Inorganic Chemistry with Doc M.

Fall Semester, 2012

Day 12. Ionic Thrills Part II.

Name(s):	Element:

Topics:

1. The cesium chloride lattice
2. The fluorite lattice
3. The zinc blende lattice
4. Diamond
5. Close packing
6. Hexagonal close packed lattice (hcp)
7. Cubic close packing (ccp)

1. The cesium chloride lattice. The CsCl lattice is usually encountered when we have cations that are similar in radius to the anions. Both anion and cation sub-lattices form a simple cube, however one sub-lattice is offset by one-half the edge distance in all three dimensions (that is to say that the cation sub-lattice occupies the body-centered positions of the anion sub-lattice (or visa versa).

(a) Sketch the CsCl lattice on this template placing the anions so that they are on the corners of the cube.
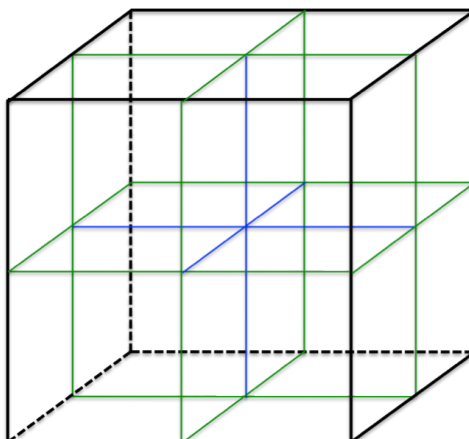
(b) Complete the following table for NaCl and CsCl. Write either Na^+ (or Cs^+) or Cl^-.

	Corner	Face-center	Body-center	Edge-center
NaCl				
CsCl				

(c) What sub-lattices does Cl^- have in the CsCl structure?

(d) What is the ratio of Cs^+ to Cl^- in the unit cell? How does this compare to its formula?

(e) What is the coordination number for Cs^+ and Cl^- in the CsCl structure? What is the coordination number for Na^+ and Cl^- in the NaCl structure?

(f) The density of CsCl is 3.988 g/cm^3. Knowing that density = mass/volume, determine the volume of the CsCl unit cell and use that value to determine the length of an edge, e, in units of pm.

(g) Continuing on, use the value for the edge, e, to determine the diagonal length from one corner to the opposite corner of the cube. This distance equals 2 x r_{Cs^+} + 2 x r_{Cl^-}. Given the ionic radius for Cs^+ ion is 188 pm, calculate the r_{Cl^-} in pm.

2. The fluorite lattice. Fluorite is CaF_2. There are two equivalent ways to think about the fluorite structure.

(a) The fluorides form a simple cubic lattice. Sketch _eight_ unit cells worth of fluorides on the template,
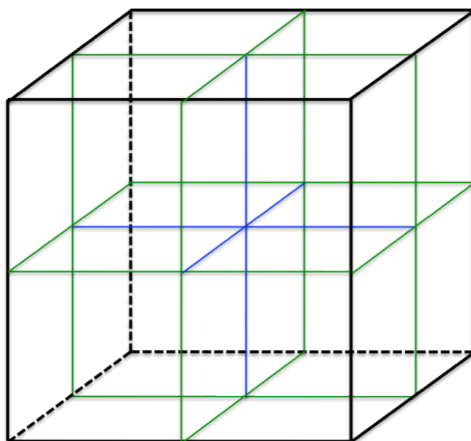
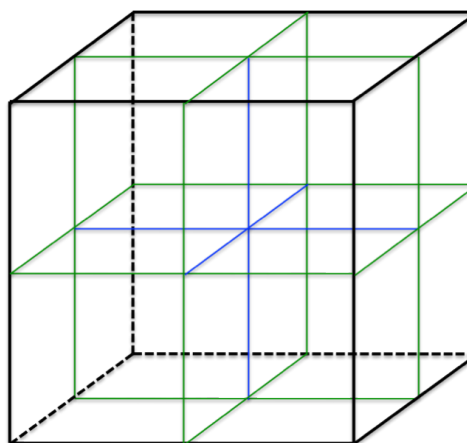(b) The calcium cations exist in alternating body-center positions. Sketch them in.

(c) What is the coordination number (number of nearest neighbors of opposite charge) for each ion?

