Experiment 7

Space-filling Spheres: Exploring Solid State Structures

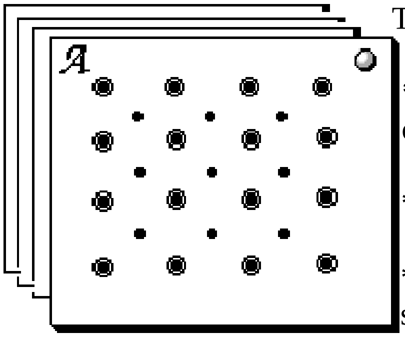
Introduction

The structures of metals and simple ionic solids are prototypes for the structures of many different inorganic compounds. For example, many complex structures, such as that of the superconductor $YBa_2Cu_3O_7$, are composed of the same basic building blocks and stacking paradigms as simple structures (in this case, the perovskite structure). This lab involves a number of problems and questions on solid state structures.

There will be no formal lab report for this experiment. Instead, you will complete your work on this handout and turn it in to your TAs when you are finished.

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);

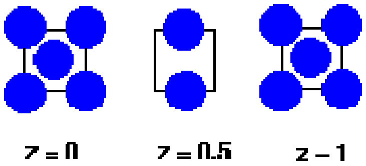
*cardboard templates (about 20 labeled A-T);

*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 shape capable of tiling a 2D plane.

In solid state structures, **x**, **y**, and **z**, refer to *fractional coordinates.* A coordinate of **z=0** describes an atom on the same plane as the origin, while an atom with **z=1/2** has a position that is half of the total height of the unit cell, or **1/2*c***, where ***c*** is one of the three vectors used to define the unit cell. Thus the bottom layer is referred to as **z=0**. We will build up our models layer by layer 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 evenly spaced 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 (to accommodate different symmetry structures) indicated by a full circle or semicircle which we will call a “moon”. You will work with one or two partners to build and view the models, but each student must hand in their own work. While discussion is encouraged, copying of answers is not permitted.

References (bring the handouts from class to this lab):

Brown, I. D. and Altermatt, D. “Bond-Valence Parameters Obtained from a Systematic analysis of the Inorganic Crystal Structure Database”, *Acta Cryst.*, **B41**, 244-7 (1985).

Brese, N. E. and O’Keefe, M. “Bond-Valence Parameters for Solids”, *Acta Cryst.*, **B47**, 192-7 (1991).

Shannon, R. D. “Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides”, *Acta Cryst.*, **A32**, 751-67 (1976).

Understanding hexagonal and cubic close packing in solids

Objective: Understand voids and coordination in HCP and CCP solids (Estimated time: 1-1.5 hr)

You can work on this hands-on modeling project in groups of two or three students. There will be a total of two stations available for this project on the table at the center of the CRC. If there is not a station available, skip ahead to the computer modeling projects, and begin work there.

Give the names of the other students in your group:

Use your model kit to build three layers of a hexagonal close packed (HCP) sequence on the ***L*** *base. Insert 28 metal rods into the circled holes and build up three layers of spheres using the plan provided to you (if you follow this plan, your first layer should have 11 spheres). Note that all the spheres in the third layer will sit exactly above spheres in the first layer. The stacking sequence we have built up would be denoted* **aba** *since the 1st and 3rd layers sit one set of columns, while the 2nd layer sits on a different set of columns. Note that the actual repeat sequence is* **$(ab)_n$**, *as the next layer that if we continued building would be another* b *layer.*

How many spheres are in your lowest, middle, and upper layers?

A fully-coordinated large sphere in the middle layer touches how many other large spheres?

How many of these neighboring spheres are in the layer below, same layer, and layer above?

Examine the demonstration stage which has an example of tetrahedral and octahedral holes. Note that all four or six spheres contact each other when the hole in the center is vacant.

What color is the largest sphere that fits in the octahedral hole, touching all of the surrounding spheres, but not disrupting the existing contacts between those spheres?

What color is the largest sphere that fits in the tetrahedral hole, touching all of the surrounding spheres, but not disrupting the existing contacts between those spheres?

Before proceeding further, check with a TA to ensure your work so far is correct.

Fill all the octahedral holes between the middle and upper layer with the largest sphere that fits in these holes. (You may wish to temporarily remove the upper layer, and replace it when you are done putting down spheres). You must verify that the holes you are filling are actually octahedral (sphere in hole touches 6 large spheres at once) after the upper layer is replaced.

