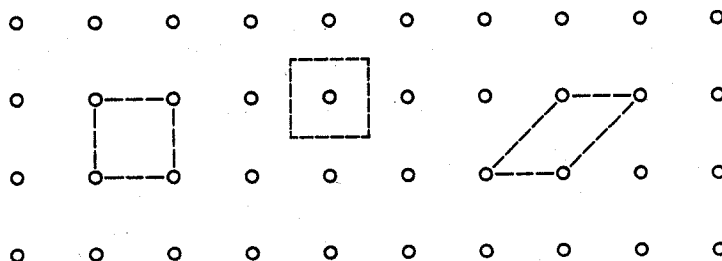


The Structure of Crystals— An Experiment Using Models

If one examines the crystals of an ordinary substance like table salt, using a magnifying glass or a microscope, one finds many cubic particles, among others, in which planes at right angles are present. This is the situation with many common solids. The regularity we see implies a deeper regularity in the arrangement of atoms or ions in the solid. Indeed, when we study crystals by x-ray diffraction, we find that the atomic nuclei are present in remarkably symmetrical arrays, which continue in three dimensions for thousands or millions of units. Substances having a regular arrangement of atom-size particles in the solid are called crystalline, and the solid material consists of crystals. This experiment deals with some of the simpler arrays in which atoms or ions occur in crystals, and what these arrays can tell us about such properties as atomic sizes, densities of solids, and the efficiency of packing of particles.

Many crystals are complex, almost beyond belief. We will limit ourselves to the simplest crystals, those which have cubic structures. They are by far the easiest to understand, yet they exhibit many of the interesting properties of more complicated structures. We will further limit our discussion to substances containing only one or two kinds of atoms, so we will be working with the crystals of some of the elements and some binary compounds.

The atoms in crystals occur in planes. Sometimes a crystal will cleave readily at such planes. This is the reason the cubic structure of salt is so apparent. Let us begin our study of crystals with a simple example, a two-dimensional crystal in which all of the atoms lie in a square array in a plane, in the manner shown below:



The first thing that you need to realize is that the array goes on essentially forever, in both directions. In this array \circ is always the same kind of atom, so all the atoms are equivalent. The distance, d_o , between atoms in the vertical direction is the same as in the horizontal, so if you knew either distance you could generate the array completely. In crystal studies we select a small section of the array, called the unit cell, that represents the array in the sense that by moving the unit cell repeatedly in either the x or y direction, a distance d_o at a time, you could generate the entire array. In the sketch we have used dotted lines to indicate several possible unit cells. All the cells have the same area, and by moving them up or down or across we could locate all the sites in the array. Ordinarily we select the unit cell on the left, because it includes four of the atoms and has its edges along the natural axes, x and y , for the array, but that is not necessary. In fact, the middle cell has the advantage that it clearly tells us that the number of \circ atoms in the cell is equal to 1. The number of atoms in whatever cell we choose must also equal 1, but that is not so apparent in the cell

on the left. However, once you realize that only $1/4$ of each atom on the corners of the cell actually belongs to that cell, because it is shared by three other cells, the number of atoms in the whole cell becomes equal to $1/4 \times 4$, or 1, which is what we got by drawing the cell in a different position.

When we extend the array to three dimensions, the same ideas regarding unit cells apply. The unit cell is the smallest portion of the array that could be used to generate the array. With cubic cells the unit cell is usually chosen to have edges parallel to the x , y , and z axes we could put on the array.

Experimental Procedure

IN THIS EXPERIMENT YOUR INSTRUCTOR MAY ALLOW YOU TO WORK WITHOUT SAFETY GLASSES

In this experiment we will mix the discussion with the experimental procedure, since one supports and illustrates the other. We will start with the simplest possible cubic crystal, deal with its properties, and then go on to the next more complex example, and the next, and so on. Each kind of crystal will be related in some ways to the earlier ones but will have its own properties as well. So get out your model set and let's begin.

Work in pairs, and complete each section before going on to the next, unless directed otherwise by your instructor.

The Simple Cubic Crystal

You can probably guess the form of the array in the crystal structure we call simple cubic (SC). It is shown on the Calculations page at the end of this section.

