Lecture 4

Atomic And Ionic Arrangements

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Points, Directions, and Planes in the Unit Cell

- Miller indices - A shorthand notation to describe certain crystallographic directions and planes in a material. Denoted by [ ] brackets. A negative number is represented by a bar over the number.
- Directions of a form - Crystallographic directions that all have the same characteristics, although their ‘‘sense’’ is different. Denoted by < > brackets.
- Repeat distance - The distance from one lattice point to the adjacent lattice point along a direction.
- Linear density - The number of lattice points per unit length along a direction.
- Packing fraction - The fraction of a direction (linear-packing fraction) or a plane (planar-packing factor) that is actually covered by atoms or ions.

Points, Directions, and Planes in the Unit Cell

Coordinates of Points We can locate certain points, such as atom positions, in the lattice or unit cell by constructing the right-handed coordinate system in Figure 3-14. Distance is measured in terms of the number of lattice parameters we must move in each of the *x*, *y*, and *z* coordinates to get from the origin to the point in question. The coordinates are written as the three distances, with commas separating the numbers.

Directions in the Unit Cell Certain directions in the unit cell are of particular importance. **Miller indices** for directions are the shorthand notation used to describe these directions. The procedure for finding the Miller indices for directions is as follows:

1. Using a right-handed coordinate system, determine the coordinates of two points that lie on the direction.
2. Subtract the coordinates of the “tail” point from the coordinates of the “head” point to obtain the number of lattice parameters traveled in the direction of each axis of the coordinate system.

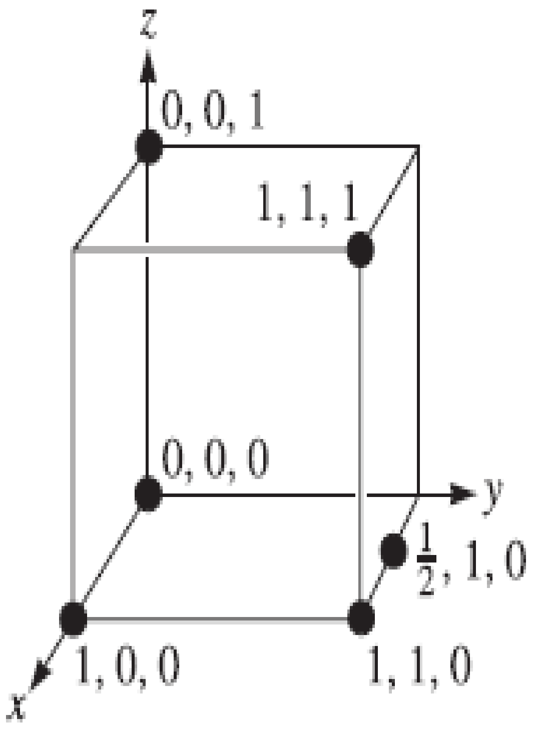


Figure 3-14
Coordinates of selected points in the unit cell. The number refers to the distance from the origin in terms of lattice parameters.

3. Clear fractions and/or reduce the results obtained from the subtraction to lowest integers.
4. Enclose the numbers in square brackets [ ]. If a negative sign is produced, represent the negative sign with a bar over the number.

Determine the Miller indices of directions *A*, *B*, and *C* in Figure 3-15.

SOLUTION

Direction *A*

1. Two points are 1, 0, 0, and 0, 0, 0
2. 1, 0, 0 − 0, 0, 0 = 1, 0, 0
3. No fractions to clear or integers to reduce
4. [100]

Direction *B*

1. Two points are 1, 1, 1 and 0, 0, 0
2. 1, 1, 1 − 0, 0, 0 = 1, 1, 1
3. No fractions to clear or integers to reduce
4. [111]

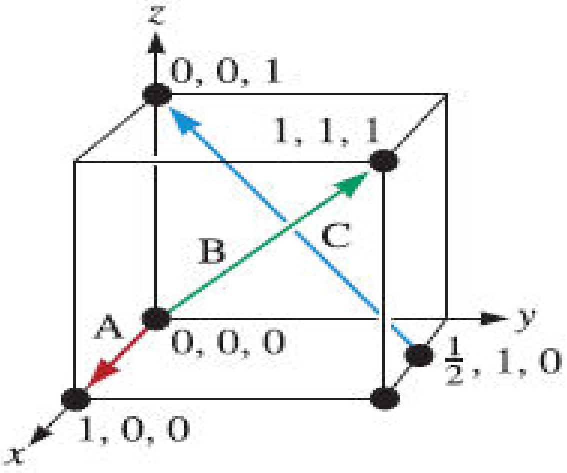


Figure 3-15
Crystallographic directions and coordinates (for Example 3-7).