Describe the location and environment of the spheres filling the octahedral holes. Make sure you comment on the number of neighboring spheres above and below the octahedral holes. You can specify the column of a site as “1”, “2”, or “3” based on the labels given in the **L** blueprint.

How many of these “octahedral” spheres fit between the middle and upper layers of spheres? Do NOT count the truncated sites on the edge which do not have six neighbors present.

Are all of the octahedral holes between these two layers found at the same height?

Use a ruler to measure the radii of the atoms making up the close-packed layer and those occupying the octahedral holes. Remember you should have one digit with uncertainty.

The radius of the smaller sphere is what percent of the radius of the larger sphere?

If the larger spheres have a radius 1.40 Å (oxygen), what will the radius of the smaller sphere be?

If the layers were infinite in size (instead of constrained to just 14 spheres), how many octahedral holes between the upper and middle layers would there be relative to the number of spheres in the <u>one</u> layer? Give your answer as a ratio (*i.e.* 3:1 ratio of sphere to holes).

Now fill all the tetrahedral holes between the <u>middle</u> and <u>upper</u> layer with the largest sphere that fits in these holes. (You may wish to temporarily remove the upper layer, and replace it when you are done putting down spheres). You <u>must</u> verify that the holes you are filling are actually tetrahedral (sphere in hole touches 4 large spheres at once) after the upper layer is replaced.

Is it necessary to remove spheres from the octahedral holes in order to fill the tetrahedral holes?

Which are larger – the tetrahedral holes or the octahedral holes?

Does it appear that atoms occupying the tetrahedral or octahedral holes would be small enough to readily diffuse throughout the structure? Justify your answer.

Describe the location and environment of the spheres filling the tetrahedral holes. Make sure you comment on the number of neighboring spheres above and below the tetrahedral holes. You can specify the column of a site as “1”, “2”, or “3” based on the labels given in the **L** blueprint.

How many of these “tetrahedral” spheres fit between the middle and upper layers of spheres? Do NOT count the truncated sites on the edge which do not have four neighbors present.

Are all of the tetrahedral holes between these two layers found at the same height?

Use a ruler to measure the radii of the atoms making up the close-packed layer and those occupying the tetrahedral holes. Remember you should have one digit with uncertainty.

The radius of the smaller sphere is what percent of the radius of the larger sphere?

If the larger spheres have a radius 1.40 Å (oxygen), what will the radius of the smaller sphere be?

If the layers were infinite in size (instead of constrained to just 14 spheres), how many tetrahedral holes between the upper and middle layers would there be relative to the number of spheres in the <u>one</u> layer? Give your answer as a ratio (*i.e.* 3:1 ratio of sphere to holes).

You should now convert the hexagonal close packed (HCP) structure to a cubic close packed (CCP) structure by removing the uppermost layer of spheres. Rebuild the upper layer by placing spheres on rods sitting above uncircled spots. You have now created a crystal lattice with the CCP ordering of layers abbreviated as ***abc***. *Verify for yourself that you can see the three distinct layer positions, and that no rod has two large spheres on it.*

How many spheres are in your lowest, middle, and upper layers

Have the locations of the tetrahedral and octahedral voids between the two uppermost layers changed relative to the **L** base below? If not, explain why not. If so, explain how they have changed.

Considering infinite layers again, have the number of octahedral and tetrahedral holes between the 2nd and 3rd layer changed? If so, how have they changed.

What would be the stoichiometry of a compound with “A” atoms in the close packed positions and “B” atoms occupying all of the octahedral holes in a CCP structure? What would be the stoichiometry of a similar compound with only half of the octahedral holes filled? (A_xB_y format)

The cubic perovskite, $CaTiO_3$

Objective: Use software to explore coordination and bonding in the solid state (Estimated time: 1-1.5 hr)

Launch Diamond from the Diamond3 folder of the Start Menu on a CRC PC. In general, you will use the arrow cursor for selecting atoms and the rotate-xy cursor (just to the right of the arrow on the bottom bar) for rotating your structure. Holding the cursor over buttons gives help.

The perovskite is one of the most ubiquitous structure families know, and many functional materials have a perovskite or perovskite-related structure. The generalized formulas for perovskites is ABX_3, where A is a large cation, B is a small cation, and X is an anion such as oxygen. Each of these three sites has a unique coordination environment.

