Crystal Structure

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Purpose: To investigate the formation of crystalline solids and the close packing of spheres.

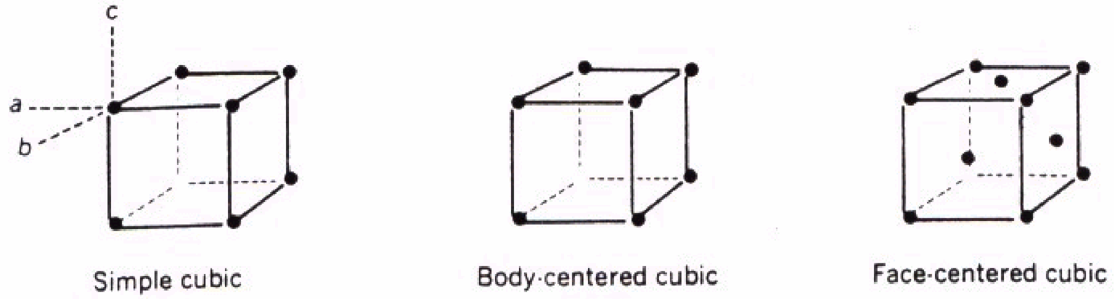
Equipment: 30 2-in. polystyrene balls, 15 1-in. polystyrene balls, 15 .5-in. polystyrene balls, wooden toothpicks

Introduction: A crystalline solid is a substance whose atoms, ions, or molecules are ordered in well-defined arrangements. The surfaces of crystalline solids are flat, and the faces of such solids make definite angles with each other. Their shapes are regular and repeating. Crystalline solids have several characteristic properties. Crystalline solids have definite melting points because all of the bonds in the solid are identical. Thus, the same amount of energy is required to break all of the bonds. Two common examples of crystalline solids are diamond and quartz.

The other type of solid is the amorphous solid. An amorphous solid is one whose particles have no orderly structure. In contrast to crystalline solids, amorphous solids lack well-defined faces and shapes. They are usually composed of large molecules or molecules that do not stack well together. Since the makeup of amorphous solids can vary, there is no definite melting point. There is, however, a melting range, over which the bonds in the solid will be broken. Two common examples of amorphous solids are glass and rubber.

A unit cell is the smallest portion of a crystal that is used as the blueprint for repeating in all directions. The unit cell is the base building block of the crystal lattice. The crystal lattice is simply a three-dimensional array of points made from the repetition of the unit cell. The atoms, ions, or molecules making up the crystal lattice are called lattice points.

The simplest type of unit cell is the simple cubic. All of the lattice edges are identical, and all of the angles formed are right angles. Other types of cubic unit cells are the body-centered cubic, in which a cube is constructed around a central sphere, and the face-centered cubic, in which a cube is constructed around a face. Space diagrams of the three types of cubics are shown below:



Simple cubic   Body-centered cubic   Face-centered cubic

Figure 15.1

Many crystalline solids employ a close-packed structure in which spherical or nearly-spherical particles are arranged to leave the least amount of empty space possible. Two forms of close packing are cubic close packing and hexagonal close packing. In both, each sphere has a coordination number of 12. The coordination number of a sphere is determined based on the number of spheres immediately surrounding it in the crystal lattice.

This experiment will employ polystyrene balls to simulate the crystal lattices of various crystalline solids.

Procedure:

Part A.

1. A single unit cell of the simple cubic lattice was constructed. Using four more balls, the model was extended in the *c* direction to create two unit cells in contact. More balls were used to extend the model in the *a* and *b* directions. The model was extended until 27 balls had been used to construct eight unit cells.

2. The edge length of one unit cell was recorded.

3. The equivalent spheres were measured and recorded.

Part B.

1. A single unit cell of a body-centered cubic lattice was constructed. The diagonal length of the cube was recorded in terms of the radius of a sphere.

Part C.

1. A single unit cell of a face-centered cubic lattice was constructed as shown in the Introduction. The face was constructed first. The face-diagonal length was recorded in terms of sphere radius.

Part D.

1. A single unit cell of the NaCl lattice was constructed. 2 inch balls were used for chloride ions and 1 inch balls were used for sodium ions. The final model contained 13 chloride ions and 14 sodium ions. The equivalent number of ions were recorded.

Part E.

1. A single unit cell of a face-centered cubic lattice was constructed so that each face center was occupied by a small ball and each corner by a large ball. The equivalent number of each type of sphere within the unit cell was determined.

Part F.

1. A tetrahedral hole was constructed by joining three large balls in a triangle with toothpicks. Another large ball was placed on top of the triangle in the center and then was removed. A small ball was placed on top of the hole in the center of the base triangle. The large ball was placed on top of the small ball to determine whether the small ball fit snugly.
2. Two triangles were constructed with three large balls per triangle. One triangle was placed on top of the other and then nestled into the other. The structure was tested to determine whether or not a small ball could fit inside the hole at the center of it.
3. A portion of a close-packed layer was constructed by placing six large balls around another large ball on the horizontal plane. The structure was replicated twice using fourteen other balls. One of the replications was placed on top of the original so that the holes were on the same vertical axis. The distance between the layers was determined. The top layer was shifted into the holes of the bottom layer. The distance between the two layers was again determined and compared with the diameter of the ball. The third layer was placed on top of the structure in as many different ways as possible to produce different close-packed structures.