(d) The other way to think about the fluorite structure is to think of a fcc of calcium ions (Ca^{+2} has slightly larger radius than F^-) with the fluorides in all of the tetrahedral holes. Sketch this here.
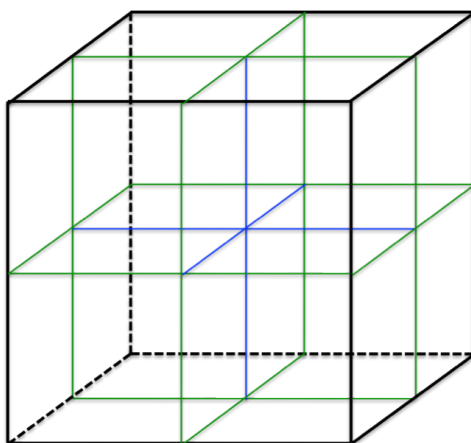

(e) What is the coordination number for each ion?

3. The zinc blende lattice. The ZnS is
"zinc blende." The lattice consists of a **fcc**
sulfide sub-lattice with Zn^{+2} cations occupying
half (alternate) of the tetrahedral holes.

(a) Sketch the ZnS lattice on this template.

(b) What is the coordination number (number of
nearest neighbors of opposite charge) for each
ion?

(c) How many S^{-2} anions are there per unit cell? Explain.

4. Diamond. Diamond has the same structure as zinc blende except that all of the occupied positions
are taken by carbons (both the zinc cation and the sulfide anion positions. Sketch diamond here and
connect every carbon to its four nearest neighbors. Do you see the tetrahedral angle?
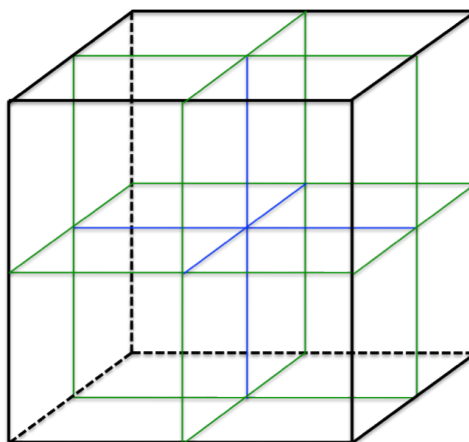
5. Close packing is a term that refers to the most highly efficient packing. In two dimensions, circles can close pack as follows. You may want to build something like this with pennies (or tiddlywinks) so that the next parts are easier.
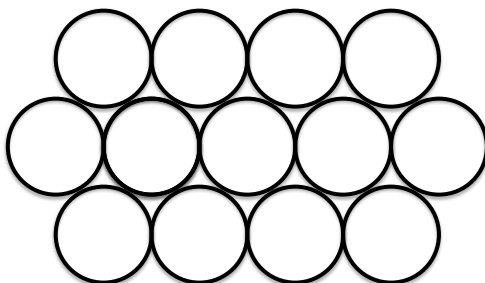

