# LAB 8: IONIC CRYSTAL STRUCTURES

I have tried to adapt this laboratory from actual three-dimensional models you could hold in your hands to computer models freely available on the internet. Some things are lost in the process, such as the space-filling aspect, which is really necessary to appreciate the importance of closest-packed layers. Nevertheless, I hope you can get some sense of the three-dimensional structures by looking at the computer models. Even if you can find a quick answer to some of the questions, make sure you really rotate the models and look at them from all angles to convince yourself that you understand the answers in three dimensions!

1. Look at the NaCl structure here: https://www.chemtube3d.com/_rocksaltfinal/.
a. What is the coordination number of each of the green atoms, *i.e.* how many purple atoms are nearest neighbors to a green atom? What is the coordination number of each of the purple atoms? Do *not* consider the atoms at the edge or face of the cube but focus on the atoms on the interior of the model.

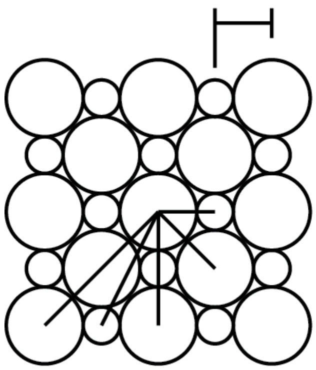
b. Rotate the model until you can clearly see a $C_4$ axis perpendicular to your screen. What other symmetry elements are evident from this perspective?

c. Now rotate the model until you can see a $C_3$ axis. What other symmetry elements are evident from this perspective?

d. Now rotate the model so that there appear to be alternating *layers* of green and purple atoms. It is very hard to see, but these layers represent *closest-packed* layers of the same kind of atoms. Can you see the line that these layers are perpendicular to? How would you describe where this line is positioned relative to the cubic structure?

You might be able to better see the relationship of the closest-packed layer with the cube in the picture on this page: http://www.ilpi.com/inorganic/structures/nacl/index.html.

e. In evaluating the energies of crystal structures, we use what is called a "Madelung constant." The Madelung constant is the sum of the number of ions at a given distance, divided by that distance in units of $r_{\pm}$, with the sign indicating whether the ions are the same charge or opposite charge. Because there is a negative in the product of the ion charges that applies to all terms of the potential, positive values indicate attractive interactions. For example, for the two-dimensional lattice depicted below, the first five terms of the Madelung constant M are shown. What are the first four terms of the Madelung constant for the three dimensional lattice that you have built?




$$\frac{M}{r_{\pm}} = \frac{4}{r_{\pm}} - \frac{4}{\sqrt{2}\,r_{\pm}} - \frac{4}{2r_{\pm}} + \frac{8}{\sqrt{5}\,r_{\pm}} - \frac{4}{2\sqrt{2}\,r_{\pm}} + \dots$$

$$M = 4 - \frac{4}{\sqrt{2}} - \frac{4}{2} + \frac{8}{\sqrt{5}} - \frac{4}{2\sqrt{2}} + \dots$$

2. Now look at the wurtzite structure: https://www.chemtube3d.com/_wurtzitefinal/

a. What is the coordination number of the yellow spheres? What is the coordination number of the gray spheres?

b. Rotate the model so that you can see hexagons, and so that the top layer is yellow. Are all the yellow atoms that look like they are at the top all in the same layer?

c. See if you can convince yourself that the top layer of atoms in this view constitutes a closest-packed layer. Make a sketch which shows a hexagon of yellow atoms around a central yellow atom, where all the atoms are in the same plane.

d. Now rotate the models so that you can see planes of yellow and gray atoms. If you look only at the yellow atom layers, is this an *a-b-a* pattern or an *a-b-c-a* pattern of stacking these layers? The key here is to look whether the atoms 2 or 3 layers away from each other are directly above the layers along a perpendicular to the layers. Another way of seeing the stacking is to click on the *hcp* link to the right of the structure. This shows you a simple *unit cell*, the smallest repeating unit of the crystal.

3. Now look at the zinc blende or sphalerite structure: https://www.chemtube3d.com/_blendefinal/

a. Is the coordination number for the yellow and gray spheres the same as you found for the wurtzite structure?

b. Look at the *ccp* link. This shows you a simple cubic unit cell. Does the arrangement of the yellow spheres remind you of any aspect of the NaCl structure? Note that the faces of this cube, although consisting of layers of yellow atoms, are not *closest packed* layers, as they form square arrangements rather than hexagonal arrangements.

c. Align this structure so that you can see *closest-packed* yellow and gray layers. The best way to do this is to hit the blue "reset" bar so you can see the whole model, and then rotate it so that you are looking directly from one edge to the diagonally opposite edge. From this angle, you should be able to determine whether this an *a-b-a* pattern or an *a-b-c-a* pattern.

4. Look at the cesium chloride structure (caesium chloride, to those in the Commonwealth): https://www.chemtube3d.com/_csclfinal/

a. This structure doesn't have as many "bonds" as the other structures, so it is harder to count the coordination numbers. Look at the *"primitive"* link and you should clearly be able to see the coordination number of the central violet atom. Now hit "reset" and see if you can see the same coordination number for the green atoms.

5. Take a look at the $BiI_3$ structure: https://www.chemtube3d.com/_bii3final/

a. What is the coordination number of the purple atoms? What is the coordination number of the white atoms? This is easier to see with the *hcp* link. Is there a rational relationship between the coordination numbers of the purple and white atoms and the chemical formula?

6. Take a look at the fluorite structure, and click on the *ccp* link to the right to see a unit cell:

https://www.chemtube3d.com/_fluoritefinal/ The unit cell is indicated by the lines; imagine a cube with these lines as edges.

a. How many green atoms are entirely within the unit cell?

b. How many orange atoms are on the corners of the unit cell? What fraction of the spherical atoms would actually be within a cube defined by the edge lines? When you multiply this fraction by the number of atoms on the corners, what do you get?

c. How many orange atoms are on the faces of the unit cell? What fraction of the spherical atoms would actually be within a cube defined by the edge lines? When you multiply this fraction by the number of atoms on the faces, what do you get?

d. Add up the total amount of green atoms within the cell and the products you get from parts b and c for the orange atoms. What is the ratio of green atoms to orange atoms within the unit cell? Which atoms represent the $F^-$ ions in $CaF_2$, the green or the orange?