The unit cell is a cube with an edge length equal to the distance from the center of one atom to the center of the next. The cell edge is usually given the symbol d_0 . The volume of the unit cell is d_0^3 , and is very small, since d_0 is of the order of 0.5 nm. Using x-rays we can measure d_0 to four significant figures quite easily. The number of atoms in the unit cell in a simple cubic crystal is equal to 1. Can you see why? Only $1/8$ of each corner atom actually belongs to the cell, since it is shared equally by eight cells.

Using your model set, assemble three attached unit cells having the simple cubic structure shown in the sketch. Use the short bonds (no. 6) and the gray atoms. Each bond goes into a square face on the atom. An actual crystal with this structure would have many such cells, in three dimensions.

If you extended the model you have made further, you would find that each atom would be connected to six others. We say that the coordination number of the atoms in this structure is 6. Only the closest atoms are considered to be bonded to each other. In the other models we will be making, *only* those atoms that are *bonded*, by covalent or ionic bonds, will be connected to one another, so the number of bonds to an atom in a large model will be equal to the coordination number.

Although the model has an open structure to help us see relationships better, in an actual crystal we consider that the atoms that are closest are touching. It is on this assumption that we determine atomic radii. In this SC crystal, if we know d_0 we can find the atomic radius r of the atoms, since, if the atoms are touching, d_0 must equal $2r$. Another property we can calculate knowing d_0 is the density, given the nature of the atoms in the crystal. From d_0 we can easily find the volume V of the unit cell. Since there is one atom per cell, a mole will contain Avogadro's number of cells. Given the molar mass of the element, we can find the mass m of a cell. The density is simply m/V . With more complex crystals we can make these same calculations, but must take account of the fact that the number of atoms or ions per unit cell may not be equal to one.

Essentially no elements crystallize in an SC structure. The reason is that SC packing is inefficient, in that the atoms are farther apart than they need be. There is, as you can see, a big hole in the middle of each unit cell that is begging for an atom to go there, and atoms indeed do. Before we go into that, let's calculate the fraction of the volume of the unit cell that is actually occupied by atoms. This is easy to do. Make the calculation of that fraction on the Calculations page.

That fraction is indeed pretty small; only about 52 percent of the cell volume is occupied by atoms. Most of the empty space is in that hole. You can calculate by simple geometry that an atom having a

radius equal to 73 percent of that of the atom on a corner would fit into the hole. Or, putting it another way, an atom bigger than that would have to push the corner atoms back to fit in. If the particles on the corners were anions, and the atom in the hole were a cation, the cation in the hole would push the anions apart, decreasing the repulsion between them and maximizing the attraction between anions and cations. We will have more to say about this when we deal with binary salts, but for now you need to note that if $r_+/r_- > 0.732$, the cation will not fit in the cubic hole formed by anions on the corners of an SC cell.

Body-Centered Cubic Crystals

In a body-centered cubic (BCC) crystal, the unit cell still contains the corner atoms present in the SC structure, but in the center of the cell there is another atom of the same kind. The unit cell is shown on the Calculations page.

Using your model set, assemble a BCC crystal. Use the blue balls. Put the short bonds in the eight holes in the triangular faces on one blue ball. Attach a blue ball to each bond, again using the holes in a triangular face. Those eight blue balls define the unit cell in this structure. Add as many atoms to the structure as you have available, so that you can see how the atoms are arranged. In a BCC crystal each atom is bonded to eight others, so the coordination number is 8. Verify this with your model. (There are no bonds along the edges of the unit cell, since the corner atoms are not as close to one another as they are to the central atom.)

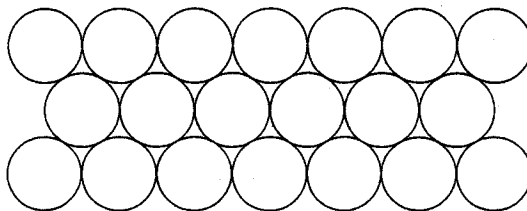
The BCC lattice is much more stable than the SC one, in part at least because of the higher coordination number. Many metals crystallize in a BCC lattice—including sodium, chromium, tungsten, and iron—when these metals are at room temperature.