Now we can extend the 2-D circles to what happens for 3-D spheres: the same thing! With spheres, however, additional layers can be added and they do so in quite specific ways in order to maintain close packing: the spheres rest in the divots. Sketch about four close-packed atoms from a second layer on top of this first layer. Shade the second layer atoms. Build a second layer with your pennies or tiddlywinks.
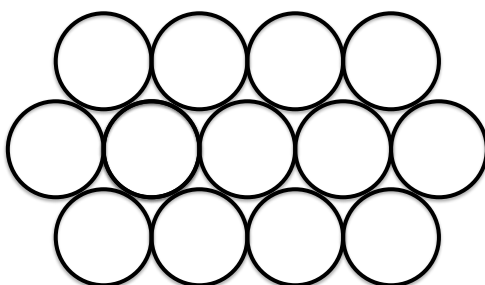
Note that of all the little triangle-shaped holes between the spheres in Layer 1, half of them will be covered with spheres from Layer 2. This brings us to Layer 3! The third layer could either (a) repeat the first layer so that the little holes from Layer 1 are still in view. When this happens, the close packed structure is called ABAB, referring to the two layers, A and B.   The ABAB layering is more commonly called "hexagonal close packed" or "hcp" or (b) the third row can position itself over the **holes** from Layer 1, creating a third unique layer. This structure is called ABC or "cubic close packed" or "ccp." Locate on this drawing where the third layer would go to create (a) an hcp arrangement or (b) a ccp arrangement.
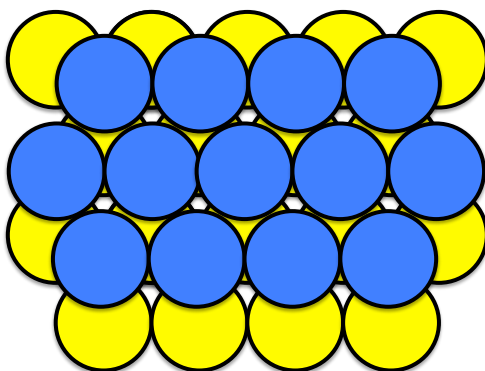
6. The hexagonal close packed lattice (hcp) forms a new type of unit cell, joining the cubic ones studied earlier. The hexagonal unit cell is shown as a group of three below. In these drawings, one of the unit hexagonal unit cells is outlined in blue. Draw the atoms present in one unit cell using what you learned above from the blue and yellow spheres.
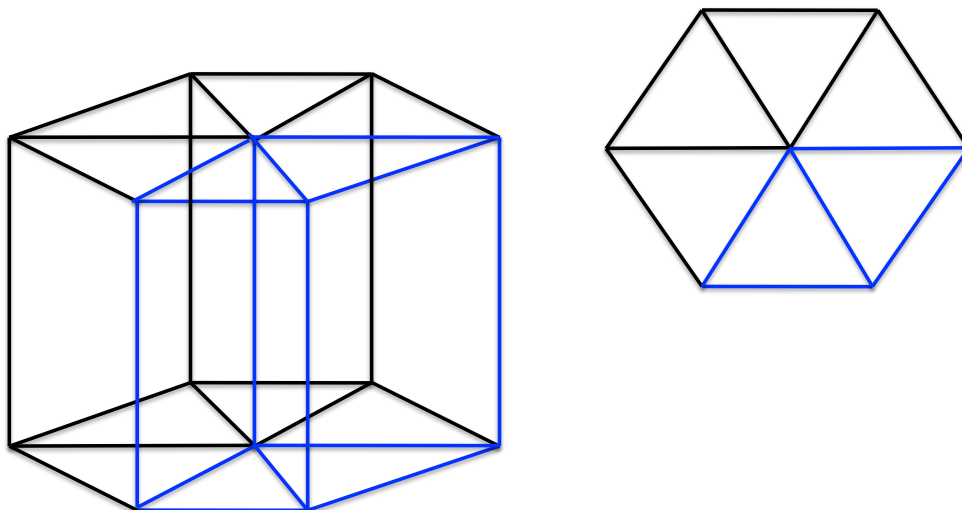
Hexagonal close packed

In the following drawings, the location of the diagrams, the relative vertical positions of the B layer and the octahedral holes are shown in more detail.


● A
● B
○ Oct hole

Hexagonal close packed
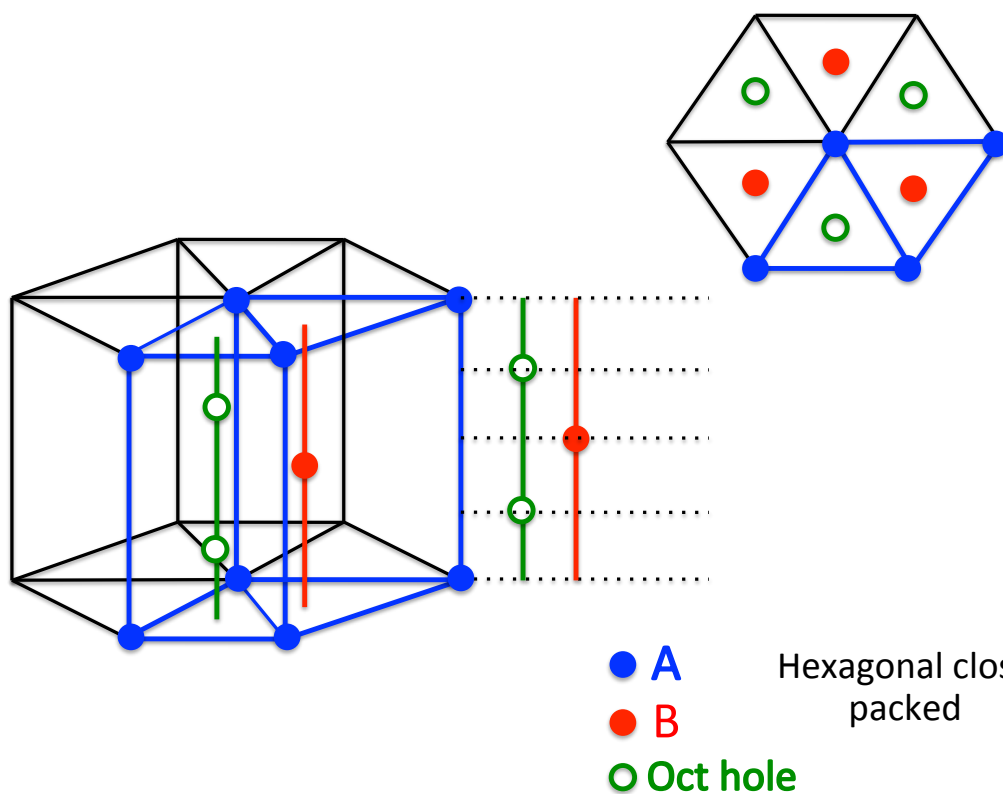
(b) How many atoms are fully contained within each unit cell?

