Learning Objectives

- To know the characteristic properties of crystalline and amorphous solids.
- To recognize the unit cell of a crystalline solid.
- To calculate the density of a solid given its unit cell.

Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays. With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the positions of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice, thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (from the Greek ámorphos, meaning "shapeless").

(left) Crystalline faces. The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS₂), or at other angles, as in quartz. (Right) Cleavage surfaces of an amorphous solid. Obsidian, a volcanic glass with the same chemical composition as granite (typically KAlSi₃O₈), tends to have curved, irregular surfaces when cleaved.
Crystalline solids, or crystals, have distinctive internal structures that in turn lead to distinctive flat surfaces, or faces. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material. The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure \(\PageIndex{1}\), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

![Cleaving a Crystal of an Ionic Compound along a Plane of Ions](image)

Figure \(\PageIndex{1}\): Cleaving a Crystal of an Ionic Compound along a Plane of Ions. Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glass. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO\(_2\) and both consist of linked SiO\(_4\) tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO\(_2\) is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of \(4 \times 10^{13}\) K/s, which prevents the atoms from arranging themselves into a regular array.
The lattice of crystalline quartz (SiO$_2$). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Crystals have sharp, well-defined melting points; amorphous solids do not.

**Crystals**

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a crystal lattice), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cell. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.
Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure \(\PageIndex{2}\)). Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in part (d) in Figure \(\PageIndex{2}\)) is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure \(\PageIndex{3}\)).
The Unit Cell

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure \(\PageIndex{4}\)). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in which all sides have the same length and all angles are 90°, but the concepts that we introduce also apply to substances whose unit cells are not cubic.

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubic (Figure \(\PageIndex{5a}\)). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc) (\(\PageIndex{5b}\)). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc) (Figure \(\PageIndex{5c}\)).

As indicated in Figure \(\PageIndex{5}\), a solid consists of a large number of unit cells arrayed in three dimensions. Any
intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because density is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 5. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as \( \frac{1}{2} \) atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes \( \frac{1}{4} \) atom per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 4. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as \( \frac{1}{2} \) atom per unit cell. The statement that atoms lying on an edge or a corner of a unit cell count as \( \frac{1}{4} \) or \( \frac{1}{8} \) atom per unit cell, respectively, is true for all unit cells except the hexagonal one, in which three unit cells share each vertical edge and six share each corner (Figure 4), leading to values of \( \frac{1}{3} \) and \( \frac{1}{6} \) atom per unit cell, respectively, for atoms in these positions. In contrast, atoms that lie entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

For all unit cells except hexagonal, atoms on the faces contribute \( \frac{1}{2} \) atom to each unit cell, atoms on the edges contribute \( \frac{1}{4} \) atom to each unit cell, and atoms on the corners contribute \( \frac{1}{8} \) atom to each unit cell.

Example 1: The Unit Cell for Gold

Metallic gold has a face-centered cubic unit cell (Figure 5). How many Au atoms are in each unit cell?

**Given:** unit cell

**Asked for:** number of atoms per unit cell

**Strategy**

Using Figure 5, identify the positions of the Au atoms in a face-centered cubic unit cell and then determine how much each Au atom contributes to the unit cell. Add the contributions of all the Au atoms to obtain the total number of Au atoms in a unit cell.

**Solution**

As shown in Figure 5, a face-centered cubic unit cell has eight atoms at the corners of the cube and six atoms on the faces. Because atoms on a face are shared by two unit cells, each counts as \( \frac{1}{2} \) atom per unit cell, giving \( 6 \times \frac{1}{2} = 3 \) Au atoms per unit cell. Atoms on a corner are shared by eight unit cells and hence contribute only \( \frac{1}{8} \) atom per unit cell, giving \( 8 \times \frac{1}{8} = 1 \) Au atom per unit cell. The total number of Au atoms in each unit cell is thus \( 3 + 1 = 4 \).

**Exercise**

Metallic iron has a body-centered cubic unit cell (Figure 5). How many Fe atoms are in each unit cell?
Now that we know how to count atoms in unit cells, we can use unit cells to calculate the densities of simple compounds. Note, however, that we are assuming a solid consists of a perfect regular array of unit cells, whereas real substances contain impurities and defects that affect many of their bulk properties, including density. Consequently, the results of our calculations will be close but not necessarily identical to the experimentally obtained values.

