CRYSTAL STRUCTURES

BACKGROUND

The regular geometric shapes of crystals are due to the orderly three-dimensional networks of atoms, ions, or molecules that form the crystal lattice. The purpose of today's experiment is to give you the opportunity to prepare a crystal of alum and to build models of some common crystal structures and see how atoms and ions are arranged.

Crystals are formed from a liquid (a solution of molten solid) or a gas in which particles are randomly oriented. A tiny collection of particles must form in a highly ordered manner to initiate crystal growth. A foreign material may provide a surface on which particles may be adsorbed in orientations suitable for continued crystal growth. For example, a string suspended in a supersaturated salt solution may provide sites as ions are adsorbed into the fibers.

PROCEDURE

A) PREPARING ALUM CRYSTALS

- Weigh to the nearest 0.01 g 15 g of $Al_2(SO_4)_3.18H_2O$ and 3.9 g K_2SO_4 into the same 250 ml beaker.
- Add 100 ml of deionized water.
- Heat and stir the mixture to dissolve the solid as much as you can. Note, not all solid will dissolve.
- Suspend a thread in the solution by tying it over a wooden splint-it should not touch the bottom.
- Carefully store in your locker.
- As the water evaporates, crystals of alum, $KAl(SO_4)_2.H_2O$ will form.

Next lab period, check on your growing crystal. A good alum crystal should be clear and looks like two pyramids joined at the base. If you have one good crystal forming on the thread that is the best. If you have no crystal, you can try again, by decanting the clear solution into a clean 150 ml beaker, suspend the thread, and put them back into your locker. Discard the residue on the bottom of the beaker if there is any, unless you find a nice crystal there. You may try growing the crystal as long as you like during the semester.

B) BUILDING MODELS

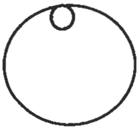
You will work in pairs. Each pair will check out a Solid State Model Kit from the stockroom. The kits are expensive, please take care not to bend any rods or lose pieces. Follow the instructions and directions on how to assemble crystal models. For additional information about the unit cell refer to the small diagram to the side of the model. It describes the building of the unit cell layers proceeding from bottom to top. If any sphere does not slide easily onto a rod, return it to the stockroom for replacement. Be sure to pick up any pieces that may fall on the floor. To take the model apart, invert the structure and allow the spheres to slowly slide off the rods. Remove the rods by grasping near the base and pulling without bending or wiggling. When you are finished sort the content of the kit

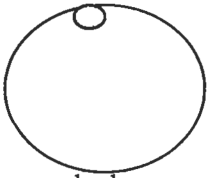
and return it to the stockroom. The Solid State Model Kit will allow you to construct three-dimensional models of metallic and ionic solids.

To get started, open the box and examine the parts. Their actual sizes are shown below.


Spacer


Blue


green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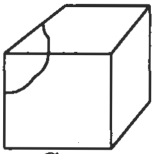
Only NaCl model requires 7.4 mm spacers. The diagram above shows the actual size of spacer required.

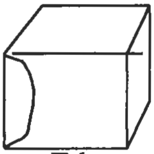
For the three cubic unit cells that you will build (simple cubic, body-centered cubic, and face-centered cubic) you will be asked to determine:

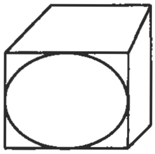
a) the coordination number of the unit cell.
b) the number of atoms per unit cell.
c) the percent of the unit cell occupied by atoms.

To find the number of atoms per unit cell you need to know the following:

Counting Atoms in Cubic Lattices: it is important that you can count atoms in the unit cells. Here are some guidelines for doing so:


Corner


Edge


Face

i) An atom at the **corner** of a cubic cell is shared with 7 other neighbor unit cells. Thus, only **1/8** of that atom can be assigned to the unit cell of interest.

ii) An atom along the **edge** of a cubic unit cell is shared among 4 unit cells. Thus, only **1/4** of that atom can be assigned to the unit cell of interest.

iii) An atom in a **face** of a cubic unit cell is shared between 2 unit cells. Thus, only **1/2** of that atom can be assigned to the unit cell of interest.

To find the percent of the unit cell occupied by atoms you need to know the following:

$V_{atom} = (4/3)\Pi r^3$ (where" r "is the radius of the atom)

$V_{unit\ cell} = a^3$ (where, " a " is the length of the side of the cube)

To find the percent of volume of cubic unit cell occupied by atoms, you need to find the volume of all atoms within the unit cell, and then divide that volume by the volume of the unit cell. The answer should be multiplied by 100 to get percent.

$$\text{Percent of unit cell occupied by atoms} = \frac{\text{Volume of all spheres}}{\text{Volume of unit cell}} \times 100$$

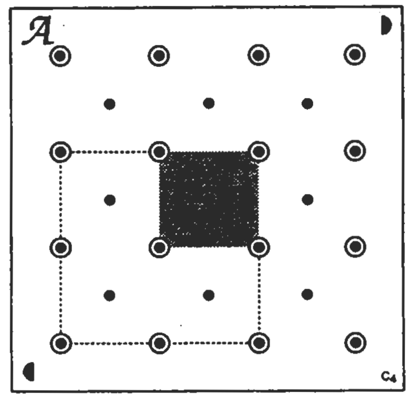
If you compare the values of packing efficiency for the three unit cells, you will see that packing efficiency increases in the order : simple cubic< body-centered cubic < face-centered cubic.