Load the structure of $CaTiO_3$ into Diamond. Accept all the defaults during the structural import. When the structure creation wizard is launched, accept the first page defaults, change the Range drop-down menu on the second page to 3 x 3 x 3 cells, edit the third page to check “Create Polyhedra”, and create them about Ti, and on the 4th screen change from “Ellipsoids” to a “Ball and Stick” representation. Edit the polyhedra to make them transparent (Go to the Build->Polyhedra->Add Polyhedra menu, and choose Ti as the central atom and O as the ligand by deselecting all the other atoms, and make sure the Replace Polyhedra box is checked. Then click on the Design button, and raise the Transparency to about 0.3 in this submenu. *If you need or would like to make the O atoms visible,* go again to the Polyhedra->Add Polyhedra menu, revisit the Design submenu, and choose the “Others” tab. Change the Ligand Atoms reducing factor from 0 to a larger value, such as 0.2 or 0.4 – if this number is zero, atoms at the corners of coordination polyhedra will be invisible).

<u>What are the oxidation numbers of Ca, Ti, and O in $CaTiO_3$?</u>

<u>What are Shannon’s atomic radii for Ca, Ti, and O with a coordination number (CN) of 6 and the above oxidation states (refer to paper distributed in previous lecture)?</u>

To determine the coordination number of Ti, count the number of oxygen atoms that are with 2.2 angstroms of the Ti. (This cutoff distance is taken as the sum of the radii of Ti and O plus an extra 10-20%). To quickly see this, on the top-right corner of the screen, click on the “Distances-Angle” tab. A value that reads as “8x” indicates that there are 8 equivalent bonds with the same distance. You can adjust the minimum (Dmin) and maximum (Dmax) cutoff distances as necessary. The row with the Ti on the left describes the coordination sphere about Ti, while other rows describe the environment about O or Ca. *Click on the “Picture” tab to return to the structure view when you are finished.* (You can alternatively measure each Ti-O distance individually if you have made the oxygen atoms visible. Go to the Tool->Measure Distance feature via the top menu, or click on the icon that looks like the mm scale on a ruler at the bottom of the screen. If you now click on two atoms in sequence, the program will measure the distance. These values will be saved in the program, though you will have to go to the “Data Sheet” drop down menu and change it to “Table of Distances” to access the saved values”

<u>What is the coordination number for Ti in this structure?</u>

In general, the coordination environment of Ti and other transition metals are well-defined, and the M-O distances fall within a narrow spread. How close is the nearest oxygen which does not fall within the 2.2 Angst. cutoff?

The coordination environments for large cations such as Ca, Sr, Ba, Na, K, La, Y, Cd, Hg, Pb, Bi, and the lanthanides and actinides are often inhomogenous and have a wide range of bond lengths. A reasonable cutoff for the coordination environment of the Ca in this structure is about 3.2 angst. How many O atoms are within 3.2 Angst of Ca in this structure?

What is the atomic radius of Ca for this coordination number, and how does it differ from the radius of Ca with a CN 6?

Now open the file CaTiO3-CP.dsf to examine the close-packed layers of atoms that form the core of this structure. Notice how this close-packed layer is made up of Ca and O atoms in a 1:3 ratio, and that the atoms form the expected equilateral triangles within their planes. How are the O and Ca atoms arranged within the close packed layer?

Examine how these planes are aligned relative to the cubic unit cell of $CaTiO_3$. You can display this cell by going to the Build->Cell Edges… menu. Are these planes aligned parallel to a cubic face, parallel to a face diagonal, or parallel to the body diagonal of the cube?

Why do you think this structure forms with diatomic CaO_3 close packed layers instead of monoatomic close packed layers (ie O only or Ca only).

What fraction of the possible octahedral voids do the Ti atoms in this structure occupy? Your work on the hands-on modeling exercise may help with this?

Bond valence sum analysis of $La_{4.87}Ru_2O_{12}$

Objective: Use BVS analysis to assign oxidation numbers in solids (Estimated time: 30-60 min)

Download the structure of $La_{4.87}Ru_2O_{12}$ from the Chem242 web site and open it up in Diamond. You may wish to change the background color (Picture->Layout, choose background tab, and choose a reasonable color from the palette) to a lighter color or to white.

In oxides, La atoms are almost always found with an oxidation number of 3, while oxygen atoms can be generally assumed to have an oxidation number of -2. Knowing this, what is the average oxidation number of Ru in this structure?

What color are the La atoms?

What color are the Ru atoms?

