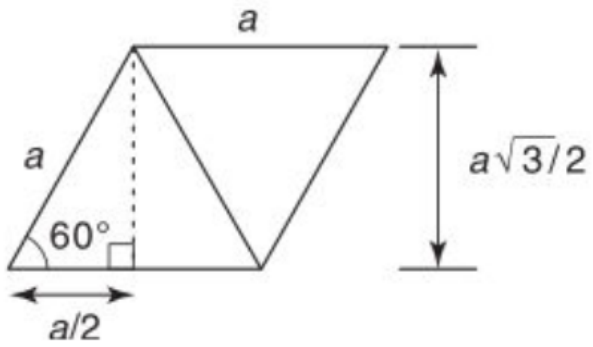
$$V_{\text{total}} = 1.571 \times 10^{-21}\ \text{m}^3$$

The volume of a unit cell is

$$V_{\text{cell}} = A_{\text{base}}c$$

Where A_{base} is the area of the base of the unit cell and c the height of the unit cell.

The geometry of the unit cell is shown here:



$$V_{\text{cell}} = A_{\text{base}}c$$

$$A_{\text{base}} = 2\left(\frac{1}{2} \times a \times \frac{a\sqrt{3}}{2}\right) = \frac{a^2\sqrt{3}}{2}$$

$$V_{\text{cell}} = \left(\frac{a^2\sqrt{3}}{2}\right)c$$

$$V_{\text{cell}} = \left(\frac{[3.24 \times 10^{-10}\ \text{m}]^2\sqrt{3}}{2}\right)(5.19 \times 10^{-10}\ \text{m})$$

$$V_{\text{cell}} = 4.718 \times 10^{-29}\ \text{m}^3$$

$$N_{\text{atoms}} = \left(\frac{V_{\text{total}}}{V_{\text{cell}}}\right)\left(4\ \frac{\text{atom}}{\text{cell}}\right)$$

$$\boxed{N_{\text{atoms}} = 1.33 \times 10^8\ \text{atom}}$$