(c) What is the area of the parallelogram, in units of r, that defines the top and bottom of each unit cell?

(d) What is the vertical length of the unit cell in units of r?

(e) What is the volume of the unit cell in units of r?

The location of the tetrahedral holes in the hexagonal close packed unit cell are shown in this drawing:

● A
● B
○ Oct hole
○ Tetr hole

Hexagonal close packed
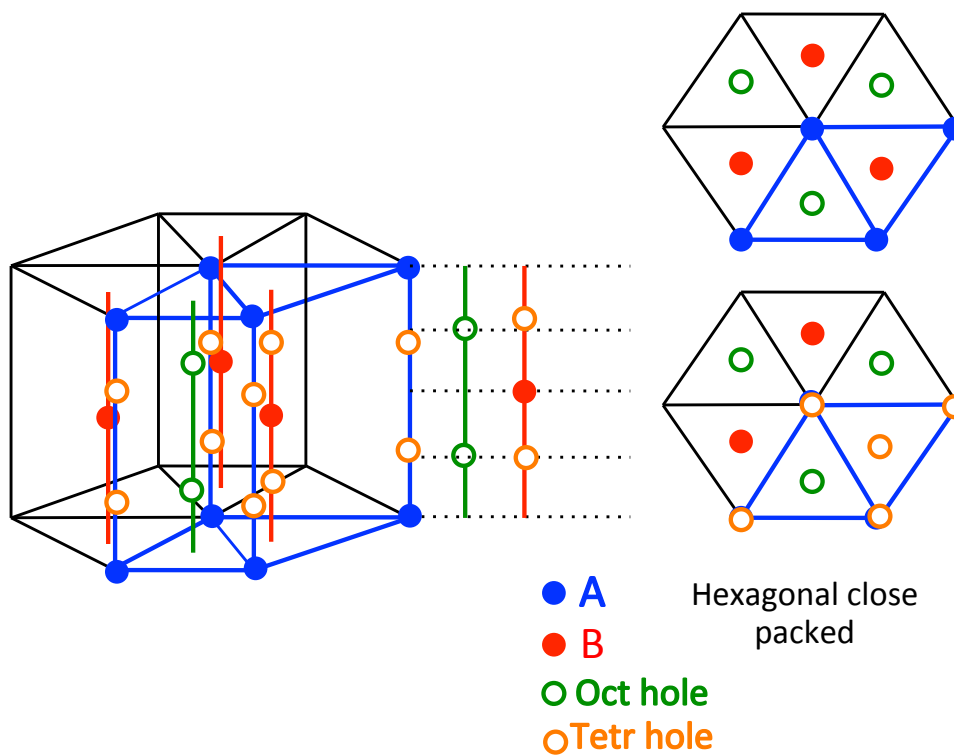
(f) How many tetrahedral holes are within each hexagonal unit cell?

(g) Magnesium, scandium, titanium, cobalt and zinc are just a few examples of elements that exhibit hexagonal close packed structure. Given that the atomic radius of magnesium is 160 pm, calculate the density of magnesium and compare it to the known density given on your colorful and informative periodic table.

