

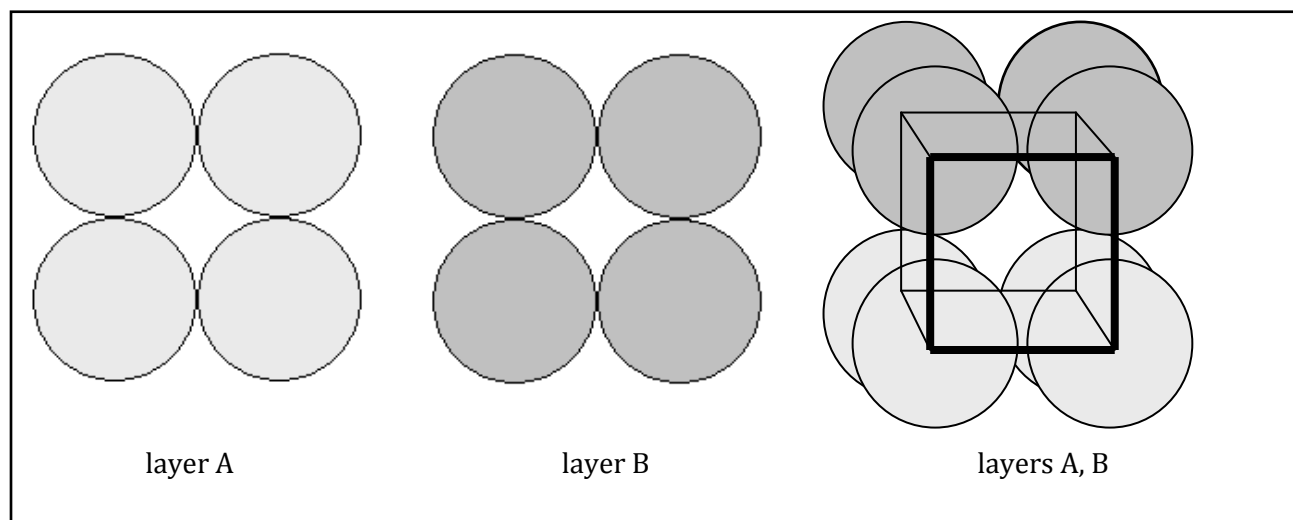
## Experiment 7: Understanding Crystal Structures

To do well in this laboratory experiment you need to be familiar with the concepts of lattice, crystal structure, unit cell, coordination number, the different types of holes in a lattice and the simple cubic structures studied in class.

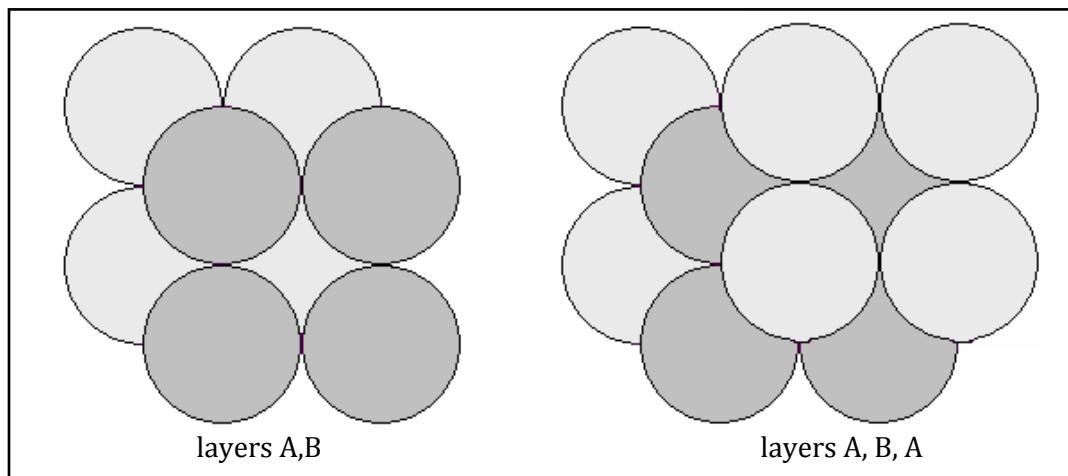
### 1. Brief review about packing

When a solid crystallizes, the atoms or ions that form it try to pack as tightly as possible. In the case of ions, repulsive forces between ions of the same kind of charge get minimized and attractive forces between ions of opposite charges get maximized. If we assume that atoms and ions can be represented by spheres let's use these to figure out different packing schemes.