There are several properties of the BCC structure that you should note. The number of atoms per unit cell is two, one from the corner atoms and one from the atom in the middle of the cell, where it is unshared. As with SC cells, there is a relation between the unit cell size and the atom radius. Given that in sodium metal the cell edge is 0.429 nm, calculate the radius of a sodium atom on the Calculations page. When you are finished, calculate the density of sodium metal.

The fraction of the volume that is occupied by atoms in a BCC crystal is quite a bit larger than with SC crystals. Using the same kind of procedure that we did with the SC structure, we can show that in BCC crystals about 68 percent of the cell volume is occupied.

Close-Packed Structures

Although many elements form BCC crystals, still more prefer structures in which the atoms are close packed. In such structures there are layers of atoms in which each atom is in contact with six others, as in the sketch below:

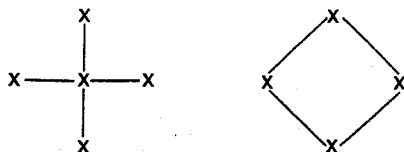


This is the way that billiard balls lie in a rack, or the honeycomb cells are arranged in a bees' nest. It is the most efficient way one can pack spheres, with about 74 percent of the volume in a close-packed structure filled with atoms. It turns out that there is more than one close-packed crystal structure. The layers all have the same structure, but they can be stacked on one another in two different ways. This is certainly not apparent at first sight. The first close-packed crystal we will examine is cubic, amazingly enough, considering all those triangles in the layers of atoms.

Face-Centered Cubic Crystals

In the face-centered cubic (FCC) unit cell there are atoms on the corners and an atom at the center of each face. There is no atom in the center of the cell (see the sketch on the Calculations page, where we show the bonding on only the three exposed faces).

Constructing an FCC unit cell, using bonds between closest atoms, is not as simple as you might think, so let's do it the easy way. This time select the large gray balls, the ones with the most holes. Make the bottom face of the unit cell by attaching four gray balls to a center ball, using short bonds, and holes that are in rectangular faces. You should get the structure on the left below:



To make the middle layer of atoms, connect four of the balls in a square, again using short bonds and the holes in rectangular faces, as in the right sketch. The top layer is made the same way as the bottom one. Then connect the layers to one another, again using holes in the rectangular faces. You should then have an FCC cubic unit cell. Because the atoms in the middle of adjacent faces are as close to one another as they are to the corner atoms, there should be bonds between them. There are quite a few bonds in the final cell, 32 in all. Put them all in. As with BCC there are no bonds along the edges of the cell.

The FCC, or cubic close-packed, structure is a common one. Among the metals with this type of crystal are copper, silver, nickel, and calcium.

In close-packed structures the coordination number is the largest that is possible. It can be found by looking at a face-centered atom, say on the top face of the cell. That atom has eight bonds to it and would also have bonds to atoms in the cell immediately above, four of them. So its coordination number, like that of every atom in the cell, is 12.

Having seen how to deal with other structures, you should now be able to find the number of atoms in the FCC unit cell and the radius of an atom as related to d_0 . From these relationships and the measured density, you can calculate Avogadro's number. On the Calculations page, find these quantities, using copper metal, which has a unit cell edge d_0 equal to 0.361 nm and a density equal to 8.92 g/cm³.

In the center of the unit cell there is a hole. It is smaller than a cubic hole but of significant size nonetheless. It is called an octahedral hole, because the six atoms around it define an octahedron. In an ionic crystal, the anions often occupy the sites of the atoms in your cell, and there is a cation in the center of the octahedral hole. On the Calculations page, find the maximum radius, r_+ , of the cation that would just fit in an octahedral hole surrounded by anions of radius r_- . You should find that the r_+/r_- ratio turns out to be 0.414.

There is another kind of hole in the FCC lattice that is important. See if you can find it; there are eight of them in the unit cell. If you look at an atom on the corner of the cell, you can see that it lies in a tetrahedron. In the center of the tetrahedron there is a tetrahedral hole, which is small compared to an octahedral or cubic hole. However, in some crystals small cations are found in some or all of the tetrahedral holes, again in a close-packed anion lattice. The cation-anion radius ratio at which cations would just fit into a tetrahedral hole is not so easy to find; r_+/r_- turns out to be 0.225.