3. The cubic close packed lattice (ccp) also has a surprise for us! Look at two close-packed lattices shown below.

(a) Which one is ABC and which one packs ABAB?
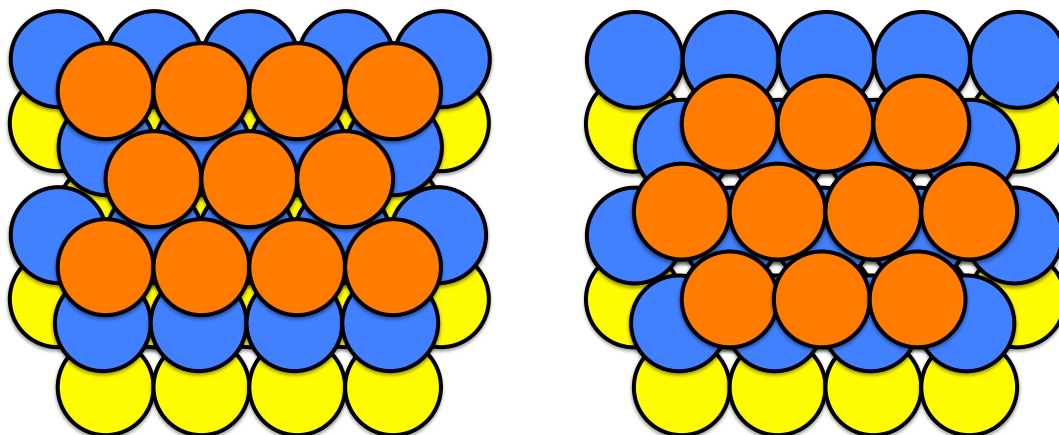
Hexagonal close packed (hcp) is equivalent to ABAB packing. The face-centered cubic lattice is equivalent to ABC or cubic close packing (ccp) as we see in the following figure. The face-centered unit cell is shown in its traditional cubic view as shown at left. The connection to ABC packing is seen if we view the fcc unit cell from one corner, down through the unit cell to the completely opposite corner as

shown in the right figure. The layers are shown in colors for both layers with Layer A being orange, Layer B being shown in blue and Layer C in green:
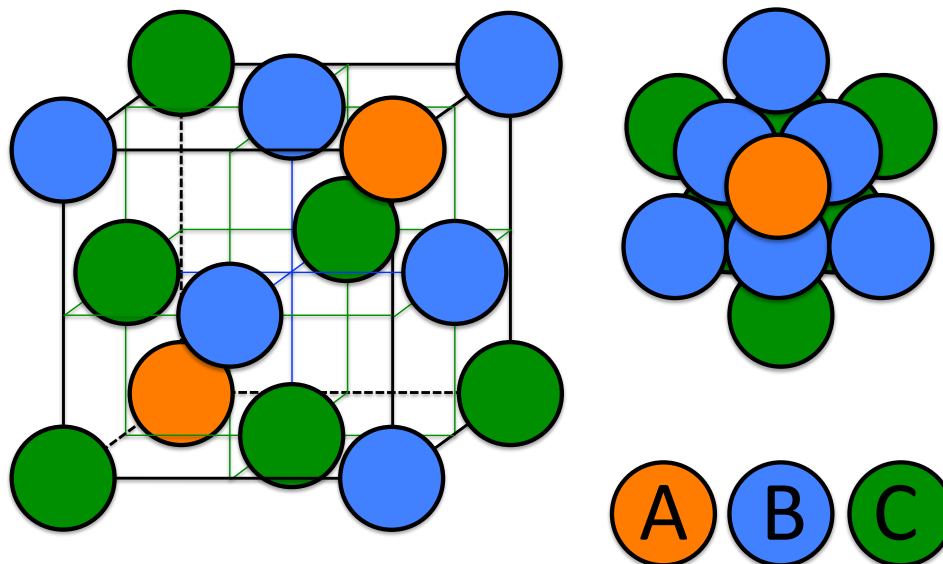
(b) Could body-centered cubic or simple cubic also be examples of close packing? Explain.

(c) Given your answer to (b), if you were to calculate the density for a metal, for example, using simple cube, **bcc** and **fcc** unit cells, for which would the density be greatest?

