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Laboratory Safety

DISCLAIMER

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Experiment 2

Solid-State Structure and Properties

George C. Lisensky and Ludwig A. Mayer

Notes for Instructors

Purpose

To construct portions of extended three-dimensional solids; on the basis of the structure, to determine the coordination number and geometry for each atom and the empirical formula of the material; to relate the structure to physical properties.

Method

See Chapters 3, 5, and the Experiment 2 laboratory introduction.

Materials

Spheres in radius-ratio sizes, 1.000:0.732:0.414:0.225. The Solid-State Model Kit, available from the Institute for Chemical Education, is convenient and comes with directions for assembling the structures in this experiment.

Copper wire. *See* Demonstration 6.4

Graphite pencil (a normal pencil), diamond-tipped pencil (Aldrich), and glass microscope slides. *See* Demonstration 7.8

Rock salt (sold for water softeners) and flat spatulas to use in cleaving crystals

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Cellophane or Scotch tape

A sample of molybdenum sulfide (rock or gem shop or Wards Natural Science; *see* Supplier Information). *See* Demonstration 5.5

Solid-State Structure and Properties

Purpose

To construct portions of extended three-dimensional solids; on the basis of the structure, to determine the coordination number and geometry for each atom and the empirical formula of the material; to relate the structure to physical properties.

Introduction

Crystalline materials in the solid state, including metals, semiconductors, and ionic compounds, have a patterned arrangement of atoms that in principle can extend infinitely in all three dimensions. This patterned arrangement of objects forms an extended structure that can be described by layers of stacked spheres.

More than two-thirds of the naturally occurring elements are metals. Most of the metallic elements have three-dimensional structures that can be described in terms of close-packing of spherical atoms. Many of the other metallic elements can be described in terms of a different type of extended structure that is not as efficient at space-filling, called body-centered cubic. The packing arrangements exhibited by metals will be explored in this activity.

In any scheme involving the packing of spheres there will be unoccupied spaces between the spheres. This void space gives rise to the so-called interstitial sites. A very useful way to describe the extended structure of many substances, particularly ionic compounds, is to assume that ions, which may be of different sizes, are spherical. The overall structure then is based on some type of sphere-packing scheme exhibited by the larger ion, with the smaller ion occupying the unused space (interstitial sites). Salts exhibiting these packing arrangements will be explored in this lab activity.

The coordination number and geometry for sphere packing schemes are shown in Figure 1.

Another useful and efficient way to describe the basic pattern of an extended structure is to conceive of a three-dimensional, six-sided figure having parallel faces that encloses only a portion of the interior of an extended structure. A cube is one example, but the more general case does not have 90° angles and is called a parallelepiped. If the parallelepiped is chosen so that when replicated and moved along its edges, by a distance equal to the length of that edge, it generates the entire structure of the crystal, it is a unit cell. The unit cell is a pattern for the atoms as well as for the void spaces among the atoms. The contents of the unit cell give the

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chemical formula for the solid. Figure 2 corresponds to one large ion for each small ion with a formula of (large ions)$_4$(small ions)$_4$.

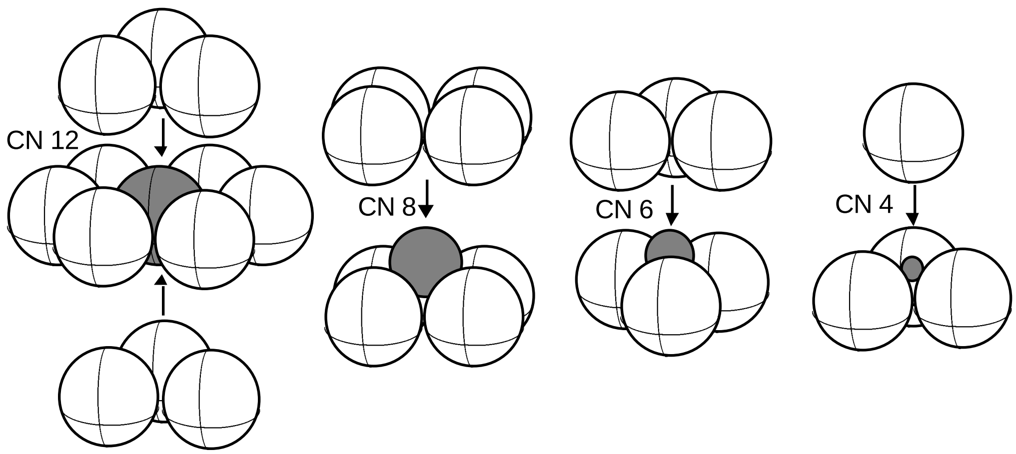


Figure 1. Close-packing of spheres gives a coordination number (CN) of 12 and leaves interstitial sites capable of coordination numbers 6 or 4. Square-packing of spheres leaves an interstitial site capable of coordination number 8.