Direction C

1. Two points are 0, 0, 1 and $\frac{1}{2}$, 1, 0
2. 0, 0, 1 $-\frac{1}{2}$, 1, 0 = $-\frac{1}{2}$, −1, 1
3. 2 ($-\frac{1}{2}$, −1, 1) = −1, −2, 2
4. [$\bar{1}\bar{2}2$]

Several points should be noted about the use of Miller indices for directions:

1. Because directions are vectors, a direction and its negative are not identical; [100] is not equal to [$\bar{1}00$]. They represent the same line, but opposite directions.
2. A direction and its multiple are *identical*; [100] is the same direction as [200].
3. Certain groups of directions are *equivalent*; they have their particular indices because of the way we construct the coordinates. For example, in a cubic system, a [100] direction is a [010] direction if we redefine the coordinate system as shown in Figure 3-16. We may refer to groups of equivalent directions as **directions of a form** or **family**. The special brackets ⟨⟩ are used to indicate this collection of directions. All of the directions of the form ⟨110⟩ are listed in Table 3-3. We expect a material to have the same properties in each of these twelve directions of the form ⟨110⟩.

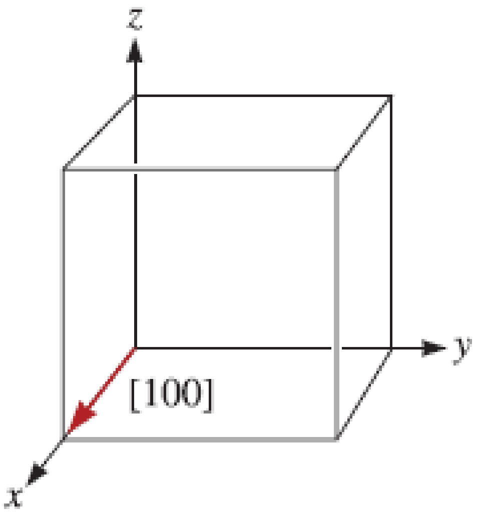
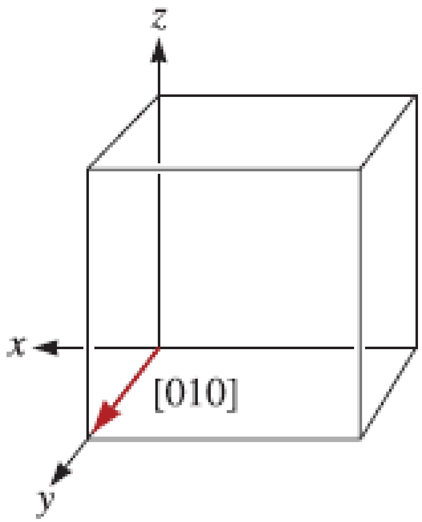
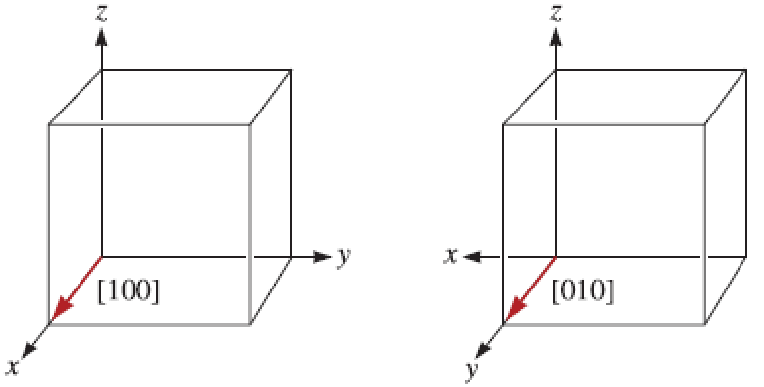


Figure 3-16 Equivalency of crystallographic directions of a form in cubic systems.

Significance of Crystallographic Directions Crystallographic directions are used to indicate a particular orientation of a single crystal or of an oriented polycrystalline material. Knowing how to describe these can be useful in many applications. Metals deform more easily, for example, in directions along which atoms are in closest contact. Another real-world example is the dependence of the magnetic properties of iron and other magnetic materials on the crystallographic directions. It is much easier to magnetize iron in the [100] direction compared to the [111] or [110] directions. This is why the grains in Fe-Si steels used in magnetic applications (e.g., transformer cores) are oriented in the [100] or equivalent directions.

