Experiment 2a
Models of the Solid State*

*This lab is adapted from solid-state labs offered at Purdue and Rice Universities.

Introduction
The structures of metals and simple ionic solids are prototypes for the structures of many different inorganic compounds. For example, many extended covalent solids have structures that can be described in the same way as those of ionic solids. The internet resource “Materials Explorer, http://copper.chem.umass.edu/~dv/matex/ will be used to manipulate CHIME computer models, and the model kits will allow you to manipulate 3-D models, of several solid-state structures. The lab involves a number of problems and questions based on these models of solid state structures.

There will be no formal lab report for this experiment. Instead, you will complete your work on this handout, and turn this in at the beginning of the next lab period.

Use of the Solid State Kit

We will use the Institute for Chemical Education (ICE) Solid-State Model Kits which are designed for creating a variety of common and important solid state structures. Please be careful with these materials as they are quite expensive. There is a list of kit components on the inside of the lid of each box - be sure that you have a complete kit, and that you return all parts.

There are four major part types in each model kit:

*2 off-white, thick plastic template bases with holes (one with a circle, the other a semicircle);
*cardboard templates (about 20 labeled A-T);
*metal rods (to be inserted in the holes to support the plastic spheres);
*plastic spheres in 4 sizes and colors.

The spheres can represent atoms, ions, or even molecules depending upon the kind of solid it is.

You will be given directions for the use of a specific base, template, placement of the rods, selection of spheres, and arrangement of the spheres as you progress. The ICE model kits make use of Z-diagrams to represent how the structure will be built up. Each type of sphere will be numbered with the \( z \) layer in which it belongs.
As we build each structure in three-dimensional space, we will be drawing figures to represent the unit cell structures. Each level or layer of atoms, ions, or molecules in a unit cell can be represented by a two-dimensional base which is a square, hexagon, parallelogram, or other packable shape.

The bottom layer is referred to as $z=0$. We then proceed layer by layer up the unit cell until we reach a layer which is identical to the $z=0$ layer. This is $z=1$. Since $z=0$ and $z=1$ are identical by definition, we do not have to draw $z=1$, although you might want to do so as you are learning how to work with solid state figures. The layers between top and bottom are given $z$ designations according to their positions in the crystal. So, for example, a unit cell with 4 layers (including $z=0$ and $z=1$) would also have $z=0.33$ (1/3) and $z=0.67$ (2/3).

Each solid-state kit has two types of bases (one using rectangular coordinates, the other using polar coordinates) indicated by a full circle or semicircle which I call a “moon”, so two structures can be built simultaneously as long as there are spheres available. You will work with a partner, to build and view the models, but each student must hand in their own work. To expedite things, half of the partners will work initially with the moon base, while the other half works initially with the circle base.

**Use of Materials Explorer**

Materials Explorer uses the Chime program. Using the Chime representations you can rotate a model, change its size, measure distances, and change from ball-and-stick representations to wireframe or space filling views.

*To rotate a model:*

Click and hold down the left mouse button (left click) while over the graphic and drag the arrow to manually rotate the structure on display.

*To get a close up of part of a structure:*

Click and hold down the left mouse button and simultaneously depress the “shift” key while over the graphic. Dragging the arrow will change the size of the model displayed.

*To change the display mode:*

Click and hold down the right mouse button (right click) while over the graphic. A menu will pop up. While holding the right button down drag the “display” and then select the type of display in the second pop-up menu.

*To measure distances between atoms:*

Click and hold down the right mouse button (right click) while over the graphic. A menu will pop up. While holding the right button down drag to “select” then to “Mouse Click Action” and then to “Distance”. Left click on one atom then left click on a second atom to determine the distance between them. The distance is displayed in the gray bar at the bottom of the screen. Unfortunately, you need to reselect “Distance” if you change models.