I. SIMPLE CUBE (PRIMITIVE CUBE)

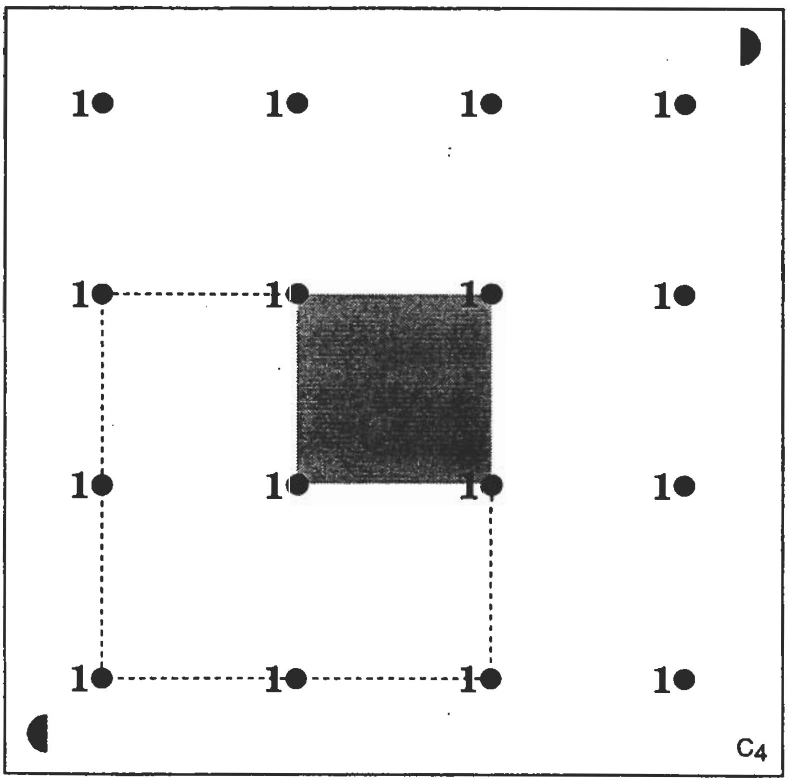
Construct a model of a simple cubic unit cell:

- Position the ◗ on template **A** in the same as the matching ◗ on the base and align holes.
- Insert rods in the **4 circled holes in the shaded region.**
- Build layer 1 first as described below.
- Complete the unit cell by repeating the first layer (1')

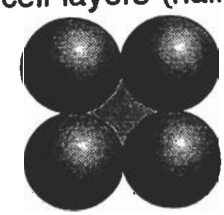
Template A –Half size



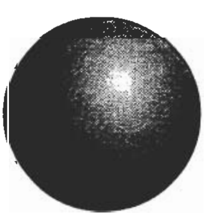
Pattern (actual size)



Unit cell layers (half-size)



layer 1

1, 1' = 

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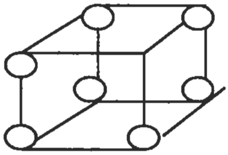
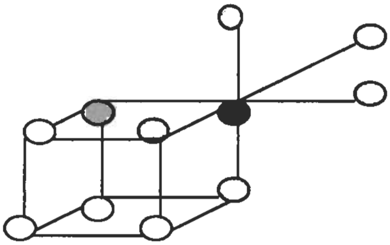
Questions: Simple Cube:

Coordination number: A simple cubic structure is formed when a second layer is laid down directly over the first in a square array. When the structure is extended beyond the unit cell as in the figure above, the coordination number becomes apparent .





Simple Cubic Extended Simple Cubic

1) What is the coordination number for each atom? ____________.

2)The structure above is drawn with a large distance between the spheres for clarity. However, the actual packing of atoms in solids is sufficiently close, it can be assumed that the spheres are touching. Where do atoms actually touch in the simple-cubic structure? a)Along the edge of the cube, b)along the body-diagonal, or c)along the face diagonal?

____

3) Establish a mathematical relationship between the side of the cube, a, and the radius of the sphere, r. ____________

4) What is the number of atoms in the simple-cubic unit cell? ____________

setup:

5) What is the volume of all atoms inside the unit cell? ____________

Setup:

6) What is the volume of the cube in terms of "r"? ____________

Setup: $V_{\text{unit cell}} = a^3 =$ ....

7) Calculate the percent of unit cell occupied by atoms. ____________

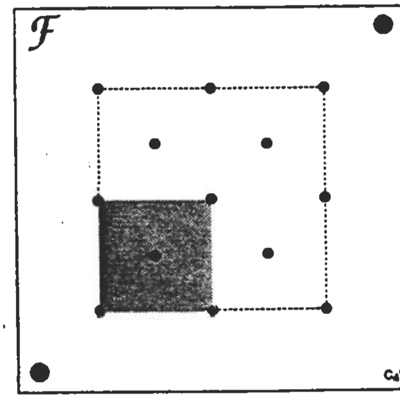
setup:

II. BODY-CENTERED CUBE

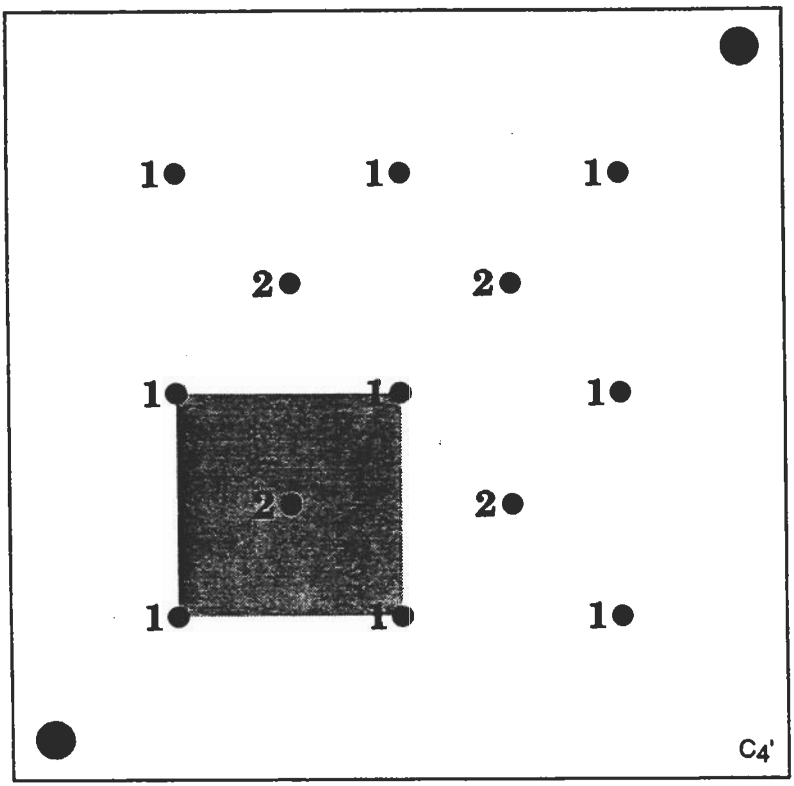
Construct a model of a body-centered cubic unit cell:

- Position the ● on template 𝓕 in the same corner as the matching ● on the base and align holes.
- Insert rods in all 5 **holes in the shaded region.**
- Build each layer in numerical order, **1** through **2** As described in the directions. Finish each layer before starting the next layer.
- Complete the unit cell by repeating the first layer (**1'**)

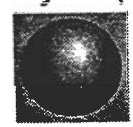
Template 𝓕 –Half size



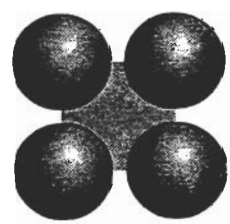
Pattern (actual size)



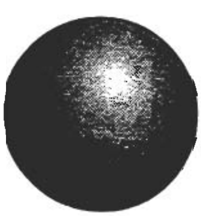
Unit cell layers (half-size)



layer 2



layer 1

1, 2, 1' = 

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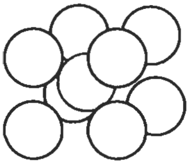
Questions: Body Centered Cube

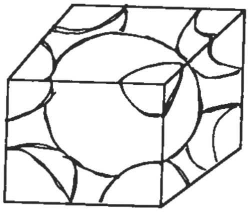
1) What is the coordination number for each atom?

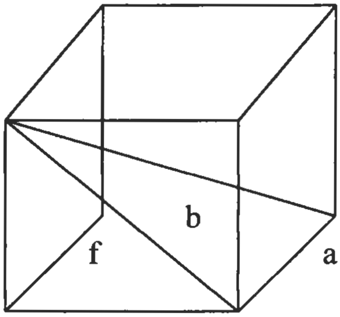
2) Where do atoms actually touch in the body-centered cubic structure? Along the edge of the cube, the body-diagonal, or the face diagonal?

3) Use the Pythagorean theorem to establish a mathematical relationship between the body diagonal, **b**, and the side of the cube, **a** .

Setup:







4) Establish a relationship between the body diagonal , **b**, and the radius of the atom, **r**.

5) From steps (3) and (4) establish a mathematical relationship between" **a**" and " **r**".

Setup:

6) What is the number of atoms in the body-centered unit cell?

7) What is the volume of all atoms inside the unit cell?

Setup:

8) What is the volume of the cube in terms of "r"?

Setup: $V_{\text{unit cell}} = a^3$ = ...

9) Calculate the percent of unit cell occupied by atoms.

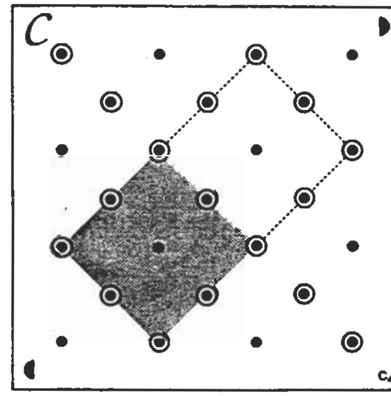
setup:

III. FACE-CENTERED CUBE

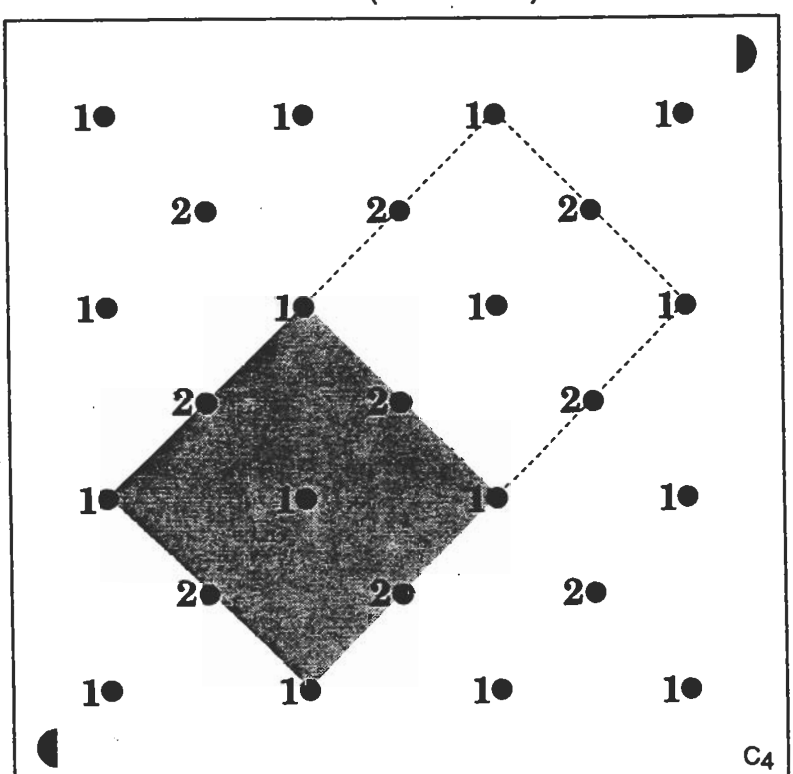
Construct a model of a face-centered cubic unit cell:

- Position the ◗ on template C in the same corner as the matching ◗ on the base and align holes.
- Insert rods in all **9 holes in the shaded region.**
- Build each layer in numerical order, **1** through **2** as described in the directions. Finish each layer before starting the next layer.
- Complete the unit cell by repeating the first layer (**1'**)

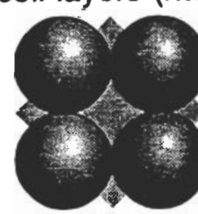
Template C–Half size



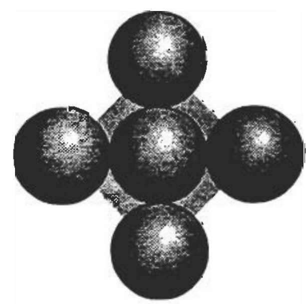
Pattern (actual size)



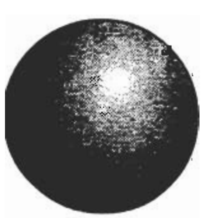
Unit cell layers (half-size)



layer 2



layer 1

1, 2, 1' = 

colorless

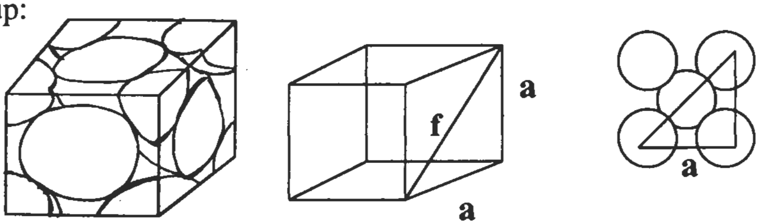
Questions: Face Centered Cube

The coordination number here is 12, although it is not obvious from the model. However, it will be apparent after you build the cubic close-packed, ccp, model on page 11 .