(d) Close packed lattices are very important for monatomic elements such as the metals. Why is that so? Why are close packed models less important for ionic compounds?

Review for the ACS Final Exam: Solid State

1. Which of the following best describes the cesium chloride lattice?

  (a) A face-centered cubic sublattice of one ion with the other ion occupying edge-centered positions.

  (b) A body-centered cubic sublattice of one ion with the other ion occupying edge-centered positions.

  (c) A face-centered cubic sublattice of one ion with the other ion occupying body centered positions.

  (d) A body-centered cubic sublattice of one ion with the other ion occupying edge-centered positions.

  (e) A primitive cubic sublattice of one ion with the other ion occupying body centered positions.

2. Palladium metal has an atomic radius of 137 pm and exists as a cubic close packed solid. What is its density?

  (a) $\dfrac{106.4}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 4/\sqrt{2})^3)}$

  (b) $\dfrac{106.4 \times 4}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 2)^3)}$

  (c) $\dfrac{106.4 \times 4}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 4/\sqrt{2})^3)}$

  (d) $\dfrac{106.4 \times 4}{(137 \times 10^{-10} \times 4/\sqrt{2})^3}$

  (e) $\dfrac{106.4 \times 2}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 4/\sqrt{3})^3)}$

Answers: E, C

Answers to Day 11

1. (a) List properties of ionic compounds: high melting, possibly soluble in water, in which case it will conduct electricity, hard but brittle; (b) How would one identify a compound as either ionic or covalent? Formula contains metal cation and non-metal or polyatomic anion, solutions conduct electricity, must be a solid.

3. The simple cubic unit cell.
  (a) Sketch in the atoms for a **simple cube**. Example: polonium

(b) atoms/ions touch along edge; (c) 1 atom is present per unit cell: 8 corners x $^1/_8$ = 1; (d) e = 2r; (e) V = e^3 = $(2r)^3$; (f) percent of the space occupied = 100% x $V_{one\ atom}/V_{one\ unit\ cell}$ = 100% x $(^4/_3 \pi r^3)/(2r)^3$ = 52.4%
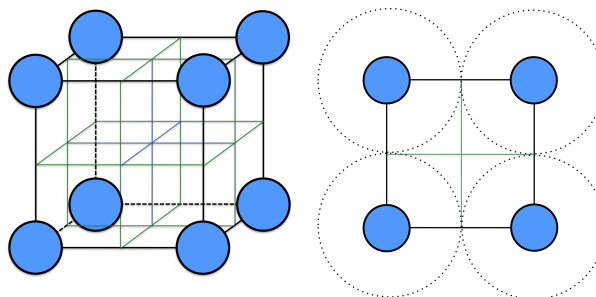
4. The face-centered cube Note that the yellow balls are the face-centered positions and the blue balls are the corners, BUT both yellow and blue are the SAME atom/ion in the fcc. Color is used only to accentuate the two different positions.
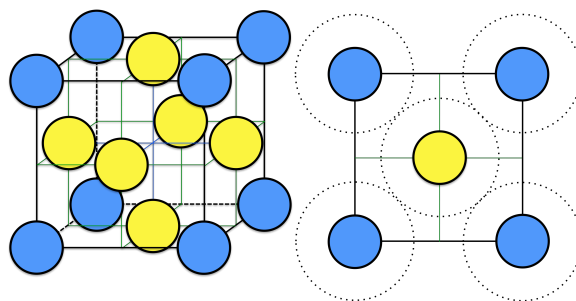
(a) see figure above; (b) 4 atoms are present per unit cell: 8 corners x $\frac{1}{8}$ + 6 face centers x $\frac{1}{2}$ = 4;
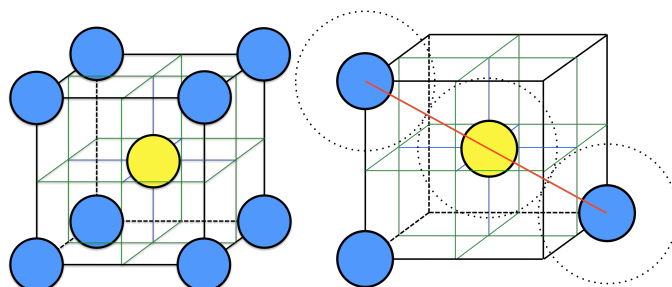
(c) $4r = 2^{0.5}e$, therefore $e = 4r / 2^{0.5}$; (d) $V = e^3 = (4r/2^{0.5})^3$;