We can start by packing the spheres as follows, with layer A exactly on top of layer B. The resulting structure has a cube of eight spheres for the repeating unit. This results in the simple cubic lattice, with a large amount of empty space between the spheres.

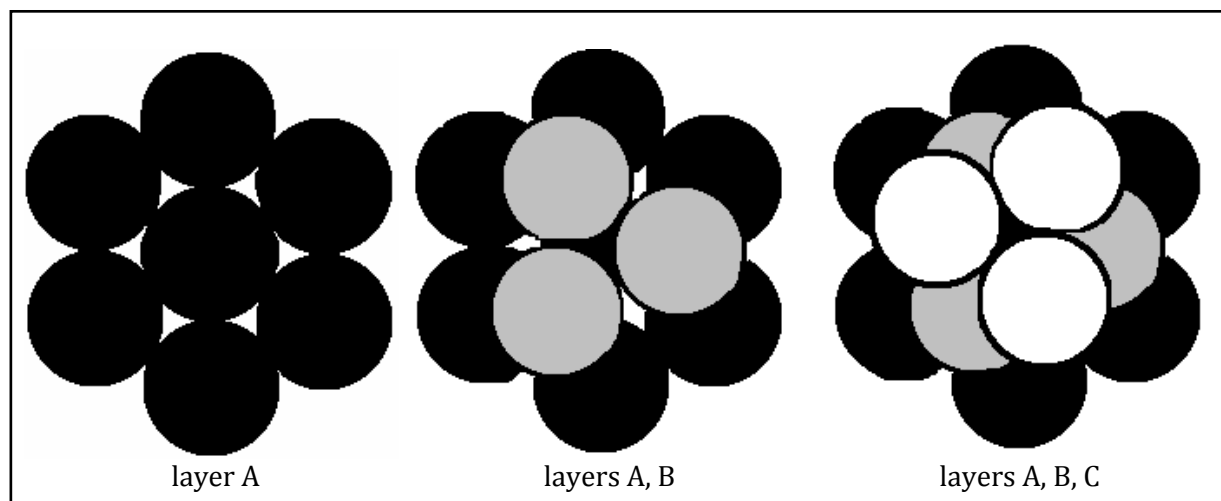


We can pack the spheres in a slightly different way, with those in the second layer above the holes in the first layer and those atoms in the third layer exactly above those in the first layer (ABABAB scheme).



This way of packing leads to the body centered cubic lattice with 8 atoms in the corners of a cube and one more atom in the center.

We can also start by packing spheres so that each sphere touches six others oriented towards the corners of a hexagon (the way billiard balls lie in a rack). The second layer can be set so that the spheres occupy half of the holes left by the spheres in the first layer.