Some pages have buttons you can click to change the display – for example, to view the packing of a particular ion, rather than the unit cell.
Go to [http://www-unix.oit.umass.edu/~mjknapp/Chem242/](http://www-unix.oit.umass.edu/~mjknapp/Chem242/) the course web site. A link to the computer portion of this lab (Materials Explorer) can be found on the “weekly handouts” page. Open this link to view and manipulate CHIME models of the following structure:

- CsCl, a primitive cubic structure
- NaCl, a face-centered cubic structure
- diamond, related to the body-centered cubic structure
- ZnS, zinc blende
- ZnO, isostructural with an isomer of ZnS called wurtzite, is also of interest.
- BaTiO$_3$, a perovskite

Now use your models and the computer representation to get the data necessary to solve the following problems:

**Problem 1. moon base**

Cesium Chloride crystallizes as primitive cubic lattice, with a unit cell edge, $a = 412$ pm. View the CsCl unit cell on the computer, and build a 3-D model of one unit cell of CsCl (stay within the shaded cube of template A of your ICE kit). Show your work!

A. If the radius of a chloride ion is 167 pm, what is the radius of a cesium ion?

B. How many cesium ions surround each chloride ion?

C. Sketch a unit cell of CsCl, indicating fractional ions at the corners. Indicate each type of ion.
D. What is the coordination number of the cesium ion? What are the shapes of the coordination polyhedra?

E. The structure of CsCl shows that there is space between chloride ions that are nearest to each other (along the face of each unit cell – wherever you can see the Cs⁺). Using the radius of the chloride ion determined above, calculate the radius of the largest ion that could move through this opening without distorting the structure. Is there an ion this small? If so, give an example (go ahead and look this up – but cite your source).
Problem 2. moon base
In order to determine terms in the Madelung series for the NaCl structure we need to know the relative interionic distances, the number of each type of neighbors in the structure, and whether the interaction between the ions is attractive or repulsive. Use your model kit to build a NaCl unit cells (use pattern C). Using these models and assuming the nearest neighbor M⁺ - X⁻ distance is 1, determine the relative distances between ions, the number of neighbors, and whether the interaction between ions is attractive or repulsive for the 1ˢᵗ, 2ⁿᵈ, and 3ʳᵈ nearest neighbors about a given ion.

Problem 3. circle base
Carbon (diamond form) and silicon crystallize with a cubic unit cell that has atoms in the same positions as the zinc and sulfur ions in the unit cell of cubic ZnS (zinc blende); however, all atoms in the carbon and silicon unit cells are identical to one another. Build a model of the diamond structure (use pattern F), and view the diamond unit cell on the computer. Measure the C-C bond distance. Diamond and silicon crystallize in the diamond structure with \( a = 356.6 \) pm and 542.8 pm, respectively. Carborundum (silicon carbide) has the zinc blende structure with \( a = 436.0 \) pm.

A. Calculate the C-C distance in diamond, the Si-Si distance in silicon and the Si-C distance in Carborundum. Note that you can verify the C-C distance in diamond using the CHIME model, as a means to double check your method.
B. From the C-C and Si-Si distances determined above, calculate covalent radii for C and Si and predict the Si-C bond distance in Carborundum.

C. How does the calculated value of the Si-C distance compare to the experimental value?

Problem 4. moon base

Barium titanate, BaTiO$_3$ crystallizes with the perovskite structure. Build 3 unit cells of the isostructural CaTiO$_3$ (use pattern C of your model kit), and view the perovskite structure on Materials Explorer. In the 3-D models, the green spheres represent Ba$^{2+}$, while the blue spheres represent Ti$^{4+}$.

A. The unit cell is characterized by $a = 401.0$ pm. The radius of Ba$^{2+}$ is 142 pm, and the radius for Ti$^{4+}$ is 61 pm. Assuming that everything packs tightly, what is the calculated (or, maximal) radius of O$^{2-}$ in BaTiO$_3$?
B. How does this compare with a tabulated value of \( r \) for \( \text{O}^{2-} \)? Coordination number matters.