<u>Observations</u>:

Part A.

Edge length in terms of sphere radius *r*: **2r**

Fraction of interior sphere in each unit cell: **1/8**

Number of spheres per unit cell: **1**

Part B.

Cube-diagonal length in terms of *r*: **4r**

Number of spheres per unit cell: **2**

Part C.

Face-diagonal length in terms of *r*: **4r**

Number of spheres per unit cell: **4**

Part D.

Sodium ions per unit cell: **4**

Chloride ions per unit cell: **4**

Part E.

A spheres per unit cell: **3**

B spheres per unit cell: **1**

Part F.

Observations on tetrahedral hole: The sphere did not fit snugly into the tetrahedral hole.

Observations on octahedral hole: The sphere fit snugly into the octahedral hole.

Observations on close-packed layers: The layers nestled together snugly. Each layer was in the shape of a hexagon. There were two different kinds of stacking possible when three layers were used.

Results:

Part A.

Volume of unit cell in terms of *r*: The volume of the unit cell is the length of the edge cubed. $(2r)^3 = \mathbf{8r^3}$

Volume of spheres within unit cell in terms of *r*: The volume of the spheres within the unit cell is equal to the volume of a sphere with radius *r* times the number of equivalent spheres within the unit cell. $4\pi r^3/3 = \mathbf{4.19r^3}$

Fraction of unit cell that is empty space: The fraction of the unit cell that is empty space is equal to the total volume of the unit cell minus the volume of the spheres within the unit cell. $(8r^3 – 4.19r^3) / 8r^3 =$ **47.63% empty space.**

Part B.

Edge length of unit cell in terms of *r*: The edge length of the unit cell is part of a right triangle formed by two edges and the cube-diagonal. The cube-diagonal length is 4r. Using the Pythagorean theorem, the calculation is as follows:

$16r^2 = 3E^2$

$\sqrt{(16r^2/3)} = E$

$E = \mathbf{2.31r}$

Volume of unit cell in terms of *r*: The volume of the body-centered unit cell is simply the edge length cubed. $(2.31r)^3 = \mathbf{12.3r^3}$

Volume of spheres within unit cell in terms of *r*: The volume of the spheres within the unit cell is the volume of a sphere with radius *r* times the number of equivalent spheres in the unit cell. $4\pi r^3/3 \text{ x } 2 = \mathbf{8.4r^3}$

Fraction of unit cell that is empty space: The fraction of the unit cell that is empty space is equal to the total volume of the unit cell minus the volume of the spheres within the unit cell. $(12.3r^3 – 8.4r^3) / 12.3r^3$ = **31.71% empty space.**

Part C.

Edge length of unit cell in terms of *r*: In order to find the edge length of the unit cell, the face-diagonal length must be squared. This value must be divided by two, and the square root of this value must be obtained.

$(4r)^2 = 16r^2$

$16r^2/2 = 8r^2$

$\sqrt{(8r^2)}$ = **2.83r**

Volume of unit cell in terms of *r*: The volume of the unit cell is the edge length cubed.

$(2.83r)^3 = \mathbf{22.7r^3}$

Volume of spheres within unit cell in terms of *r*: The volume of spheres within the unit cell is the volume of a sphere with radius *r* times the number of equivalent spheres in the unit cell. $4\pi r^3/3 \text{ x } 4 = \mathbf{16.8r^3}$

Fraction of unit cell that is empty space: The fraction of the unit cell that is empty space is equal to the total volume of the unit cell minus the volume of the spheres within the unit cell. $(22.7r^3 – 16.8r^3) / 22.7r^3$ = **25.99% empty space.**

Part D.

Simplest formula: The simplest formula for a compound can be found by reducing the ratio of ions per unit cell to the smallest possible whole numbers. In this model, there were four sodium ions and four chloride ions per unit cell. This reduces to a one-to-one ratio. Thus, the simplest formula for this compound is **NaCl**.

Part E.

Simplest formula: The simplest formula for a compound can be found by reducing the ratio of ions per unit cell to the smallest possible whole numbers. In this model, there were three A spheres and one B sphere per unit cell. This reduces to a three-to-one ratio. Thus, the simplest formula for this compound is $\mathbf{A_3B}$.

Part F.

Size of tetrahedral hole:

Edge length of tetrahedron in terms of *r*: By observation, the edge length of the tetrahedron is **2r**.

Distance from vertex to center in terms of *r*: Using right triangles and the Pythagorean theorem, this value can be calculated.

$(2r)^2 = 4r^2$

$4r^2 / 2 = 2r^2$

$\sqrt{(2r^2)} = \mathbf{1.414r}$

Distance from vertex occupied by large sphere: By observation, the distance from the vertex occupied by the large sphere is the length of one radius, **1r**.