1) Where do atoms actually touch in the face-centered cubic structure?
Along the edge of the cube, the body-diagonal, or the face diagonal? ___________

2) Use the Pythagorean theorem to establish a mathematical relationship between the face diagonal, **f**, and the side of the cube, **a** . f =_________

Setup:



3) Establish a relationship between the face diagonal , **f**, and the radius of the atom, **r**. f =_________

4) From steps (2) and (3) establish a mathematical relationship between" **a**" and " **r**".
Setup: ____________

5) What is the number of atoms in the face centered cubic unit cell?
Setup: ____________

6) What is the volume of all atoms inside the unit cell? ____________
Setup:

7) What is the volume of the cube in terms of "r"? ____________
Setup: $V_{unit\ cell} = a^3$ = ...

8) Calculate the percent of unit cell occupied by atoms. ____________
setup:

SAVE THIS MODEL FOR LATER REERENCE AND PROCEED TO THE NEXT PART

C. CLOSEST PACKING ARRANGEMENTS

In two dimensional space, metal atoms (identical size) can be arranged as either figure (i) or figure (ii).

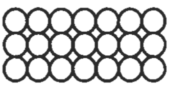


Figure (i)

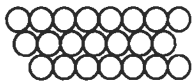
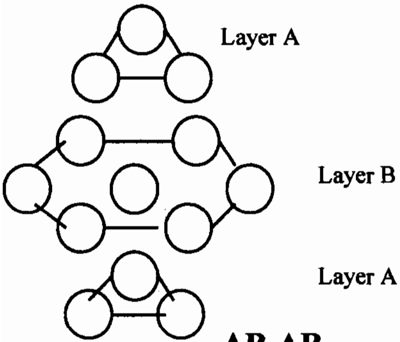


Figure (ii)
(close packed array)

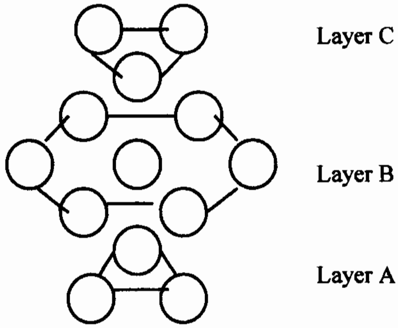
1) What is the coordination number in figure (i) ? _____ In figure (ii)? ______
2) Which of the two packing arrangements allows for the most efficient use of space? ____________
3) Which would have a higher density? ____________

The arrangement in Figure (ii) allows the largest possible number of spheres to fit in a given area, i.e. the density of spheres is maximum.

There are two different packing arrangements for 3-dimensional crystals formed from a closed packed array. They are called hexagonal closest packing or "hcp" and cubic closest packing or "ccp". In both arrangements, the second layer is shifted and placed over holes between atoms in the first layer rather than lying directly over the atoms.



AB-AB
Hexagonal close packing, hcp



ABC-ABC
Cubic close packing , ccp

The packing arrangement in hcp and ccp differ in the formation of the third layer of atoms. In hcp, the third layer is identical to the first layer and its atoms lie directly over the atoms in the first layer. This packing arrangement is often called **"AB-AB-"** referring to the repeating order of the layers. In ccp structure the third layer is different from both the first and second layers, again shifting to cover holes between atoms in the second layer. This arrangement is called **"ABC-ABC-"**. Both structures (hcp and ccp) have identical coordination number and density.

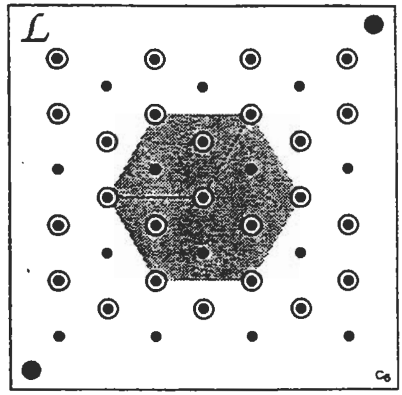
I. HEXAGONAL CLOSE PACKING (INVOLVE AB..AB –TYPE PACKING AND HAS HEXAGONAL PRISM UNIT CELL)

<u>Construct a model of a hexagonal close packing:</u>

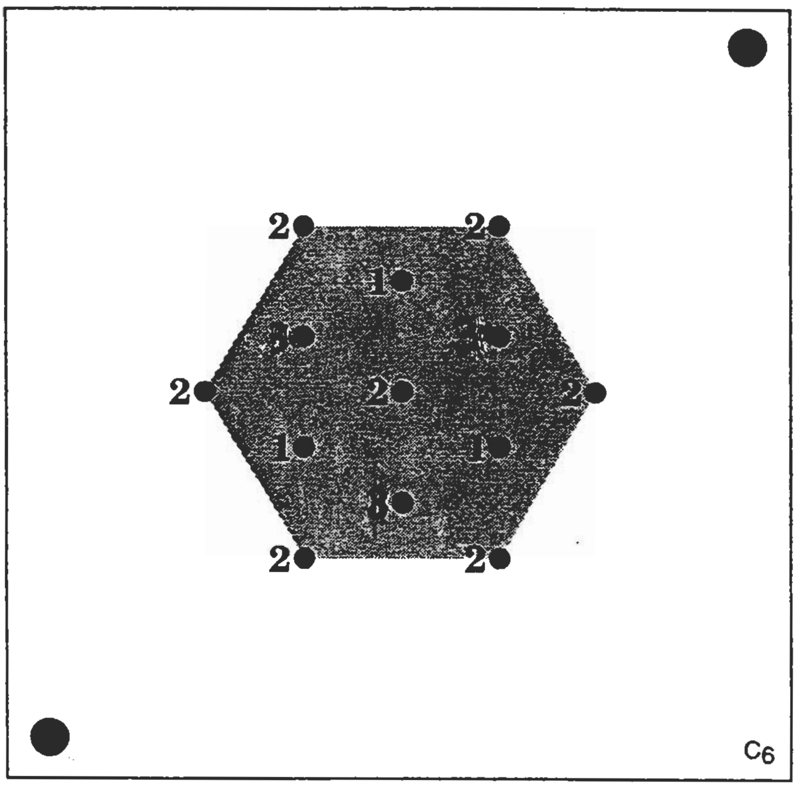
- Position the ● on template $\mathcal{L}$ in the same corner as the matching ● on the base and align holes.
- Insert rods in **all 13 holes in the shaded region.**
- Build each layer in numerical order, **1** through **2** as described in the directions. Finish each layer before starting the next layer.
- Repeat the first layer (**1'**)
- Complete the unit cell by repeating the second layer (**2'**).

