Although the symmetry and beauty of crystals have always excited curiosity and wonder, the science of crystallography did not begin until the latter part of the 18th century. In these closing days of the Age of Enlightenment, when Lavoisier led the modern approach to chemistry, another brilliant French thinker established the fundamental laws of crystallography. René Just Haüy was struck by the fact that when he accidentally dropped a crystal of calcite (a form of calcium carbonate), it fractured into smaller crystals that had the same interfacial angles between their plane surface as did the original crystal. The consistency of the interfacial angles observed when crystals are cleaved is known as Haüy’s law. Haüy drew the conclusion that the outward symmetry of crystals implies an internal regularity and the existence of a smallest crystal unit. The first experimental evidence for the periodicity of the structure was reported in 1912 by Laue using x-ray diffraction by crystals. In the late 1990s, direct images of crystal structure have been produced by scanning tunneling microscopy (STM). One exploits the large variations in quantum tunneling as a function of the height of a fine metal tip above the surface of a crystal. The image in Figure
9.1 was produced this way. An STM method has been developed that will assemble single atoms into an organized layer nanometer structure on a crystal substrate.

![Figure 9.1 A scanning tunneling microscope image of atoms on a surface of fcc platinum at 4 K. The nearest-neighbor spacing is 2.78 Å. (Photo courtesy of D. M. Eigler, IBM Research Division) (Kittel, 2005)](image)

### 9.1 Atomic Mass

The *molar mass* is defined as the mass in grams of one mole of an element, which is numerically equal to the *atomic mass unit* (amu) of that element. One *mole* of a substance is the amount that contains *Avogadro's number* of atoms, or molecules.

**Avogadro's number**

*Avogadro's number* \( (N_o = 6.022137 \times 10^{23}) \) is defined as the number of atoms contained in exactly 12 g of isotope \(^{12}\text{C}\). This number of atoms forms *one mole* for any element.

**EXAMPLE 9.1 Mass of One Atom**

One of the heaviest atoms found in nature is uranium \(^{238}\text{U}\). What is the mass of one atom of the uranium?
Solution:
From the periodic table, the molar mass of $^{238}$U is 238.0289 g/mol. The mass of one atom of the uranium is calculated as

$$\text{Mass of one atom} = \frac{M}{N_\circ} = \frac{238.0289 \text{ g/mol}}{6.022137 \times 10^{23} \text{ #/mol}} = 3.952565 \times 10^{-22} \text{ g}$$

9.2 Unit Cells of a Crystal

A crystal is a periodic arrangement of atoms. A periodic array of mathematical points called a lattice (or reciprocal lattice) replicates the inherent periodicity of the crystal. A group of atoms in a lattice is called the basis. The lattice is formed from a unit cell like a small box having three lattice vectors, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, of which the magnitudes are called the lattice constants. Lattice points are the positions occupied by atoms. (One lattice point counts for one complete atom. A lattice point may share the count with surrounding lattices as a fraction). There could be more than one unit cell in a crystal depending on the chosen lattice points. The smallest volume of a unit cell is called a primitive unit cell. The primitive unit cell must have one lattice point or equivalently one atom.

Consider a two-dimensional lattice as shown in Figure 9.2. One may have more than one unit cell as shown in Figure 9.2 (cells 1 and 2). The primitive unit cell is the smallest volume cell shown as cell 1 in the figure. Cell 3 is not a primitive unit cell, but often chosen due to its regularity and symmetry, which is called a conventional unit cell. Another way of choosing a primitive unit cell is the Wigner-Seitz primitive cell as shown in Figure 9.2, which has the full symmetry of the Bravais lattice. The Wigner-Seitz primitive cell of the reciprocal lattice is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin, which is shown in Figure 9.3 in a two dimensional lattice and Figure 9.4 in a three dimensional lattice. Although the terms “Wigner-Seitz primitive cell” and “first Brillouin zone” refer to identical geometrical constructions, in practice the latter term is applied only to the $k$-space cell.
Different choices of primitive lattice vectors $a$ and $b$ and primitive cells are possible. The Wigner-Seitz primitive cell is one way to uniquely construct a primitive unit cell. Vectors $a$ and $b$ are not a set of primitive lattice vectors and the shaded area is not a primitive unit cell. This area is, however, often used due to its regular shape and is called a conventional cell.

A primitive cell may also be chosen for following procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells.
Figure 9.4 The Wigner-Seitz cell for the body-centered cubic Bravais lattice (a “truncated octahedron”). The surrounding cube is a conventional body-centered cubic cell with a lattice point at its center and on each vertex. The hexagonal faces bisect the lines joining the central point to the points on the vertices (drawn as solid lines). The square faces bisect the lines joining the central point to the central points in each of the six neighboring cubic cells (not drawn). The hexagons are regular.

Bravais Lattices

There are fourteen different lattices in seven crystal systems as shown in Figure 9.5. The fourteen lattices are called as the Bravais lattices. There are 3 lattices in the cubic system, 2 in the tetragonal (tetrahedral), 4 in the orthorhombic, 2 in the monoclinic, and 1 each in the hexagonal, rhombohedral (Trigonal), and triclinic systems (See Table 9.1 and Figure 9.6 for lattice vectors and angles). In many calculations involving properties of crystals it is important to know how many atoms are contained in each unit cell.
Figure 9.5 Unit cells of the 14 Bravais lattices of the seven crystal systems. Courtesy of Segal (1989).