The close-packed layers of atoms in the FCC structure are not parallel to the unit cell faces, but rather are perpendicular to the cell diagonal. If you look down the cell diagonal, you see six atoms in a close-packed triangle in the layer immediately behind the corner atom, and another layer of close-packed atoms below that, followed by another corner atom. The layers are indeed closely packed, and, as one goes down the diagonal of this and succeeding cells, the layers repeat their positions in the order ABCABC . . . , meaning that atoms in every fourth layer lie below one another.

Clearly there is another way we could stack the layers. The first and second will always be in the same relative positions, but the third layer could be below the first one if it were shifted properly. So we

can have a close-packed structure in which the order of the layers is ABABAB. . . . The crystal obtained from this arrangement of layers is not cubic, but hexagonal. It too is a common structure for metals. Cadmium, zinc, and manganese have this structure. As you might expect, the stability of this structure is very similar to that of FCC crystals. We find that simply changing the temperature often converts a metal from one form to another. Calcium, for example, is FCC at room temperature, but if heated to 450°C it converts to close-packed hexagonal.

Crystal Structures of Some Common Binary Compounds

We have now dealt with all of the possible cubic crystal structures for metals. It turns out that the structures of binary ionic compounds are often related to these metal structures in a very simple way. In many ionic crystals the anions, which are large compared with cations, are essentially in contact with each other, in either an SC or FCC structure. The cations go into the cubic, or octahedral, or tetrahedral holes, depending on the cation-anion radius ratios that we calculated. The idea is that the cation will tend to go into a hole in which it will not quite fit. This increases the unit cell size from the value it would have if the anions were touching, which reduces the repulsion energy due to anion-anion interaction and increases to the maximum the cation-anion attraction energy, producing the most stable possible crystal structure. According to the so-called radius-ratio rule, large cations go into cubic holes, smaller ones into octahedral holes, and the smallest ones into tetrahedral holes.

The deciding factor for which hole is favored is given by the radius ratio:

If $r_+/r_- > 0.732$	cations go into cubic holes
If $0.732 > r_+/r_- > 0.414$	cations go into octahedral holes
If $0.414 > r_+/r_- > 0.225$	cations go into tetrahedral holes

The NaCl Crystal

To apply the radius-ratio rule to NaCl, we simply need to find r_+/r_- , using the data in Table 16.1. Since $r_{\text{Na}^+} = 0.095$ nm, and $r_{\text{Cl}^-} = 0.181$ nm, the radius ratio is $0.095/0.181$, or 0.525. That value is less than 0.732 and greater than 0.414, so the sodium ions should go into octahedral holes. We saw the octahedral hole in the center of the FCC unit cell, so Na^+ ions go there, and the Cl^- ions have the FCC structure. Actually, there are 12 other octahedral holes associated with the cell, one on each edge, which would be apparent if we had been able to make more cells. An Na^+ ion goes into each of these holes, giving the classic NaCl structure shown on the Calculations page. (Again, only the ions and bonds on the exposed faces are shown.)

Make a model of the unit cell for NaCl, using the large gray balls for the Cl^- ions and the blue ones for Na^+ ions. Clearly the Na^+ ion at the center of the cell is in an octahedral hole, but so are all of the other sodium ions, because if you extend the lattice, every Na^+ ion will be surrounded by six Cl^- ions. The coordination number of Na^+ , and of Cl^- , ions is 6. The crystal is FCC in Cl^- and also in Na^+ , because you could put Na^+ ions on the corners of the unit cell and maintain the same structure. The unit cell extends from the center of one Cl^- ion to the center of the next Cl^- along the cell edge; or, from the center of one Na^+ ion to the center of the next Na^+ ion.

On the Calculations page find the number of Na^+ and of Cl^- ions in the unit cell.

The CsCl Crystal

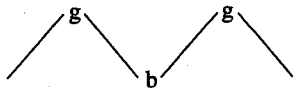
Cesium chloride has the same type of formula as NaCl, 1:1. The Cs^+ ion, however, is larger than Na^+ , and has a radius equal to 0.169 nm. This makes r_+/r_- equal to 0.933. Because this value is greater than 0.732, we would expect that in the CsCl crystal the Cs^+ ions will fill cubic holes, and this is what is observed. The structure of CsCl will look like that of the BCC unit cell you made earlier, except that the ion in the center will be Cs^+ and those on the corners Cl^- . If you put gray balls in the center of each BCC unit cell you made from the blue balls, you would have the CsCl structure. This structure is *not*

BCC, because the corner and center atoms are not the same. Rather it consists of two interpenetrating simple cubic lattices, one made from Cl^- ions and the other from Cs^+ ions.