(e) percent of the space occupied = 100% x $V_{4\ atoms}/V_{one\ unit\ cell}$ = 100% x $(4 \times \frac{4}{3} \pi r^3)/(4r/2^{0.5})^3$ = 74.0%; (f) volume of a calcium unit cell of calcium in 1.73×10^{-22} cm^3;

(g) density of calcium = $m_{Ca\ in\ one\ unit\ cell}/V_{one\ unit\ cell}$ =

$(4 \times 40.08$ g mol$^{-1}/6.02 \times 10^{23})/(1.73 \times 10^{-22}$ cm$^3) = 1.54$ g/cm^3, same as the actual density
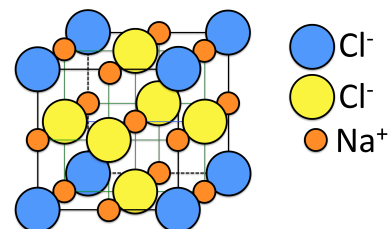
5. The body-centered Cube

(a) shown above; (b) Contact occurs along the body diagonal – the body center and the two opposite corners touch in a distance of 4r; (c) 2 atoms are present per unit cell: 8 corners x $\frac{1}{8}$ + 1 body centered entirely within the cell = 2; (d) $e = 4r / 3^{0.5}$; (e) $V = e^3 = (4r/3^{0.5})^3$; (f) percent of the space occupied = 100% x $V_{2\ atoms}/V_{one\ unit\ cell}$ = 100% x $(2 \times \frac{4}{3} \pi r^3)/(4r/3^{0.5})^3$ = 68.0%

6. The sodium chloride lattice.

(a) chlorides are the large spheres and sodium cations are the small ones; (b) fcc; (c) see figure; (d) There are 12 edge-centered positions in the fcc unit cell; (e) Edge-centered positions are only $\frac{1}{4}$ inside each a particular unit cell.

There are 12 x $\frac{1}{4}$ = 3 ions in edge-centered positions within each unit cell; another sodium cation is at the body-centered position.

(g)

|	Corner	Face-centered	Body-centered	Edge-centered
Simple cube	Yes	No	No	No
Face-centered cube	Yes	Yes	No	no
Body-centered cube	Yes	No	Yes	no
NaCl lattice	Yes	Chlorides	Sodium cations	Sodium cations

(h) The ratio of Cl$^-$ to Na$^+$ in the unit cell is 4:4 or 1:1, same as the formula

(i) $e = 2 \times 116$ pm + 2 x 167 pm = 566 pm; and the volume is 1.81×10^{-22} cm^3
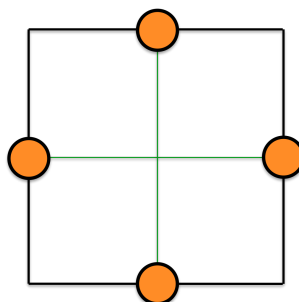
(j) density of NaCl = $m_{NaCl\ in\ one\ unit\ cell}/V_{one\ unit\ cell}$ =

$(4 \times 58.44$ g mol$^{-1}/6.02 \times 10^{23})/(1.81 \times 10^{-22}$ cm$^3) = 2.15$ g/cm^3, about the same as the actual density
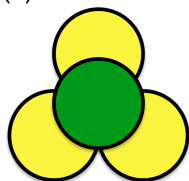
7. Octahedral and tetrahedral holes.
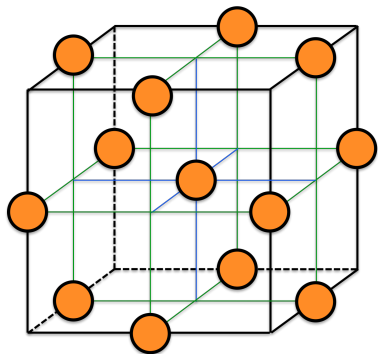
octahedral holes   octahedral holes

(a) There are 8 tetrahedral holes are present within a fcc unit cell;

(b) ratio of spheres : octahedral holes : tetrahedral holes fully contained within the fcc unit cell is 4:4:8.

(c)

(d) Each ion in NaCl has 6 nearest neighbors of opposite charge.