What color are the O atoms?

Verify for yourself that this compound has a layered structure. Use diamond to draw in the unit cell of this compound (Build->Cell Edges). How many layers are present in each unit cell?

Display the unit cell vectors for this structure (Objects->Coordinate System). The layers are stacked on top of each other along which unit cell direction, *a, b, or c*? (You can use the Picture ->Viewing direction menu to set the view to specific crystal directions)

How many different varieties of layers are present in this compound? How can you distinguish them?

If you examine the data sheet for this compound, you will notice that there are two unique types of ruthenium atoms. They are denoted Ru1 and Ru2. If you examine the Wyckoff symbol for each of these, you will notice that they are labeled 4e. The 4 in the Wyckoff symbol means that the multiplicity of that type of atom is four. In other words, there are four equivalent Ru1 atoms and four equivalent Ru2 atoms in each unit cell. Although all of the Ru atoms are blue, the software will tell you whether you are looking at a Ru1 or Ru2 when you move your cursor over an atom.

Which type of Ru atom(s) can you find in the thicker layer?

Which type of Ru atom(s) can you find in the thinner layer?

What is the approximate ratio of La atoms to Ru atoms in the thicker layer (circle one)?

3:1 2:1 1:1

What is the ratio of La atoms to Ru atoms in the thinner layer (circle one)?

3:1 2:1 1:1

It appears that one type of Ru site is surrounded by more electropositive La atoms than the other site. Ru can adopt a wide range of oxidation states in oxides, ranging from +3 to +6 and including many non-integer values. It is likely that the Ru1 and Ru2 atoms have different oxidation states since they are in significantly different environments. We can check this by calculating the bond valence sums for these two atoms.

Calculate the bond valence sum (BVS) contributions for each of the six Ru1-O bonds and each of the six Ru2-O bonds, *showing sample calculations to demonstrate your knowledge of this approach*. List the distance and bond valence sum for each bond, ***sorting the results in order of increasing bond distance and keeping the values for the two different Ru atoms separate***. Use a r_0 value of 1.888 angst. for Ru, and keep the common *b* value of 0.37. You may wish to use Excel to speed your calculations. Although the BVS method was first described by Brown and Altermatt (1985), Breese and O'Keefe (1991) have a better parameter set (which you won't need here…)

Ru1	distance	$V_{Ru1\text{-}Oj}$		**Ru2**	distance	$V_{Ru2\text{-}Oj}$
O1				O1		
O2				O2		
O3				O3		
O4				O4		
O5				O5		
O6				O6		
Total oxid. num. of Ru1:				Total oxid. num. of Ru2:		

Based on your results from the Bond Valence Sum calculations, would you assert that the two Ru atoms have the same or different oxidation states, within an estimated error of 0.1 in charge?

How well does the average of your two calculated BVS oxidation numbers match the average oxidation number calculated at the beginning of the lab?

Inorganic Crystal Structure Database

Objective: Learn to download and analyze solid state structures (Estimated time: 30-60 min)

What is your favorite transition element?

Visit the ICSD web site (http://icsd.ill.fr/icsd/) and click on the "Login or use the Demo link". We will be using the demo, so don't worry about logging in. Search for an oxide structure of your favorite element (choose a new favorite if you are having problems with your original favorite). Enter your element and oxygen into the Elements field, leaving a space between them ("W O" if your favorite is tungsten), then click on the search button. Check the box for one of the structures, and then hit the "details" button. In the new window that pops up, click on the "Export" button, which should be configured to save the data for that structure in the .cif format, which Diamond can import. Clicking on the "Structure" button (and "Display" afterwards) will give you a structural preview if the CHIME plug-in is installed on your computer.

Pick out an oxide structure of your favorite transition element to study in more detail in Diamond. (If you are having trouble finding good ones, ask your Prof. for suggestions).

What is the formula of this compound?

What is its lattice symmetry (triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, or cubic), as listed in the data sheet for this compound?

What are its lattice parameters, a, b, and c, and its cell angles, α, β, and γ?

Generate an informative structural picture of your compound in Diamond. Have diamond create all appropriate coordination polyhedra (tetrahedra and octahedral). Your work so far should give you insights into what type (and size) atoms are at the center of the oxygen polyhedra, and which atoms are at the vertices. Print out a picture of this structure (ignoring the Demo version banner which will most likely be attached). Describe the atomic arrangements for this structure, giving as many insights into this structure as you can.