Possible radius for small sphere in hole: To calculate the possible radius for the small sphere in the hole, the distance from the vertex to the center must be subtracted from the distance from the vertex occupied by the large sphere.

$1.414r - 1r = \mathbf{.414r}$.

Size of octahedral hole:

Edge length of octahedron in terms of *r*: By observation, the edge length of the octahedron is **2r**.

Distance from vertex to center in terms of *r*: Using right triangles and the Pythagorean theorem, this value can be calculated.

$(2r)^2 = 4r^2$

$4r^2 / 2 = 2r^2$

$\sqrt{(2r^2)} = \mathbf{1.414r}$

Distance from vertex occupied by large sphere: By observation, the distance from the vertex occupied by the large sphere is the length of one radius, **1r**.

Possible radius for small sphere in hole: To calculate the possible radius for the small sphere in the hole, the distance from the vertex to the center must be subtracted from the distance from the vertex occupied by the large sphere.
1.414r – 1r = **.414r**.

Distance between close-packed layers:
Edge length of tetrahedron in terms of *r*: By observation, the edge length of the tetrahedron is **2r.**

Perpendicular distance from vertex to opposite face in terms of *r*: Using the same right-triangle geometry from previous calculations, this distance is **1.414r**.

Discussion: There is no potential calculation of percent error in this experiment. There are no sources of error in this experiment. All of the models were made using standard-sized polystyrene balls. All observations that were made were absolute and were made using applied mathematics, not measuring tools. Thus, there is no error.

The theory associated with this experiment is the atomic theory of matter as it relates to bonding. Close-packing is caused by inherent characteristics of atoms and ions. Dalton's atomic theory incorporated laws demonstrated by this experiment, such as the law of constant composition, which states that all samples of a compound contain the same proportions of the elements that comprise it. This was visually demonstrated by this experiment by constructing models of sodium chloride unit cells. In addition, all of the spheres used in this experiment that represented identical atoms were identical in size, just like actual atoms.

There are several ramifications to this experiment. This was the first experiment involving polystyrene balls and wooden connectors, so laboratory experience was gained. In addition, critical thinking processes were exercised, as all of the observations were made using applied mathematics. Furthermore, the industrial ramifications of this experiment include the possibility of using expanded unit-cell models to predict the behavior of certain compounds, or to calculate whether producing synthetic compounds would be feasible based on the size of its components.

<u>Questions</u>:

1. The unit cell density of cubic unit cells can be found by multiplying the density of the spheres (given as 2.00 g/cm^3) by the number of equivalent spheres in the unit cell, then multiplying this by the percent of space taken up by the spheres, which is 1 minus the percent of empty space in each unit cell, as calculated above.

a. Simple cubic: 2.00 g/cm^3 x 1 e.s. x (1 - .4763) = 1.05 g/cm^3

b. Body-centered cubic: 2.00 g/cm^3 x 2 e.s. x (1 - .3171) = 2.73 g/cm^3

c. Face-centered cubic: 2.00 g/cm^3 x 4 e.s. x (1 - .2599) = 5.92 g/cm^3

2. a. In a close-packed three-dimensional structure composed of identical spheres, the ratio of the number of spheres to the number of octahedral holes is 6:1.

b. In a close-packed three-dimensional structure composed of identical spheres, the ratio of the number of spheres to the number of tetrahedral holes is 4:1.

3. In order to find the density of copper, the volume of the unit cube must be found. The volume of the unit cell is $22.7r^3$, and r is .128 nm. Thus, the volume of the unit cell is .0476 nm^3. The following equation can be used to calculate density.

$$\frac{\left(\left(\frac{63.5\text{ grams}}{1\text{ mole}}\right)\left(\frac{1\text{ mole}}{6.02\times10^{23}\text{ molecules}}\right)\left(\frac{4\text{ formula units}}{1\text{ unit cell}}\right)\right)}{.0476\text{ nm}^3}=8.86\times10^{-21}\text{ g/nm}^3=8.86\times10^{-3}\text{ g/cm}^3$$

4. In order to find Avogadro's number given the edge length of tungsten metal and its density, the following calculation must be performed.

$$\left(\frac{183.9\text{ amu}}{(3.16\times10^{-8}\text{ m})^3}\right)\left(\frac{1\text{ g}}{19.35\text{ g/cm}^3}\right)\cdot 2\text{ spheres}=6.0238\times10^{23}$$

5. The empirical formula of an oxide with a cubic closest-packed structure with oxygen atoms located at every lattice site and metal atoms in each tetrahedral hole is MO_4.

6. The largest sphere that could be placed inside the hole located at the center of a face-centered cubic cell can be calculated using the edge length. The edge length of a face-centered cubic cell is 2.83r. The edge length crosses the center hole plus two radii. Thus, the center hole's radius is 2.83r – 2r / 2, or .414r.

Conclusion: The goal of the experiment was achieved successfully. The formation of crystalline solids was explored and insight into the formation of crystal lattices was gained.