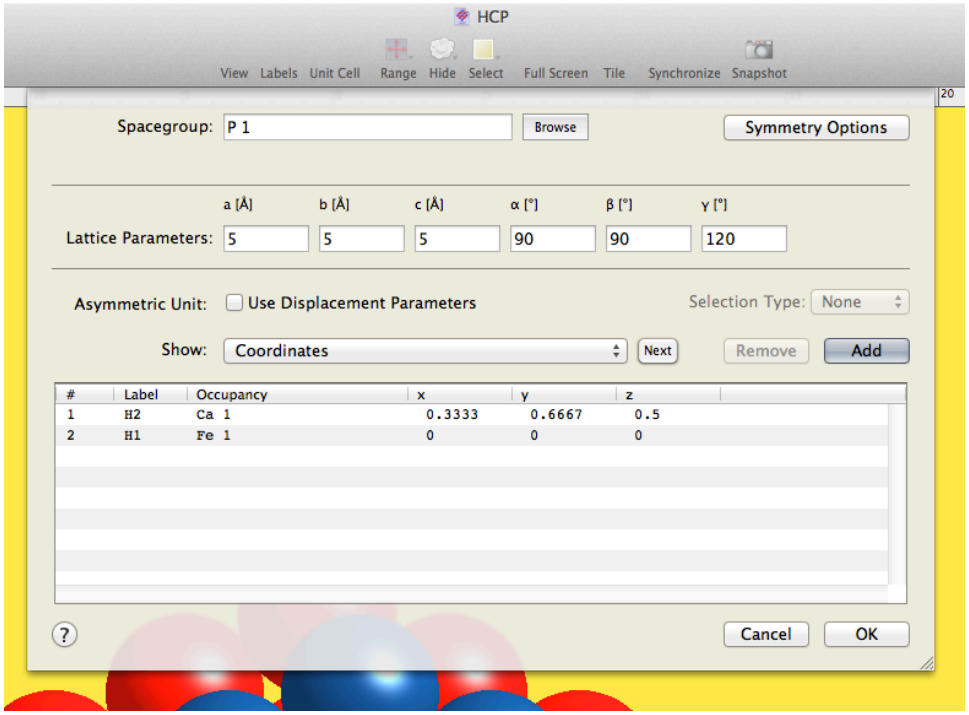
Bonding and Packing in Ionic Solids

The relationship between crystal structure and composition is called crystal chemistry. We will explore some concepts of crystal chemistry using the alkali halides as guides. The group of alkali halides comprises the compounds NaCl, KCl, NaBr, NaI, KI, and so on. These are constructed from an alkali element plus a halogen. The group exhibits ionic bonding par excellence. We will also consider some of the alkaline-earth halides, especially fluorite, CaF_2, to see how the structure changes with changes in the cation:anion ratio. This week we begin by looking at packing schemes and at the structure of halite.

1. We'll start by looking at closest-packing schemes. There are cork spheres glued together to form sheets. Each sphere is surrounded by six spheres, and all are touching. Place two sheets one on top of the other, pick the layers up, and notice the voids (interstices). Now place a third layer so that the voids are covered up; this is cubic closest packed. Can you see the face-centered cube created by this packing?

   Shift the third layer so that it is directly above the first layer. You should be able to see through the packed spheres through one set of interstices. This is hexagonal closest packing. The spheres are just as closely packed as they are in the cubic closest packed arrangement, but the symmetry is different.

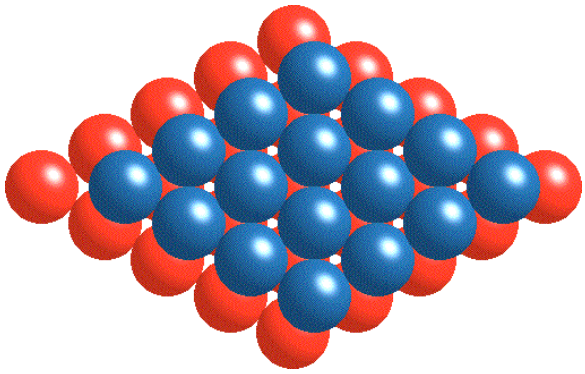


   Construct a model of hexagonal and cubic closest-packing schemes on the computer in the Department's computer lab. You have to use one of the Macintoshes. Launch the Crystal-Maker program, which should be in the Applications folder. Once the program launches, you

will need to create a new crystal. From the File menu, choose New Crystal. A dialog sheet will open to be filled in. Fill the box to look like the example above.