Figure 9.6 One unit cell. The length along the coordinate axes are denoted $a$, $b$, $c$. The angles between the axes are $\alpha$, $\beta$, $\gamma$ and are defined as shown in the diagram.
Crystal structures are pictured in Figure 9.7 as resulting from the packing of spheres in which nearest neighbors are in contact. In a simple or primitive lattice, lattice points are located only at the corners of each unit cell. In a body-centered cubic (bcc) structure, lattice points are located at the center of the cell as well as at the corners (Figure 9.7). In a face-centered cubic (fcc) structure, lattice points are found at the center of each of the six faces of the cell, as well as at each of the eight corners (Figure 9.8).

![Figure 9.7](image)

Table 9.1 The Seven Crystal Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Axes</th>
<th>Angles</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>NaCl, CsCl</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>TiO$_2$ (rutile)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>CdSO$_4$, HgBr$_2$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
<td>CaCO$_3$ (calcite)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$</td>
<td>KIO$_3$, NaHCO$_3$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
<td>NaHSO$_4$, CuF$_2$</td>
</tr>
</tbody>
</table>

Figure 9.7 The body-centered cubic crystal structure, (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Reprinted by permission of John Wiley & Sons, Inc.)
Figure 9.8 For the face-centered cubic crystal structure: (a) a hard structure unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Reprinted by permission of John Wiley & Sons, Inc.)

EXAMPLE 9.2
Gold Au forms an fcc cubic unit cell. Its atomic radius is 1.44 Å. Calculate the lattice constant of the gold, and also calculate the density of gold.

Solution:
Lattice constant = $a$

Atomic radius of gold $R = 1.44 \text{ Å}$

From the figure, we have $a^2 + a^2 = (4R)^2$. Solving for $a$ gives

$$a = 2\sqrt{2}R = 4.073 \times 10^{-8} \text{ cm} = 4.073 \text{ Å}$$

Density = total mass of lattice/volume of lattice

Mass of gold atom = $\frac{196.97 \text{ g/mol}}{6.022137 \times 10^{23} \text{ mol}} = 32.708 \times 10^{-23} \text{ g}$

The gold cubic unit cell has 4 lattice points (4 atoms) per cell as shown in the figure. Therefore,

$$
\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{4 \times 32.708 \times 10^{-23}}{(4.073 \times 10^{-8})} = 19.36 \text{ g/cm}^3
$$

9.3 Crystal Planes

The orientation of a plane is determined by three points in the plane, provided they are not collinear. If each point lay on a different crystal axis, the plane could be specified by giving the coordinates of the points in terms of the lattice constant $a_1, a_2, a_3$. However, it turns out to be more useful for structure analysis to specify the orientation of a plane by the Miller indices determined by the following rules (Figure 9.9).
• Find the intercepts on the axes in terms of the lattice constants \( a_1, a_2, a_3 \). The axes may be those of a primitive or nonprimitive cell.
• Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses \((hkl)\), is called the index of the plane.

Figure 9.9 This plane intercepts the \( a_1, a_2, a_3 \) axes at \( 3a_1, 2a_2, 2a_3 \). The reciprocals of these numbers are \( \frac{1}{3}, \frac{1}{2}, \frac{1}{2} \). The smallest three integers having the same ratio are 2, 3, 3, and the indices of the plane are (233).
Figure 9.10 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (î00).

For the plane whose intercepts are 3, 2, 2, the reciprocals are \( \frac{1}{3}, \frac{1}{2}, \frac{1}{2} \); the smallest three integers having the same ratio are (233) by multiplying \( \frac{1}{3}, \frac{1}{2}, \frac{1}{2} \) by numbers (6 in this case) to have three integers. For an intercept at infinity, the corresponding index is zero. The indices of some important planes in a cubic crystal are illustrated in Figure 9.10. The indices \((hkl)\) may denote a single plane or a set of parallel planes. If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index. The cube faces of a cubic crystal are (100), (010), (001), (î00), (0î0), and (00î). Planes equivalent by symmetry may be denoted by curly brackets (braces) around indices; the set of cube faces is \{100\}. When we speak of the (200) plane we means a plane parallel to (100) but cutting the \( a_1 \) axis at \( \frac{1}{2}a \).

The indices \([uvw]\) of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction, referred to the axes. The \( a_1 \) axis is the \([100]\) direction; the \(-a_1\) axis is the \([0î0]\) direction. In cubic crystals the direction \([hkl]\) is perpendicular to a plane \((hkl)\) having the same indices, but this is not generally true in other crystal systems.

Crystal planes and directions are often determined by using X-rays or transmission electron microscopy. Semiconductor wafers are sold with the major crystallographic directions and dopant types marked by the wafer flats. A wafer typically has a primary flat representing a crystal plane and a secondary flat that is positioned to denote the dopant type and the surface crystallographic direction for a 4-in silicon wafer.

**EXAMPLE 9.3 Indices of a Plane**

Intercepts of two planes are 4, 2, 3 and 0.8, 0.4, 0.6, respectively. Determine the Miller indices of the planes.

**Solution:**

Reciprocals: 1/4, 1/2, 1/3 = 12/4, 12/2, 12/3 = (364)
Reciprocals: $1/0.8, 1/0.4, 1/0.6 = 24/8, 24/4, 24/6 = (364)$
These two planes are in the same direction.

**Problems**

9.1 Calculate the mass of one atom of sodium.

9.2 Iron Fe holds a bcc cubic unit cell having an atomic radius of 1.25 Å. Calculate the lattice constant of the iron, and also calculate the density of the iron.

9.3 Intercepts of a plane are 4, 1, 2. Determine the Miller indices of the plane.

9.4 Indices of a plane is (123). Determine the intercepts for the smallest integers.