<u>SAVE THIS MODEL FOR LATER REERENCE AND PROCEED TO THE NEXT PART</u>

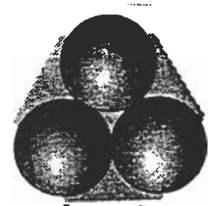
Template $\mathcal{L}$–Half size



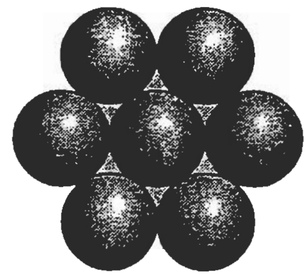
Pattern (actual size)



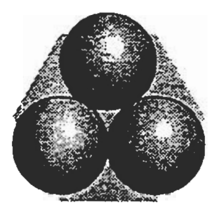
Layer sequence (half-size)



layer 3

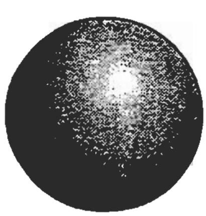


layer 2



layer 1

hcp: 1, 2, 1'



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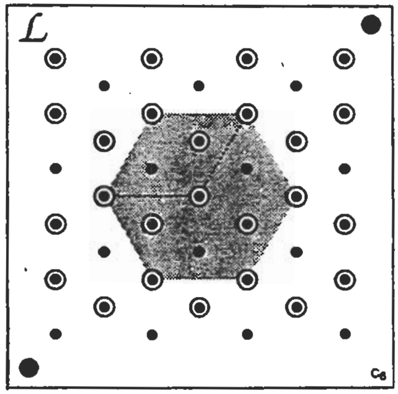
II. CUBIC CLOSE PACKING (INVOLVE ABC..ABC –TYPE PACKING AND HAS FACE-CENTERED UNIT CELL)

Construct a model of a cubic closest packing:

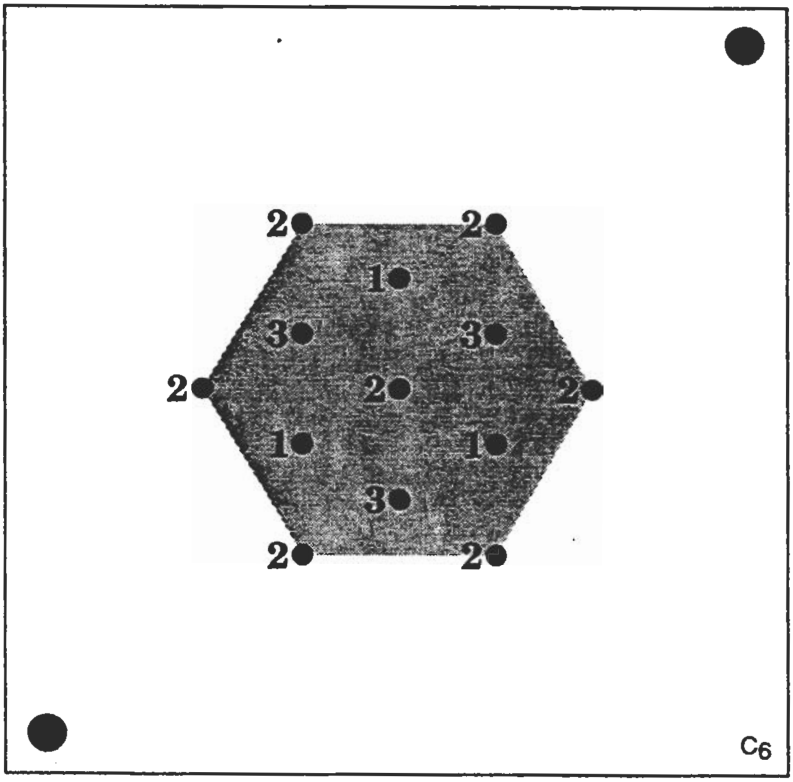
- Position the ● on template $\mathcal{L}$ in the same corner as the matching ● on the base and align holes.
- Insert rods in **all 13 holes in the shaded region.**
- Build each layer in numerical order, **1** through **3** as described in the directions. Finish each layer before starting the next layer.

SAVE THIS MODEL TO ANSWER THE QUESTIONS ON THE FOLLOWING PAGE

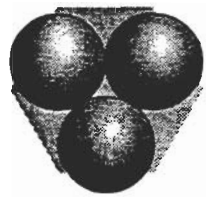
Template $\mathcal{L}$–Half size



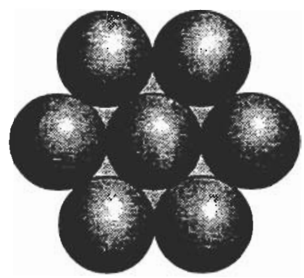
Pattern (actual size)



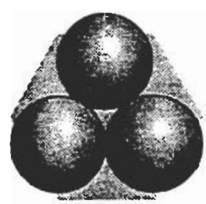
Layer sequence (half-size)



layer 3

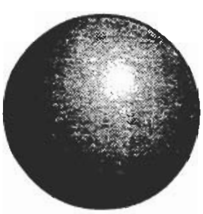


layer 2



layer 1

ccp: 1, 2, 3
hcp: 1, 2, 1'



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Questions: Close Packed Arrangements

Notice the similarities and differences between hcp and ccp packing arrangements.