Large ions	**Small ions**
8 corners $\times \frac{1}{8}$	12 edges $\times \frac{1}{4}$
6 faces $\times \frac{1}{2}$	1 center $\times$ 1
4 large ions	4 small ions

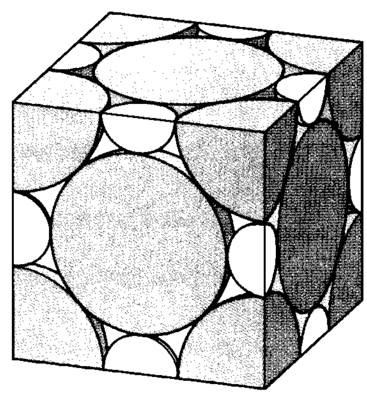
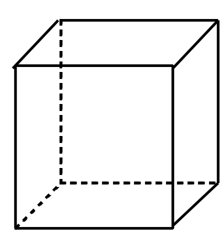


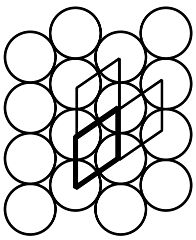
Figure 2. Counting ions in a unit cell.

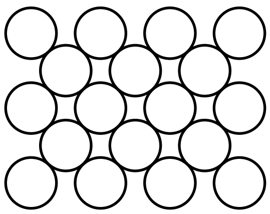
Warm-up Exercises

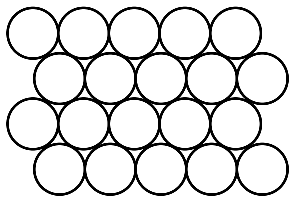
1. A cube has ____ corners, ____ edges, and ____ faces.

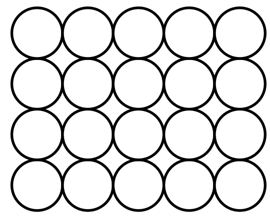


2. In two dimensions, the unit cell is a parallelogram. If the unit cell pattern is moved repeatedly in the plane of the paper in the same directions as its sides and for distances equal to the length of its sides, it must replicate the entire structure. See Structure A as an example, where the original unit cell is shown as a dark parallelogram. The light parallelograms show the start of the process. The replicated structure must include the circles as well as all the spaces between the circles. In structures B, C, and D, draw the outline of their two-dimensional unit cells.


Structure A

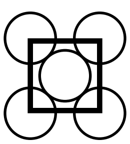

Structure B

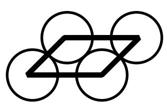

Structure C

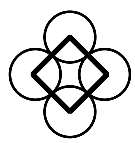

Structure D

Can a structure have more than one choice of unit cell ? _______

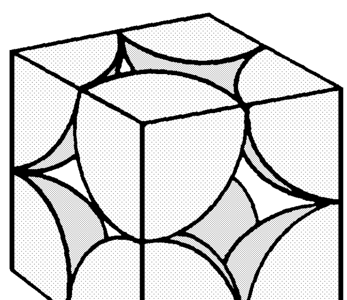
3. If the circle segments enclosed inside each of the bold-faced parallelograms shown here were cut out and taped together, how many whole circles could be constructed for each one of the patterns?

 _____

 _____

 _____

4. Shown at the right is a three-dimensional unit cell pattern for a structure of packed spheres. The center of each of eight spheres is at a corner of the cube, and the part of each that lies within the boundaries of the cube is shown. If all of the sphere segments enclosed inside the unit cell boundaries could be glued together, how many whole spheres could be constructed ? ____



5. Consult your textbook and find examples of metallic elements that adopt the following kinds of structures:

   Hexagonal closest packed (hcp): ________________________________
   Cubic closest packed (ccp): ____________________________________
   Body-centered cubic (bcc): ____________________________________

Procedure

This investigation involves two teams working together. Team A should build one structure while Team B builds another. Both teams then compare and contrast their structures and together answer the questions. The Work Sheet can be used to examine the structures in more detail. (Some Work Sheet entries will be blank for some structures such as questions about small spheres when only one size sphere is used in the structure; or questions about face-centered spheres when there are none).