C. How many \( \text{Ba}^{2+} \) ions are within the two unit-cells that you made?

D. Are the octahedral holes occupied by \( \text{Ti}^{4+} \) located at the edge, face, or corner of the unit cell?

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**Problem 5. baseless**

An ultra pure sample of silicon was found to have the following isotopic composition:

<table>
<thead>
<tr>
<th></th>
<th>(^{28}\text{Si})</th>
<th>(^{29}\text{Si})</th>
<th>(^{30}\text{Si})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic %</td>
<td>92.228948</td>
<td>4.669981</td>
<td>3.101071</td>
</tr>
<tr>
<td>Nuclide Mass</td>
<td>27.9769286</td>
<td>28.9764969</td>
<td>29.9737722</td>
</tr>
</tbody>
</table>

Calculate a value for the atomic weight of silicon to eight significant figures. Precise measurements lead to a density value of 2.3290017 g/cm³ and careful x-ray measurements to a unit cell dimension, of 543.10661 pm. Taken together these data provide one of the most precise values available for Avogadro’s Number, \( N \). Calculate that value for \( N \), continue on the reverse if you need the room. Remember to use the appropriate number of significant digits. The original report may be found in *Physical Review Letters* (1974) 33, 463.
Close-packed Models of Ionic Solids

So far we have emphasized lattices and unit cells in our discussions of the solid state. A somewhat more descriptive approach is to describe structures in terms of closest-packed structures, such as hexagonal close-packed (hcp) or cubic-close packed (ccp). Many metals pack into these structures. In addition, many ionic solids can be viewed as comprising a close-packed array of anions with the smaller cations packed into the octahedral and/or tetrahedral holes between the anions. If the cations are sufficiently small, anion/anion “contact” occurs and each anion is in contact with 12 other anions with nearest-neighbor cations sitting in some or all of the interstices.

More commonly, the cations are big enough so that the anions are not in direct contact, instead, they simply occupy the same relative positions that they would in a close-packed array (hence the same mode of description may be used). Nevertheless, for the next problem we will use very small cations to better demonstrate the concept of close-paced structures.

We shall compare hexagonal closest-packing with cubic closest packing, as well as identify the tetrahedral and octahedral holes in these lattices. By the way: It may not be immediately apparent that the cubic closest-packed arrangement is identical with the familiar face-centered cubic structure, as the 3-fold axis in the standard approach to ccp lies along the space diagonal of the face-centered cubic unit cell.

Problem 6. circle base

Use your model kit to build a hexagonal close-packed (hcp) and cubic close-paced (ccp) unit cells (plate L’ – you should use 14 rods). Now focus on the hcp cell. Note that the third layer exactly overlays the first layer – thus, hcp is described as a repeat of layers in an \( abab \ldots \) pattern.

Now, you will look at a tetrahedral hole and an octahedral hole by adding spheres to the rods labeled “holes” on plate L’. Tetrahedral holes exist wherever four ions (large spheres) pack; octahedral holes exist wherever 6 ions pack together.

A. Place a pink sphere onto the rod #2 (labeled “holes”) between layers 2 and 1’ of the hcp anion array. Is the pink cation in a tetrahedral or an octahedral hole?

B. Place a blue sphere onto the un-numbered rod (labeled “holes”) between layers 2 and 1’ of the hcp anion array. Is the blue cation in a tetrahedral or an octahedral hole?

D. Which is larger, the tetrahedral hole or the octahedral hole? Switch the pink sphere with the blue sphere to help answer this question.
**Problem 7. circle base**

This problem demonstrates concepts regarding how cations pack into tetrahedral vs. octahedral holes. For this problem compare ZnS (zinc blende) to NaCl on Materials Explorer, as well as contrasting the 3-D models.

Construct the NaCl cubic-close packed model (template L).

A. Viewing this as a close-packed lattice of anions (Cl⁻), how many octahedral holes are present in this hexagonal unit cell? How many tetrahedral holes?

B. Into which type of hole are the Na⁺ cations packed?

Construct the zinc blende structure (template L).

C. Viewing this as a close-packed lattice of anions (S²⁻), how many octahedral holes are present in this hexagonal unit cell? How many tetrahedral holes?

D. Into which type of hole are the Zn²⁺ cations packed?

E. If every hole named in part D were occupied by a zinc ion, the charge of Zinc, and the stoichiometry of zinc sulfide, would be need to change. What would the charge of zinc have to be if every hole that you named in part D were fully occupied by zinc? What would the stoichiometry of this structure be?