1) What is the coordination number (the number of nearest neighbors) of an atom in hcp structure?________ In a ccp structure? ___________

Notice the similarities between ccp packing arrangement and the face-centerd cubic unit cell

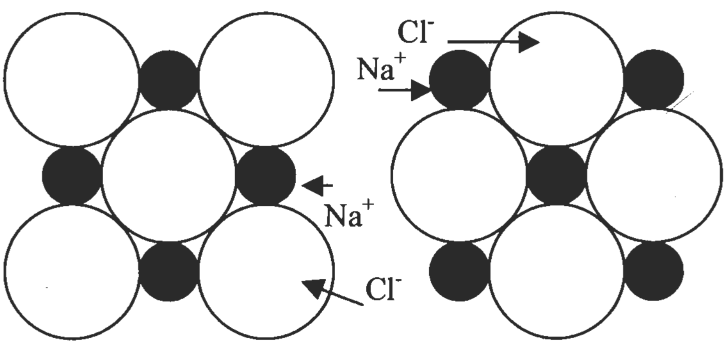
Compare this ccp model to the face-centered unit cell that you saved from page 7. Look along a body diagonal in the ccp to see a square layer of 4 spheres close to you, a second layer of 5 spheres underneath. This shows that the arrangement of atoms in a ccp structure is identical to a face-centered cubic structure. DO NOT PROCEED UNTIL YOU CAN FIND THIS ARRANGEMENT OF LAYERS. MAKE SURE YOU FIND THE FACE-CENTERED CUBE IN YOUR CCP STRUCTURE. If you want help, ask the instructor.
2) What is the coordination number in the face-centered cube model? This should be the same as the coordination number in the ccp structure. ___________________
3) What is the unit cell of the ccp structure? ___________________

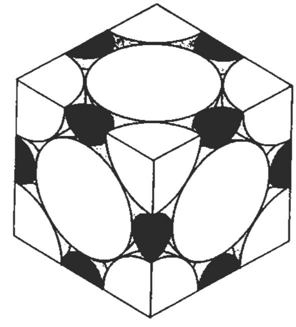
D. MODELS OF IONIC CRYSTALS

Ionic crystals differ from metallic crystals because the bonds are ionic, and the particles have different sizes. The ratio of the size of the cation to that of the anion controls the kind of packing that is possible in an ionic crystal.

I. NaCl (FACE CENTERED CUBIC LATTICE)

NaCl consists of two interpenetrated face-centered cubic lattices. Na^+ in holes of a face-centered cube of Cl^- ions, and Cl^- ions in the holes of a face-centered cube of Na^+ ions





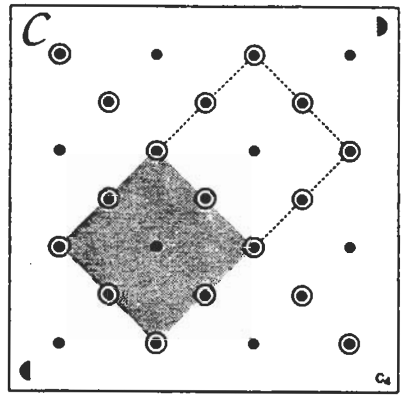
NaCl Unit Cell

Construct a NaCl model (face-centered):

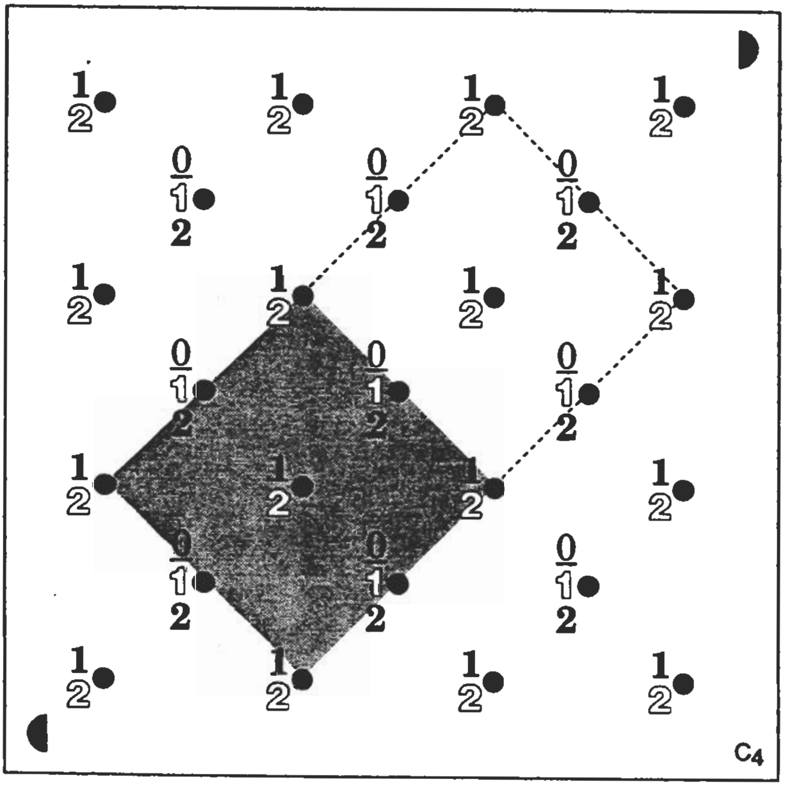
- Position the ◗ on template C in the same corner as the matching ◗ on the base and align holes.
- Insert rods in all 9 holes in the shaded region.
- Build each layer in numerical order, 0 through 2 as described in the directions. Finish each layer before starting the next layer. (0 is a 7.4 mm spacer)

- Complete the unit cell by repeating the first layer(1',1').