The Zinc Sulfide Crystal

Zinc sulfide is another 1:1 compound, but its crystal structure is not that of NaCl or of CsCl. In ZnS, the Zn^{2+} ions have a radius of 0.074 nm and the S^{2-} ions a radius of 0.184 nm, making r_+/r_- equal to 0.402. By the radius-ratio rule, ZnS should have close-packed S^{2-} ions, with the Zn^{2+} ions in tetrahedral holes. In the ZnS unit cell, we find that this is indeed the case; the S^{2-} ions are FCC, and alternate tetrahedral holes in the unit cell are occupied by Zn^{2+} ions, which themselves form a tetrahedron.

To make a model for ZnS, first assemble an SC unit cell, using blue balls and the long bonds. Use gray balls for the zinc ions, and assemble the unit shown below, using the short bonds and the holes in triangular faces:



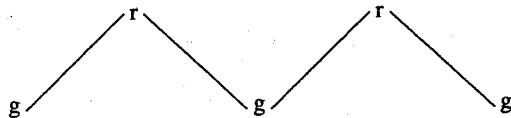
Attach this unit to two corner atoms on the diagonal of the bottom face. Make another unit and attach it to the two corner atoms in the upper face that lie on the face diagonal that is not parallel to the bottom face diagonal. The gray balls should then form a tetrahedron. Then attach the four other FCC blue balls to the gray ones. In this structure the coordination number is four (the long bonds do not count, they just keep the unit cell from falling apart). If the gray balls in the unit cell are replaced with blue ones, so that all atoms are of the same element, we obtain the diamond crystal structure.

These are the three common cubic structures of 1:1 compounds. The radius-ratio rule allows us to predict which structure a given compound will have. It does not always work, but it is correct most of the time. On the Calculations page, use the rule to predict the cubic structures that crystals of the following substances will have: KI, CuBr, and TlBr.

The Calcium Fluoride Crystal

Calcium fluoride is a 1:2 compound, so it cannot have the structure of any crystal we have discussed so far. The radii of Ca^{2+} and F^- are 0.099 and 0.136 nm, respectively, so r_+/r_- is 0.727. This makes CaF_2 on the boundary between compounds with cations in cubic holes or octahedral holes. It turns out that in CaF_2 , the F^- ions have a simple cubic structure, with half of the cubic holes filled by Ca^{2+} ions. This produces a crystal in which the Ca^{2+} ions lie in an FCC lattice, with 8 F^- ions in a cube inside the unit cell.

Use your model set to make a unit cell for CaF_2 . Use gray balls for the Ca^{2+} ions and red ones for F^- . The cations and anions are linked by short bonds that go into holes in nonadjacent triangular faces. The Ca^{2+} ions on each face diagonal are linked to F^- ions as shown below:



To complete the bottom face, attach two red and two gray balls to the initial line, so that the four red balls form a square and the gray ones an FCC face. The top of the unit cell is made the same way. Attach the two assemblies through four gray balls, which lie at the centers of the other faces. When you are done, the red balls should form a cube inside an FCC unit cell made from gray balls. Extend the model into an adjacent unit cell to show that every other cube of F^- ions has a Ca^{2+} ion at its center.

When you have completed this part of the experiment, your instructor may assign you a model with which to work. Report your results as directed. Then disassemble the models you made and pack the components in the box.