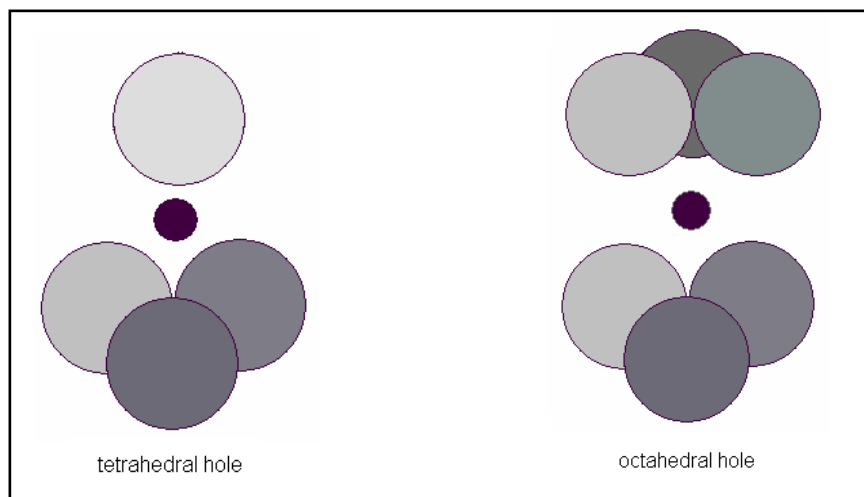


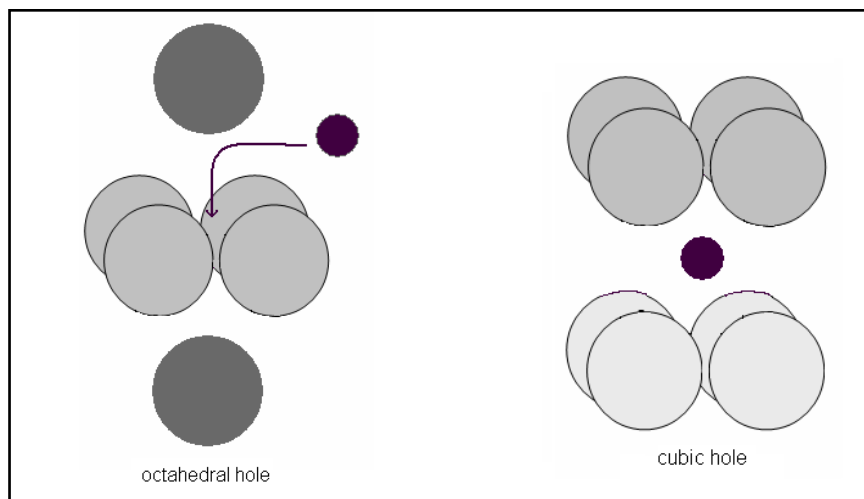
The spheres in the third layer could be set up in two different ways: they could occupy the space above the holes in the first layer that were not used to form the second layer, generating an A, B, C type of structure. This produces the cubic closest packed lattice, which is identical to the face centered cubic structure.

Another way of generating the third layer would be to repeat the first layer, generating the A, B, A, B type of lattice, also called hexagonal closest-packed structure (we won't work with this type of lattice in this lab).

## 2. Interstitial holes and coordination numbers

In ionic compounds the larger ions (usually the anions) define the unit cell and the smaller ions occupy the interstitial holes between the larger ions. We can find three types of holes: cubic, tetrahedral and octahedral. They are illustrated in the following figures.





When studying crystal structures we represent ions and atoms by spheres.

The coordination number of an atom (or ion) is the number of spheres that are closest to it (the number of its closest neighbors)

If a cation occupies a **tetrahedral** hole its coordination number is **4**. It is located in the center of a **tetrahedron** with vertices occupied by four anions.

If an ion occupies an **octahedral** hole its coordination number is **6**. It is positioned in the center of an **octahedron** (a regular polyhedron with 8 sides)

Finally, if a cation occupies a **cubic** hole it has a coordination number **8**. It is surrounded by 8 anions occupying the vertices of a **cube**.

### 3. Models and calculations of metallic structures

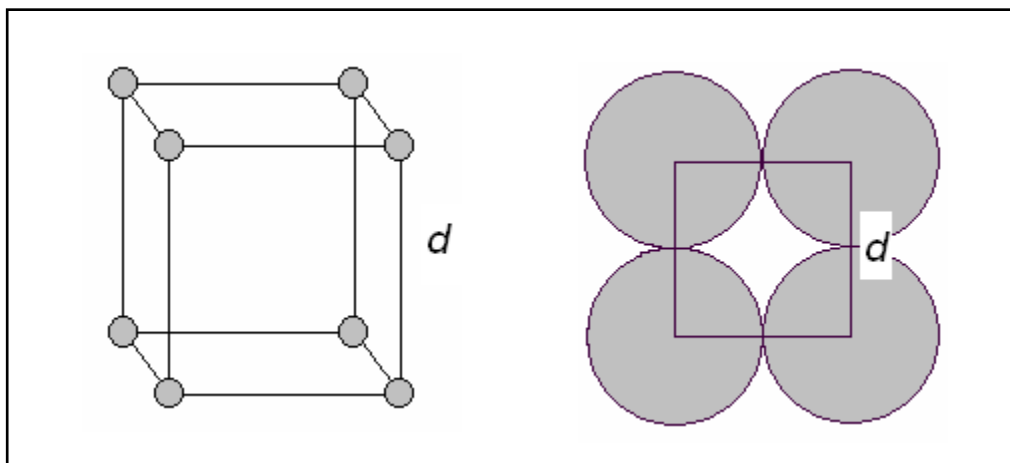
Atom	Molar mass (g/mol)	Empirical atomic radius (nm)	Pauling ionic radius (nm)
Na	22.99	0.180	0.095
Cu	63.55	0.135	0.096
Cl	35.45	0.100	0.181
Cs	132.9	0.260	0.169
Zn	65.38	0.135	0.074
S	32.06	0.100	0.184

You will need the values in this table for different calculations throughout the lab.

