Crystal Structure of Alkali Halides

This lab continues our study of the alkali halides. This week you will determine the roles of radius ratio and ionic charge on crystal structure.

1. Let's look at NaCl again. You can refer to your structure that you created in last week's lab. What is the coordination of the Na^+ ion? Calculate the radius ratio (ie., r_c/r_a) for NaCl. How does the ratio compare with the ideal value for this coordination?

   The unit cell of a crystal structure is the fundamental building block. All the chemical and structural information is embodied in the unit cell. What is the shape of the unit cell of NaCl? Using the values of ionic radii from the text, Appendix A, what do you think the length of the unit-cell edge should be? How does your guess for the unit cell edge length compare with the length determined by x-ray diffraction as 5.637 Å?

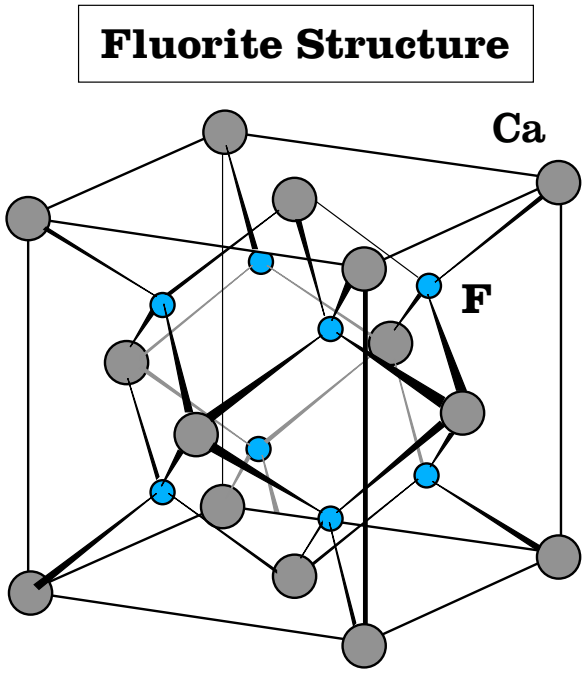
2. Many alkali halide compounds have the NaCl structure. KCl, KI, and KBr all do. With the help of the TA, choose one of these compounds to construct a model in CrystalMaker. You first have to fill out the form for the new crystal structure. Estimate the size of the unit cell from the ionic radii. The x, y, and z values are equal for cubic closest packed (face-centered cubic) structures. The angles are all 90°. The space group is $Fm3m$ for all these compounds. Enter the two atoms and plot the structure. Change the background of the plot window to white from the BACKGROUND... item in the MODEL OPTIONS menu. Rotate the model to a desired view and print the image. What are the radius ratios for these compounds? Are they all within the acceptable range for octahedral coordination?

   CsCl is another alkali halide, but its structure is different from that of NaCl. What is the radius ratio for CsCl? What should the coordination be? The Cl atoms are not closest packed because the Cs is too big to fit in the available interstices. Make a model of the CsCl structure in the same way as before, putting Cl at (0, 0, 0) and Cs at (0.5, 0.5, 0.5). Change the space group to $P1$. The change in coordination and consequent structure because of the change in radius ratio is one aspect of crystal chemistry—the mutual influence between crystal composition and crystal structure.

   If the coordination of Cs is cubic, what polyhedral elements are shared among other cubes? To figure this out, determine the electrostatic valency on the Cs^+ ion and on the Cl^- ion. How many Cs^+ ions must be bonded to a Cl^- ion for electrostatic neutrality? Is this true for all the Cs^+ ions? How, then, are the Cs cubes connected together?

3. Two factors influence the structures of the alkali halides, size (radius ratio) and charge. So far, all the structures we have considered are based on a cubic closest packing of anions with the cations filling the octahedral interstices (with the exception of CsCl). The ratio of octahedral interstices to ccp anions is 1, so this structural type works for the alkali halides for which the charges on the cation and anion are equal in magnitude. What about the alkaline earth halides? Our example is fluorite, CaF_2. Ca is divalent, whereas F is monovalent. The structure has to be different from that of halite. Determine the radius ratio for fluorite. What should the coordination of Ca be? Use CrystalMaker to construct a model of fluorite. The space group is still $Fm3m$; use a unit-cell edge of 5.46 Å; put Ca at (0, 0, 0) and F at (0.25,

0.25, 0.25). You should find that the fluorite structure can be thought of as a ccp array of Ca atoms with F in the tetrahedral interstices. What is the coordination number of Ca? What is it for F? What is the electrostatic valency of the Ca^{+2} ion? How about the F^{-} ion? What polyhedral elements are shared in the F tetrahedra? The Ca cubes?



The examples of the alkali and alkaline earth halides show that the concepts of ionic bonding work very well in explaining simple crystal structures.

4. You should be wondering how the program can generate a crystal structure containing many atoms simply by entering the coordinates of only two atoms. The secret is in the space group symbol. The short-hand notation embodies all the symmetry elements of the crystal. It is the symmetry that dictates the positions of the all the atoms from the positions of the basic group of atoms (sometimes called the motif). We will explore the mysteries of symmetry in the next lab exercise.