Example \(\PageIndex{2}\): Density of Iron

Calculate the density of metallic iron, which has a body-centered cubic unit cell (Figure \(\PageIndex{5b}\)) with an edge length of 286.6 pm.

**Given:** unit cell and edge length

**Asked for:** density

**Strategy:**

A. Determine the number of iron atoms per unit cell.

B. Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro’s number. Then divide the mass by the volume of the cell.

**Solution:**

A. We know from Example \(\PageIndex{1}\) that each unit cell of metallic iron contains two Fe atoms.

B. The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro’s number and then divide the mass by the volume of the cell (making sure to use suitable units to get density in g/cm\(^3\)):

\[
\text{mass of Fe} = \left(2 \; \frac{\text{atoms}}{\text{Fe}}\right) \left(\frac{1 \; \text{mol}}{6.022 \times 10^{23} \; \text{atoms}}\right) \left(\frac{55.85 \; \text{g}}{\text{mol}}\right) = 1.855 \times 10^{-22} \; \text{g}
\]

\[
\text{volume} = \left(286.6 \; \text{pm}\right) \left(\frac{10^{-12} \; \text{m}}{\text{pm}}\right) \left(\frac{10^{2} \; \text{cm}}{\text{m}}\right) = 2.345 \times 10^{-23} \; \text{cm}^3
\]

\[
\text{density} = \frac{1.855 \times 10^{-22} \; \text{g}}{2.345 \times 10^{-23} \; \text{cm}^3} = 7.880 \; \text{g/cm}^3
\]

This result compares well with the tabulated experimental value of 7.874 g/cm\(^3\).

Exercise \(\PageIndex{2}\): Density of Gold

Calculate the density of gold, which has a face-centered cubic unit cell (Figure \(\PageIndex{5c}\)) with an edge length of 407.8 pm.
Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in Figure \(\PageIndex{5a}\). Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa.

Body-Centered Cubic Structure

The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in Figure \(\PageIndex{5b}\), the body-centered cubic structure consists of a single layer of spheres in contact.
with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped “holes” above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in Figure \( \PageIndex{6a} \). Each sphere is surrounded by six others in the same plane to produce a hexagonal arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be divided into two sets, labeled B and C in Figure \( \PageIndex{6a} \). Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

Figure \( \PageIndex{6} \): Close-Packed Layers of Spheres. (a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure.

If we place the second layer of spheres at the B positions in Figure \( \PageIndex{6a} \), we obtain the two-layered structure shown in Figure \( \PageIndex{6b} \). There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did not use for the atoms in the first or second layers (Figure \( \PageIndex{6c} \)). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB..., resulting in a hexagonal close-packed (hcp) structure (Figure \( \PageIndex{7a} \)). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC..., giving a cubic close-packed (ccp) structure (Figure \( \PageIndex{7b} \)). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in Figure \( \PageIndex{7b} \), however, simply rotating the structure reveals its cubic nature, which is identical to a fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

Figure \( \PageIndex{4} \). The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.
Table 1 compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination number. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Percentage of Space Occupied by Atoms</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>simple cubic</td>
<td>52</td>
<td>6</td>
</tr>
<tr>
<td>body-centered cubic</td>
<td>68</td>
<td>8</td>
</tr>
<tr>
<td>hexagonal close packed</td>
<td>74</td>
<td>12</td>
</tr>
<tr>
<td>cubic close packed (identical to face-centered cubic)</td>
<td>74</td>
<td>12</td>
</tr>
</tbody>
</table>

Summary

A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure. Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a crystal lattice), which results in a crystalline solid, or more or less randomly to produce an amorphous solid. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

The smallest repeating unit of a crystal lattice is the unit cell. The simple cubic unit cell contains only eight atoms, molecules, or ions at the corners of a cube. A body-centered cubic (bcc) unit cell contains one additional component in the center of the cube. A face-centered cubic (fcc) unit cell contains a component in the center of each face in addition to those at the corners of the cube. Simple cubic and bcc arrangements fill only 52% and 68% of the available space with atoms, respectively. The hexagonal close-packed (hcp) structure has an ABABAB… repeating arrangement, and the cubic close-packed (ccp) structure has an ABCABC… repeating pattern; the latter is identical to an fcc lattice. The hcp and ccp arrangements fill 74% of the available space and have a coordination number of 12 for each atom in the lattice, the number of nearest neighbors. The simple cubic and bcc lattices have coordination numbers of 6 and 8, respectively.