#### a. The simple cubic crystal (SC)

The unit cell is a cube where the side represents the distance between the centers of two adjacent atoms ( $d$ ). How do we know the value of  $d$ ? It has to be determined experimentally, by X-ray diffraction. We can obtain the value of  $d$  to four significant figures in a routine measurement even though  $d$  is a very small number, on the order of 0.5 nm.

Using your model set assemble three unit cells, one next to the other. Examine your model carefully and answer the following questions. Keep in mind that the first figure illustrates the general position of the atoms in the unit cell and the second figure illustrates the fact that we are assuming that the adjacent atoms in the crystal touch each other.



1. How many atoms are there per unit cell? *Be sure to include only the fraction of each atom that is entirely inside the unit cell.*

There are \_\_\_ corner atoms, each atom shared by \_\_\_ adjacent unit cells, so each corner atom contributes \_\_\_ of an atom, and there is (are) \_\_\_ atom(s) per unit cell.

2. What is the volume of the unit cell if the distance between the centers of two adjacent atoms is  $d$ ?

3. What is the coordination number of any atom in this crystal? (recall that the coordination number of an atom is the number of its nearest neighbors)

4. Knowing  $d$  how can you calculate  $r$ , the radius of an atom?

5. What kind of holes do you find in the simple cubic crystal, tetrahedral, octahedral or cubic?

6. What is the percentage of empty volume in one unit cell?

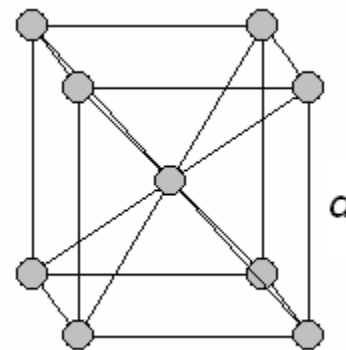
7. The only element known to crystallize with the SC structure is Polonium. Why do you think SC is such a rare structure?

**b. The body centered cubic crystal (BCC)**

The unit cell is similar to the SC cell but we have added one more atom (identical to the corner atoms) in the center of the cube.

Using your model set assemble three unit cells, one next to the other. Examine your model carefully and answer the following questions.

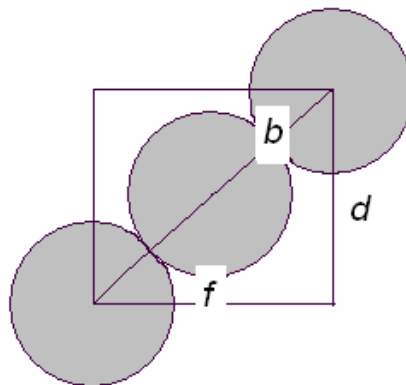
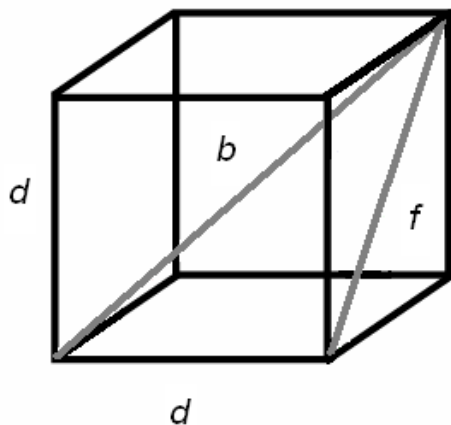
1. How many atoms are there per unit cell? Explain briefly



2. What is the coordination number of any atom in this structure?

The higher coordination number of the atoms in the BCC lattice accounts in part for the fact that the BCC lattice is much more stable than the SC lattice. All the metals in group 1A (Li, Na, K, etc) and some of the early transition metals (V, Cr, Mo, W, Fe) have the BCC structure at room temperature.

3. Knowing the length of the unit cell,  $d$ , how can you calculate the radius of one atom? Notice that the atoms touch along the body diagonal.



4. Express the density of any metal M that crystallizes in the BCC lattice in terms of the atomic weight  $m$ , its atomic radius  $r$  and any other constants you may need.

5. Use the answer to question 4 to determine the density of Na and compare it to the experimental value ( $0.97 \text{ g/cm}^3$ ).