For each pair of structures,

1. Identify a unit cell. How many atoms of each type are inside the unit cell?
2. What is the chemical formula for the material?
3. What is the coordination number and geometry of each type of atom?
4. How do the two structures differ? Answer any specific questions asked about each pair. Which of the team A and team B structures are the same?
5. Optional: What is the packing efficiency for each unit cell? Divide the volume occupied (based on the number of spheres in the unit cell and the volume of one sphere) by the volume of the unit cell (measured with a ruler). How does this relate to the density of the material?

Team A: Primitive or Simple cubic
Team B: Body-centered cubic

Which structure is more efficient at filling space? How would the density of the same element in either of these packing structures compare?

Team A: CsCl (first layer Cs)
Team B: CsCl (first layer Cl)

What is the geometric shape of just the large spheres? Of just the small spheres? What is the difference, if any, between the two structures? Which unit cell is correct? You may wish to build more than just one unit cell to check your answer.

Team A: Hexagonal close-packing
Team B: Cubic close-packing

Most of the elemental metals have close packed structures. What is the difference, if any, between the two structures? It may be useful to compare the templates on which the structures are built. How do the packing efficiencies compare qualitatively to those of the simple cubic and body-centered cubic structures?

Bend a piece of copper wire. Does it break? Explain by referring to its structure. (Copper has the cubic close-packed structure.) If you are using the Solid-State Model Kit, lift one of the bottom corner spheres of the cubic close-packing model. What happens? Does it matter which corner sphere is lifted? How do these observations of the model relate to your observations of copper?

Team A: Rock Salt (NaCl)
Team B: Rock Salt (NaCl body diagonal)

What is the structure of just the large spheres? Of just the small spheres? Show how the stoichiometry is related to the cubic unit-cell contents. Which color sphere represents Na^+ and which represents Cl^-?

Take a piece of rock salt, align a metal spatula parallel to one of its faces, as shown in Figure 3, and tap the spatula sharply with something heavier than a pencil and lighter than a hammer. How does the crystal break? The planes of cleavage in a crystal are the planes where the forces between the atoms are weakest. Which plane in the model do you think corresponds to the cleavage plane?

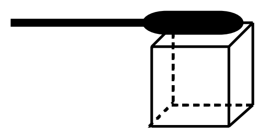


Figure 3. Breaking a crystal to reveal cleavage planes.

Team A: Diamond
Team B: Graphite

Both of these substances are composed exclusively of carbon atoms. Use a regular (graphite) pencil and a diamond-tipped scribe to write on a glass microscope slide. Why is diamond the hardest common substance while graphite is a soft, solid lubricant?

Which form of carbon do you think has the largest density? Why?

Team A: Molybdenum Sulfide
Team B: Gallium Selenide

Press a piece of cellophane tape onto a sample of molybdenum sulfide already stuck on a piece of tape. Peel apart the two pieces of tape. What happens to the molybdenum sulfide? Make a prediction about the properties of gallium selenide. Explain your reasoning.

Team A: Fluorite (CaF_2)
Team B: Zinc Blende (ZnS)

Which color sphere represents Ca and which represents F? Which color sphere represents Zn and which represents S? What is the stoichiometry of calcium fluoride? Of zinc blende? What is the structure of just the large spheres? Of just the small spheres?

Team A: Face-centered cubic
Team B: Face-centered cubic (body diagonal)

Are these structures the same as any structures you have already built?

Work Sheet (Data and Observations)

Unit Cells and Stoichiometry

How many large spheres lie with their centers
at the CORNERS of the unit cell?
on the FACES of the unit cell?
on the EDGES of the unit cell?
completely INSIDE of the unit cell?
How many small spheres lie with their centers
at the CORNERS of the unit cell?
on the FACES of the unit cell?
on the EDGES of the unit cell?
completely INSIDE of the unit cell?
With how many unit cells is a
CORNER-centered sphere shared?
FACE-centered sphere shared?
EDGE-centered sphere shared?
Inside the unit cell is how much of each
CORNER-centered sphere?
FACE-centered sphere?
EDGE-centered sphere?
How many total LARGE spheres are inside the unit cell?
How many total SMALL spheres are inside the unit cell?
What is the formula representation for the unit cell?

Coordination Number

If the structure has more than one size of spheres, nearest neighbor touching spheres will be of unequal size.
Choose a LARGE sphere. What COLOR is it?
How many nearest neighbor touching spheres are
in the layer BELOW?
in the SAME layer?
in the layer ABOVE?
What is the coordination number for large spheres?
Are the large spheres close-packed (CN 12)?
Choose a SMALL sphere. What COLOR is it?
How many nearest neighbor touching spheres are
in the layer BELOW?
in the SAME layer?
in the layer ABOVE?
What is the coordination number for small spheres?

Close-Packed Structures

Are the packing layers ABA or ABCA?