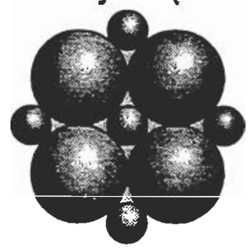
Template C–Half size



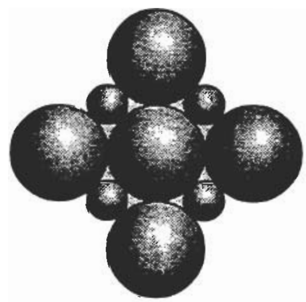
Pattern (actual size)



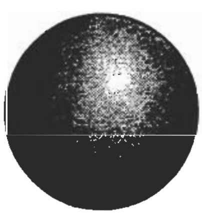
Unit cell layers (half-size)



layer 2



layer 1

0 =  1, 2, 1' =  1, 2, 1' = 

7.4

d

colorless

blue

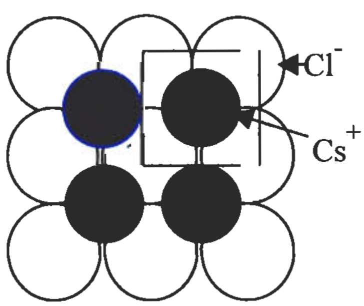
Questions: NaCl

1) Calculate the number of Na^+ ions per unit cell. ________
Setup:

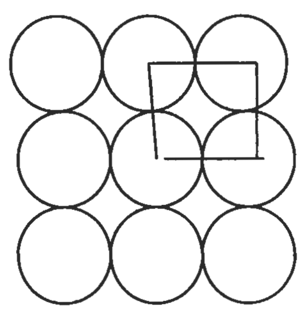
2) Calculate the number of Cl^- ions per unit cell. ________
Setup:

3) How many formula units of NaCl per unit cell? ________
4) What is the ratio of Na^+ to Cl^- in the unit cell? ________
5) Is this consistent with the 1:1 stoichiometry implied by the formula, NaCl? ________
6) What is the coordination number for each Na^+ in the structure? (i.e. the number of Cl^- touching it) ________
7) What is the coordination number for each Cl^- in the structure? (i.e. the number of Na^+ touching it) ________

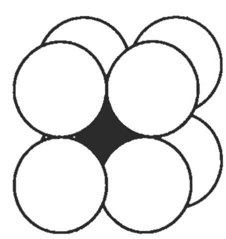
II. CsCl (SIMPLE CUBIC LATTICE)



First Layer: Cl^- ions
Second layer: Cs^+ ions



Third layer: Cl^- ions



Unit cell, CsCl

Here CsCl crystal lattice may be viewed as either Cs^+ ions in cubic holes of a simple cubic lattice of Cl^- ions, or Cl^- in cubic holes of a simple cubic lattice of Cs^+.

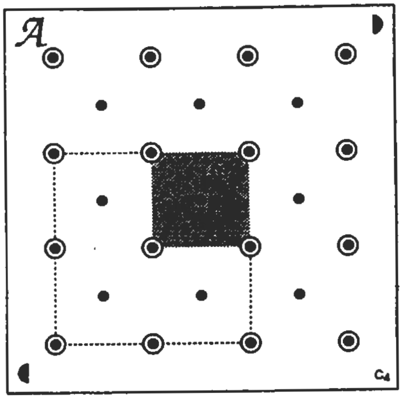
Construct a CsCl model (simple cube):

- Position the ◗ on template 𝒜 in the same corner as the matching ◗ on the base and align holes.
- Insert rods in all 5 holes in the shaded region.
- Build each layer in numerical order, **1** through **2**, as described in the directions. Finish each layer before starting the next layer.

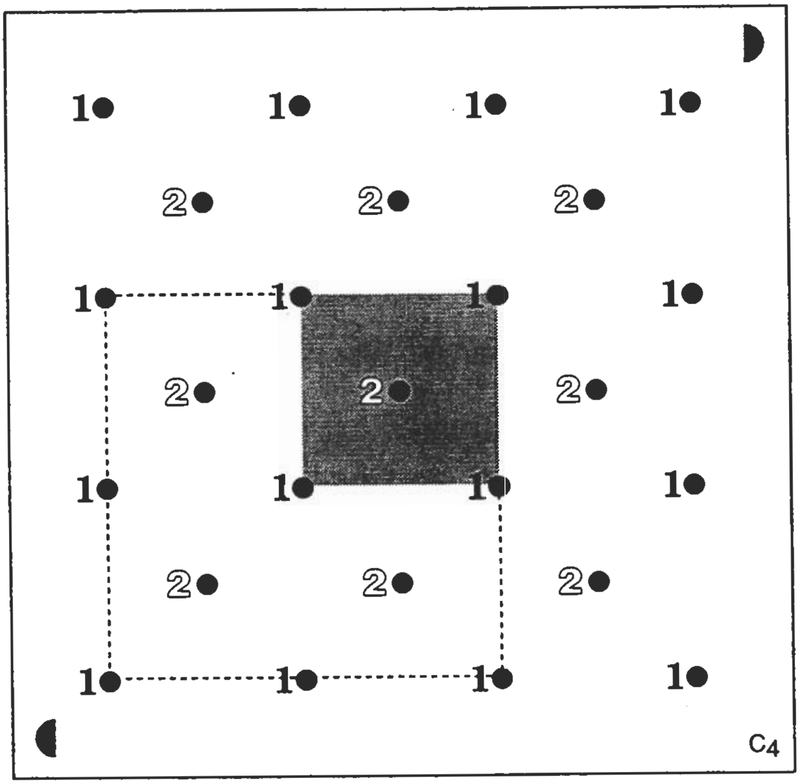
- Complete the unit cell by repeating the first layer(**1'**).
- To extend the model, place rods in additional holes before placing spheres.

Follow the same directions as above

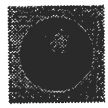
Template 𝒜–Half size



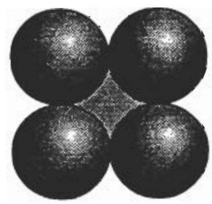
Pattern (actual size)



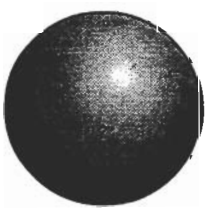
Unit cell layers (half-size)



layer 2



layer 1

1, 1' = 

colorless

2 = 

green

Questions: CsCl

1) Calculate the number of Cs^+ ions per unit cell. _____
Setup:

2) Calculate the number of Cl^- ions per unit cell. _____
Setup:

3) How many formula units of CsCl per unit cell? _____

4) What is the mass of a unit cell of CsCl? _____
Setup:

5) What is the ratio of Cs^+ to Cl^- in the unit cell? _____

6) Is this consistent with the 1:1 stoichiometry implied by the formula, CsCl? _____

7) What is the coordination number for each Cs^+ in the structure? (i.e. the number of Cl^- touching it) _____

8) What is the coordination number for each Cl^- in the structure? (i.e. the number of Cs^+ touching it) _____

9) Compare the coordination number for Cs^+ to that of Na^+ in NaCl. Which cation (Na^+ or Cs^+) has a higher coordination number? _____

10) Why? (Hint: Locate Na and Cs on the periodic table, hence compare their relative sizes.)