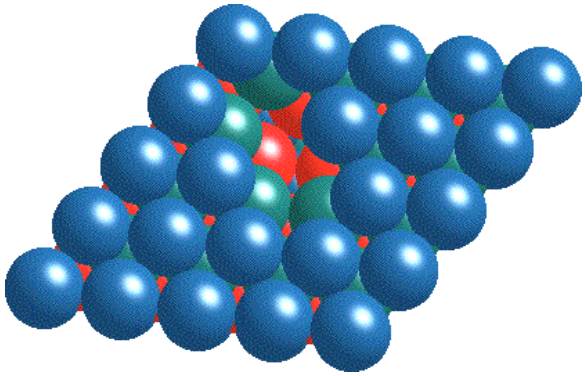
The Q and Qu are just place holders to give the separate layers different colors. You will have to edit the elements (last item in the Edit menu), Add the elements Q and Qu, make the radii 2.6, and give each a color. Click Apply. You will have a ball-and-stick model. Choose Space Filling from the Model menu. Once you have the model, go to the Transform menu and choose Set Range... to make the x range 0 to 4.0, y range 0 to 4.0, and the z range 0 to 1.5. Also choose the Model menu and choose Model Options..., which lets you set the background color to something other than black. You can also experiment with the colors of the spheres, if you wish.

To print the model on the color printer, you will need to select the Epson as your printer[1] . Go to the Apple menu and select Chooser. Click on the icon for the Epson 850, and the printer name should show in the list on the right. Select it and close the Chooser window. Then you can choose Print from the File menu in Crystal Maker. Place a copy in your notebook. Here's what I got.



You can rotate the model with the hand or rotation tools. I have it aligned to show the open spaces that are left by the stacking sequence ABAB.

To create a cubic closest-packed model, return to the Edit menu, choose Edit Structure..., and increase the value for c to 7.5. Add another atom (I called it Qz) and make its coordinates x = 0.6667, y = 0.3333, z = 0.3333. Change the coordinates for Q to z = 0.6667. Then plot. Also edit the radius of the new atom so it is also 2.6. You should have a packing sequence ABCABC with no open spaces. Print a copy for your notebook.



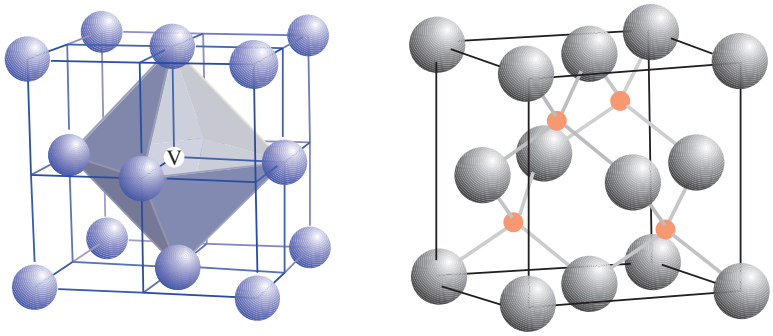
[1]The directions here change with changes in the computer lab and printer configurations. Check with your TA.

2. Ionic crystals contain anions and cations. In most crystals, the anions constitute a closest-packed array, and the cations squeeze in the spaces between the anions. Whether the anions are cubic- or hexagonal-closest packed, there are two kinds of interstices in the array: spaces surrounded by six anions, and spaces surrounded by four. If cations fit in the former, they are said to be in octahedral coordination. Cations surrounded on four sides by anions are said to be in tetrahedral coordination. Other coordinations are possible in anion arrays that are not closest packed.