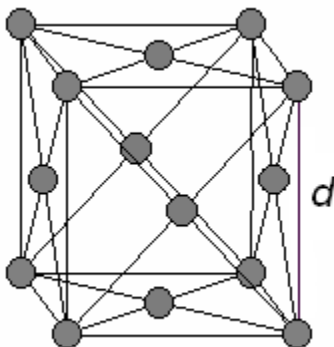
atomic weight =

atomic radius =

calculated density =

6. How much empty space is there in one unit cell?

7. What kind of holes do you find in this structure?

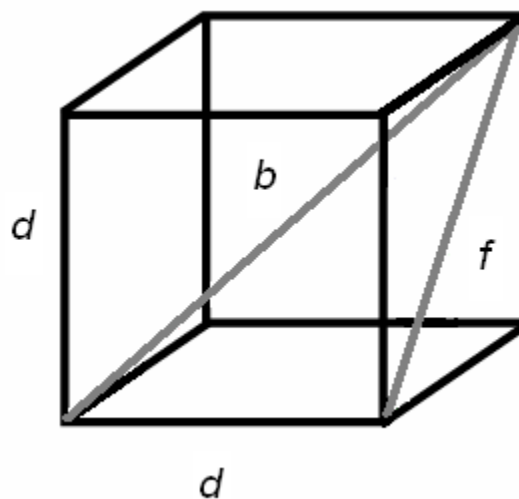
**c. The face centered cubic structure (or cubic-closed packed)**

Using your model set assemble two unit cells, one next to the other. Examine your model carefully and answer the following questions.

1. How many atoms are there per unit cell? Explain briefly.

2. What is the coordination number of any atom in this structure?

3. Knowing the size of the unit cell,  $d$ , how can you calculate the radius of one atom? Draw the atoms touching along the face diagonal on the figure to the right.



4. How much empty space is there in one unit cell?

5. What do you notice about the relationship between coordination number and the amount of empty space in the unit cell?

6. What kind of holes do you find in this structure?

6. Several metals crystallize in the FCC structure, such as Ni, Cu, Ag, Au, Ca, and Sr. Knowing that the experimental density for Cu is  $D = 8.92 \text{ g/cm}^3$  and that the size of the unit cell is  $d = 0.361 \text{ nm}$  calculate Avogadro's number  $N_A$  (without using Avogadro's number in the calculation!!)

$D = \text{mass of 1 unit cell} / \text{volume of 1 unit cell}$	
$d \text{ (in cm)} =$	
volume of 1 unit cell =	
mass of 1 unit cell =	1 unit cell = mass of ___ atoms
mass of 1 atom =	
molar mass =	= $N_A \times \text{mass of 1 atom}$
$N_A =$	

7. Add one more layer to your FCC model. Remove 2 adjacent atoms of the new layer (you need to figure out which ones) and observe the cubic-closest packed lattice.

#### 4. Crystal structures of simple binary compounds

In many ionic crystals the anions, which are usually larger than the cations, form an SC or an FCC structure. The cations fit into the cubic, octahedral or tetrahedral holes of the structure determined by the anions. The type of hole they occupy depends on the ratio of the radii of the cation and the anion. Large cations will usually occupy cubic holes, smaller ones octahedral holes and the smallest ones tetrahedral holes. The number of holes that is occupied depends on the stoichiometry of the compound.

$r_+/r_- > 0.732$	Cations go into cubic holes
$0.732 > r_+/r_- > 0.414$	Cations go into octahedral holes
$0.414 > r_+/r_- > 0.225$	Cations go into tetrahedral holes

You will be able to show how some of these limit ratios originate while answering the following questions.

A manual in your crystal model kit will include directions on how to build each of the structures below.



**a. CsCl lattice**

After you use the model set to build the CsCl structure you should be ready to answer these questions.

1. What type of lattice do the chloride ions form?
2. What is the coordination number for a  $\text{Cl}^-$  ion?
3. In what kind of holes are the  $\text{Cs}^+$  ions located?
4. Calculate  $r^+/r^-$  and see if the prediction from the radius ratio rule matches what you observed in question #3.
5. What is the coordination number of the  $\text{Cs}^+$  ions?
6. How many total  $\text{Cs}^+$  ions are there in one unit cell?
7. How many total  $\text{Cl}^-$  ions are there in one unit cell? Explain briefly.
8. Note that this structure *can't be described as a BCC structure* because the central atom is different from the corner atoms.

**b. NaCl lattice**

Answer these questions after you build one unit cell with the model set.