____

____

Report Sheet: Crystal Structures   Name________________
Section number:___________   Last   First

Simple Cube

1) What is the coordination number for each atom? ____________.

2)Where do atoms actually touch in the simple-cubic structure?
a)Along the edge of the cube, b)along the body-diagonal, or c)along the face diagonal? ____________

3) Establish a mathematical relationship between the side of the cube, a, and the radius of the sphere, r. ____________

4) What is the number of atoms in the simple-cubic unit cell? ____________
setup:

5) What is the volume of all atoms inside the unit cell? ____________
Setup:

6) What is the volume of the cube in terms of "r"? ____________
Setup: $V_{\text{unit cell}} = a^3$ = ...

7) Calculate the percent of unit cell occupied by atoms. ____________
setup:

Body Centered Cube

1) What is the coordination number for each atom? ____________.

2) Where do atoms actually touch in the body-centered cubic structure?
Along the edge of the cube, the body-diagonal, or the face diagonal? ____________

3)Use the Pythagorean theorem to establish a mathematical relationship between the body diagonal, **b**, and the side of the cube, **a** .
Setup: b =__________

4) Establish a relationship between the body diagonal , **b**, and the radius of the atom, **r**.

b =__________

5) From steps (3) and (4) establish a mathematical relationship between" **a**" and " **r**".
Setup:

____

6) What is the number of atoms in the body-centered unit cell? ____________

7) What is the volume of all atoms inside the unit cell?
Setup:

____

8) What is the volume of the cube in terms of "r"? ____________
Setup: $V_{\text{unit cell}} = a^3$ = ...

9) Calculate the percent of unit cell occupied by atoms. ____________
setup:

Face Centered Cube

1) Where do atoms actually touch in the face-centered cubic structure?
Along the edge of the cube, the body-diagonal, or the face diagonal? ____________

2) Use the Pythagorean theorem to establish a mathematical relationship between the face diagonal, **f**, and the side of the cube, **a** . f =__________

Setup:

3) Establish a relationship between the face diagonal , **f**, and the radius of the atom, **r**. f =__________

4) From steps (2) and (3) establish a mathematical relationship between" **a**" and " **r**".

Setup: ____________

5) What is the number of atoms in the face centered cubic unit cell? ____________

Setup:

6) What is the volume of all atoms inside the unit cell? ____________

Setup:

7) What is the volume of the cube in terms of "r"? ____________

Setup: $V_{unit\ cell} = a^3 = ...$

8) Calculate the percent of unit cell occupied by atoms. ____________

setup:

Close Packed Arrangements

Similarities and differences between hcp and ccp packing arrangements.

1)What is the coordination number (the number of nearest neighbors) of an atom in hcp structure?________ In a ccp structure? ___________

Similarities between ccp packing arrangement and the face-centerd cubic unit cell

2)What is the coordination number in the face-centered cube model? This should be the same as the coordination number in the ccp structure. ________

3)What is the unit cell of the ccp structure? (simple cube, body- centered, or face -centered? ________

NaCl (FACE CENTERED CUBIC LATTICE)

1) Calculate the number of Na^+ ions per unit cell. ________

Setup:

2) Calculate the number of Cl^- ions per unit cell. ________

Setup:

3) How many formula units of NaCl per unit cell? ________

4) What is the ratio of Na^+ to Cl^- in the unit cell? ________

5) Is this consistent with the 1:1 stoichiometry implied by the formula, NaCl? ________

6) What is the coordination number for each Na^+ in the structure? (i.e. the number of Cl^- touching it) ________

7) What is the coordination number for each Cl^- in the structure? (i.e. the number of Na^+ touching it) ________

CsCl (Simple Cubic Lattice)

1) Calculate the number of Cs^+ ions per unit cell. ________
Setup:

2) Calculate the number of Cl^- ions per unit cell. ________
Setup:

3) How many formula units of CsCl per unit cell? ________

4) What is the mass of a unit cell of CsCl? ________
Setup:

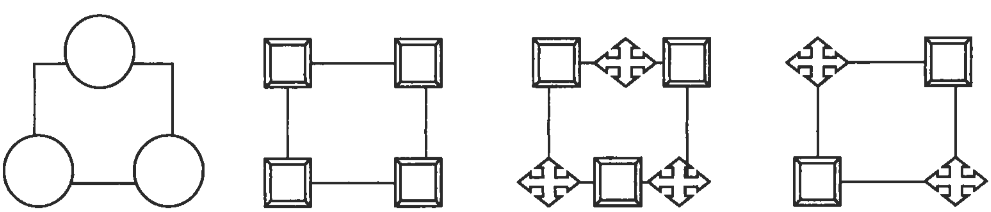
5) What is the ratio of Cs^+ to Cl^- in the unit cell? ________
6) Is this consistent with the 1:1 stoichiometry implied by the formula, CsCl? ________
7) What is the coordination number for each Cs^+ in the structure? (i.e. the number of Cl^- touching it) ________
8) What is the coordination number for each Cl^- in the structure? (i.e. the number of Cs^+ touching it) ________
9) Compare the coordination number for Cs^+ to that of Na^+ in NaCl. Which cation (Na^+ or Cs^+) has a higher coordination number? ________
10) Why? (Hint: Locate Na and Cs on the periodic table, hence compare their relative sizes.)

____

____

Exercise

1) Which of the sketches given below illustrate a 2-dimensional representation of a unit cell?



Unit cell? ______ Unit cell? ______ Unit cell? ______ Unit cell? ______

2) A metal has a body centered cubic packing structure and its density is 6.88 g/ml. The volume of one atom is 1.213×10^{-23} cm^3. Calculate the molar mass of the metal.

<u>Setup:</u>

3) Copper crystallizes in a face-centered cubic lattice. If the density of metallic copper is 8.96 g/cm^3, what is the radius of the copper atom? (molar mass of copper= 63.54 g/mole)

<u>Setup:</u>