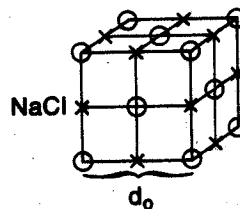
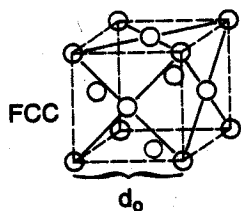
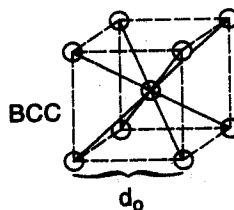
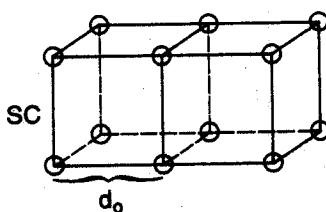
Experiment 16

Data and Calculations: The Structure of Crystals

Table 16.1

Atom	Molar Mass, g/mole	Atomic Radius, nm	Ionic Radius, nm
Na	22.99	—	0.095
Cu	63.55	—	0.096
Cl	35.45	0.099	0.181
Cs	132.9	0.262	0.169
Zn	65.38	0.133	0.074
S	32.06	0.104	0.184
K	39.10	0.231	0.133
I	126.9	0.133	0.216
Br	79.90	0.114	0.195
Tl	204.4	0.171	0.147

Some Cubic Unit Cells



Simple Cubic Crystal

Fraction of volume of unit cell occupied by atoms

Volume of unit cell in terms of d_0

Number of atoms per unit cell

Radius r of atom in terms of d_0

Volume of atom in terms of d_0 ($V = \frac{4\pi}{3} r^3$)

Volume of atom/volume of cell

_____ = _____

(continued on following page)

Body-Centered Cubic Crystal

a. Radius of a sodium atom

In BCC atoms touch along the cube diagonal
(see your model)

Length of cube diagonal if $d_o = 0.429$ nm _____ nm

$4 \times r_{\text{Na}} =$ length of cube diagonal $r_{\text{Na}} =$ _____ nm

b. Density of sodium metal

Length of unit cell, d_o , in cm ($1 \text{ cm} = 10^7 \text{ nm}$) _____ cm

Volume of unit cell, V _____ cm^3

Number of atoms per unit cell _____

Number of unit cells per mole Na _____

Mass of a unit cell, m _____ g

Density of sodium metal, m/V (Obs. 0.97 g/cm^3) _____ g/cm^3

Face-Centered Cubic Crystal

a. Number of atoms per unit cell

Number of atoms on corners _____ Shared by _____ cells _____ \times _____ = _____

Number of atoms on faces _____ Shared by _____ cells _____ \times _____ = _____

Total atoms per cell _____

b. Radius of a Cu atom

In FCC atoms touch along face diagonal (see your model and ASA)

Length of face diagonal in Cu, where $d_o = 0.361$ nm _____ nm

Number of Cu atom radii on face diagonal _____ $r_{\text{Cu}} =$ _____ nm

(continued on following page)

c. Avogadro's Number, N Length of cell edge, d_o , in cm, in Cu metal _____ cmVolume of a unit cell in Cu metal _____ cm^3 Volume of a mole of Cu metal ($V = \text{mass}/\text{density}$) _____ cm^3

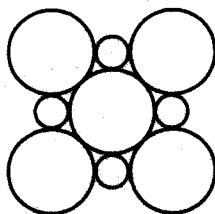
Number of unit cells per mole Cu _____

Number of atoms per unit cell _____

Number of atoms per mole, N _____

d. Size of an octahedral hole

Below is a sketch of the front face of a face-centered cubic cell with the NaCl structure. The ions are drawn so that they are just touching their nearest neighbors. The cations are in octahedral holes.

Show the length of d_o on the sketch. (See your model.)What is the relationship between r_- and d_o ?

$$r_- = \text{_____} \times d_o$$

What is the equation relating r_+ , r_- , d_o ?

$$d_o = \text{_____}$$

What is the relationship between r_+ and d_o ?

$$r_+ = \text{_____} \times d_o$$

What is the value of the radius ratio r_+/r_- ? Express the ratio to three significant figures.

$$r_+/r_- = \text{_____}$$

(continued on following page)

NaCl Crystal

Number of Cl^- ions in the unit cell (FCC) _____

Number of Na^+ ions on edges of cell _____ Shared by _____ cells

Number of Na^+ ions in center of cell _____ Shared by _____ cell(s)

Total no. Na^+ ions in unit cell _____

Radius-ratio rule (data in Table 16.1)

KI r_+/r_- _____ Predicted structure _____ Obs. NaCl

CuBr r_+/r_- _____ Predicted structure _____ Obs. ZnS

TlBr r_+/r_- _____ Predicted structure _____ Obs. CsCl

Report on unknown