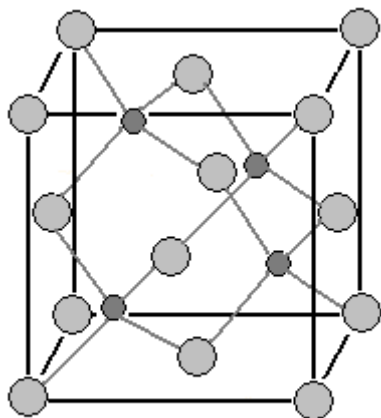
1. What type of lattice do the  $\text{Cl}^-$  ions have?
2. What is the coordination number of  $\text{Cl}^-$ ?
3. What is the coordination number of  $\text{Na}^+$ ?

4. Calculate the ratio  $r^+/r^-$ . According to the radius ratio rule, the  $\text{Na}^+$  ions should occupy what kind of hole?

5. Examine the position of the  $\text{Na}^+$  ions in your model. Is it in agreement with the prediction from question #4?

### c. ZnS lattice (zinc blende)

Build one unit cell with your model set and answer the following questions.



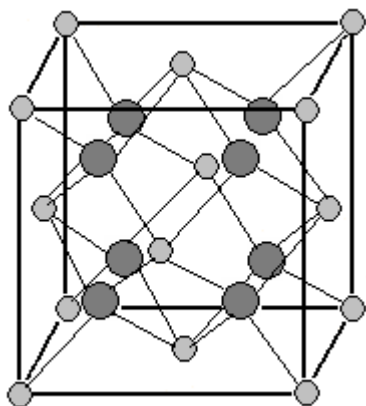
1. How many total  $\text{Zn}^{2+}$  ions and how many  $\text{S}^{2-}$  ions are there in one unit cell?

2. What kind of lattice do the  $\text{S}^{2-}$  ions form?

3. What kind of holes are occupied by the  $\text{Zn}^{2+}$  ions?

### d. $\text{CaF}_2$ (fluorite)

This is the only structure that you will build that is not 1:1, so you may want to examine it really carefully.



1. How many total  $\text{Ca}^{2+}$  ions and  $\text{F}^-$  ions are there in one unit cell?

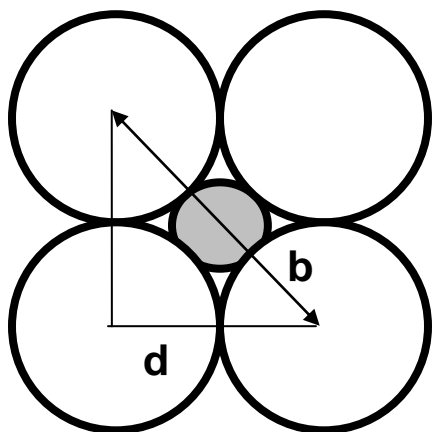
2. Does the answer to the previous question agree with the stoichiometry of the salt?

3. What kind of structure do the  $\text{Ca}^{2+}$  ions form?

4. What kind of holes are occupied by the  $\text{F}^-$  ions?

**Follow-up questions**

1. Call  $r_+$  the radius of the cation and  $r_-$  the radius of the anion. Calculate the ratio  $r_+/r_-$  in a cubic hole in a simple cubic lattice where the cation fits in the cubic hole (just like in the CsCl case). Recall that  $b = (3)^{1/2}d$ .

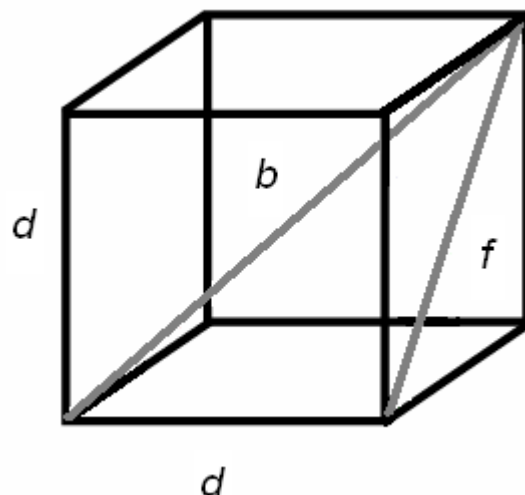


Hints:  
 $2r_- = d$   
 $2r_- + 2r_+ = b$

2. Does the ratio from question #1 sound familiar? How does it relate to the limit ratio rules?

***Pre-lab assignment—To be completed BEFORE lab!***

1. Explain in your own words what unit cell means.
2. Explain in your own words what coordination number means.
3. Calculate  $f$  as a function of  $d$  using Pythagoras' theorem.



4. Calculate  $b$  as a function of  $d$  also using Pythagoras' theorem.