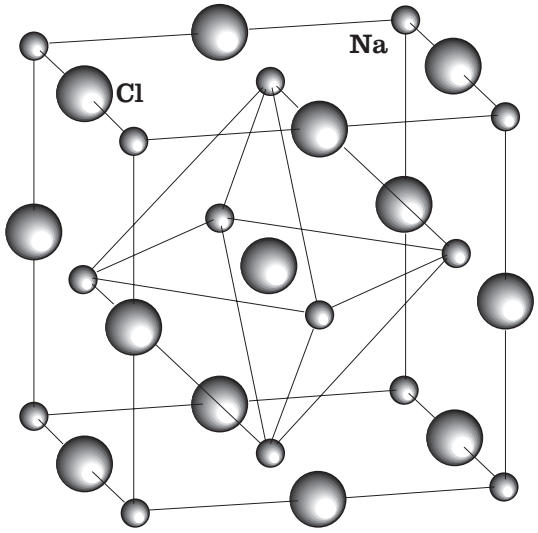
   Two factors determine the placement of cations in the closest-packed array: charge and size. If the anions are singly charged, then the number of cations is determined by their charge. If the cations are also singly charged, then the number of cations must equal the number of anions, as in NaCl. If the cations are doubly charged, then there must be half as many cations as anions, as in $CaCl_2$. The second factor in creating the crystal structure is the size of the cations, relative to the anions. Small cations fit in the tetrahedral spaces, but large cations can only fit in the octahedral interstices. The size limitation is determined by the radius ratio, r_c/r_a. The ranges for the ratio for various coordinations are shown in the text.

   Use CrystalMaker to examine the interstices in cubic and hexagonal closest packed structures. There are files on the computer for octahedral interstices and tetrahedral interstices in CCP and HCP. Feel free to experiment with the structures in the files so you can see the spaces. For the CCP structure, convince yourself that the array is the same as a face-centered cubic structure. That is, a cube is formed by connecting eight anions, and there are six anions at the center of each face. In this arrangement, the closest-packed layers are diagonal to the corners of the cube. The structure can be thought as consisting of a stacking of these cubes, which are the fundamental building blocks. We call the block the unit cell of the structure.

   Determine the number of octahedral and tetrahedral interstices per unit cell in the CCP structure. Use the Crystal Maker files CCP Octahedral and CCP Tetrahedral as aides. The structures are illustrated below.



3. Look at the ball and stick model of NaCl and pretend that the red spheres are Na and that the silver ones are Cl. Identify the layers, either red or silver, that constitute the cubic closest packed arrays. Identify a face-centered cube, either with red or with silver atoms on the corners. Convince yourself that each red atom is surrounded by six nearest silver atoms, and vice versa. Make a sketch of a unit cell of halite, similar to the one on the right, which contains an Na atom on each corner and on the center of each face with Cl atoms in the center of the cell and at the center of each edge. How many Na^+ ions are in the unit cell? How many Cl^-? What is the coordination of Na^+? What do you think the crystal form of halite crystals is? What about the cleavage? Halite is an excellent example of an ionic solid. This is a structure worth remembering.



4. Construct a model of NaCl for yourself with the use of Crystal Maker. Select New... from the file menu, and you will be presented with a window with fields for you to enter data about the new crystal.

   First enter the dimensions and angles for the unit cell. Let's use 5.637 Å for the values of a, b, and c. Leave the angles at 90°. Select the space group field with P 1 in it. Replace it with F m 3 m (put spaces between the characters). Now select the Si and replace it with Na. Change the label to Na, too. Click the Add button. Select the Na and change it to Cl; change the label to Cl, too. Change the coordinates to 0.5, 0.5, 0.5. Click the Add button. Click the OK button. You will be presented with a top-down view of a unit cell of halite. You can rotate the image with the hand to see the structure from any other vantage point (there is also a Rotator palate, which you can select from the Windows menu, for finer control). Don't like the preselected colors? You can click the color bars from the Crystal Information window or choose Atom Specs... from the Edit menu. Want to draw bonds between the atoms? Choose Bond Specs... from the Edit menu and select Na in the From Atom list and Cl in the To Atom list and click Add. The bond size can be changed in the Bond Types... item under the Model Options menu. You can increase the number of unit cells to view by choosing the Set Range... item from the Transform menu. Change the maximum values to 2.0. Now you should be able to rotate the model to see the sheets of atoms that are stacked together in a cubic closest packed arrangement. Feel free to explore the program as you build the models. Once you have a model you like, print it out and place it in your notebook.