TABLE 3-3 ■ *Directions of the form* ⟨110⟩ *in cubic systems*

$$\langle 110 \rangle = \begin{cases} [110]\ [\bar{1}\bar{1}0] \\ [101]\ [\bar{1}0\bar{1}] \\ [011]\ [0\bar{1}\bar{1}] \\ [1\bar{1}0]\ [\bar{1}10] \\ [10\bar{1}]\ [\bar{1}01] \\ [01\bar{1}]\ [0\bar{1}1] \end{cases}$$



Repeat Distance, Linear Density, and Packing Fraction

Another way of characterizing directions is by the **repeat distance** or the distance between lattice points along the direction. For example, we could examine the [110] direction in an FCC unit cell (Figure 3-17); if we start at the 0, 0, 0 location, the next lattice point is at the center of a face, or a 1/2, 1/2, 0 site. The distance between lattice points is therefore one-half of the face diagonal, or $\frac{1}{2}\sqrt{2}a_0$. In copper, which has a lattice parameter of 0.3615 nm, the repeat distance is 0.2556 nm.

The **linear density** is the number of lattice points per unit length along the direction. In copper, there are two repeat distances along the [110] direction in each unit cell; since this distance is $\sqrt{2}a_0 = 0.5112$ nm, then

$$\text{Linear density} = \frac{2 \text{ repeat distances}}{0.5112 \text{ nm}} = 3.91 \text{ lattice points/nm}$$

Note that the linear density is also the reciprocal of the repeat distance.

Finally, we can compute the **packing fraction** of a particular direction, or the fraction actually covered by atoms. For copper, in which one atom is located at each lattice point, this fraction is equal to the product of the linear density and twice the atomic radius. For the [110] direction in FCC copper, the atomic radius $r = \sqrt{2}a_0/4 = 0.1278$ nm. Therefore, the packing fraction is

$$\begin{aligned}\text{Packing fraction} &= (\text{linear density})(2r)\\ &= (3.91)(2)(0.1278)\\ &= (1.0)\end{aligned}$$

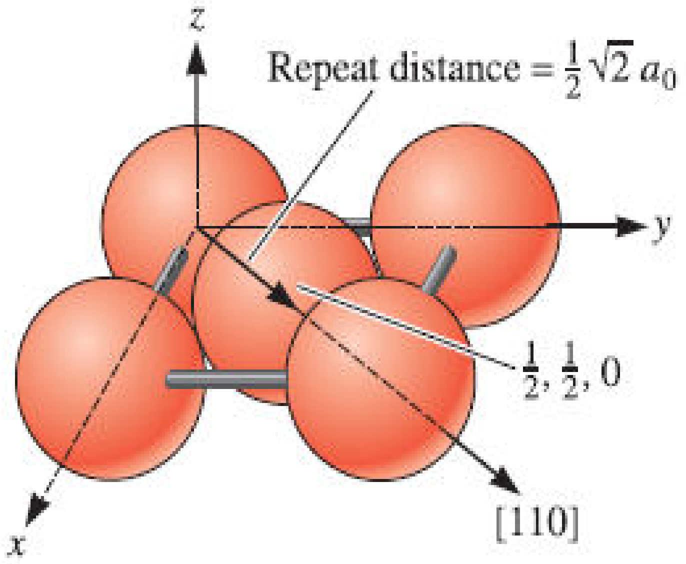


Figure 3-17
Determining the repeat distance, linear density, and packing fraction for a [110] direction in FCC copper.

Atoms touch along the [110] direction, since the [110] direction is close-packed in FCC metals.

Planes in the Unit Cell Certain planes of atoms in a crystal also carry particular significance. For example, metals deform along planes of atoms that are most tightly packed together. The surface energy of different faces of a crystal depends upon the particular crystallographic planes. This becomes important in crystal growth. In thin film growth of certain electronic materials (e.g., Si or GaAs), we need to be sure the substrate is oriented in such a way that the thin film can grow on a particular crystallographic plane.

Miller indices are used as a shorthand notation to identify these important planes, as described in the following procedure.

1. Identify the points at which the plane intercepts the x, y, and z coordinates in terms of the number of lattice parameters. If the plane passes through the origin, the origin of the coordinate system must be moved to that of an adjacent unit cell.
2. Take reciprocals of these intercepts.
3. Clear fractions but do not reduce to lowest integers.
4. Enclose the resulting numbers in parentheses (). Again, negative numbers should be written with a bar over the number.

Determine the Miller indices of planes *A*, *B*, and *C* in Figure 3-18.

SOLUTION

Plane *A*

1. $x = 1, y = 1, z = 1$
2. $\frac{1}{x} = 1, \frac{1}{y} = 1, \frac{1}{z} = 1$
3. No fractions to clear
4. (111)

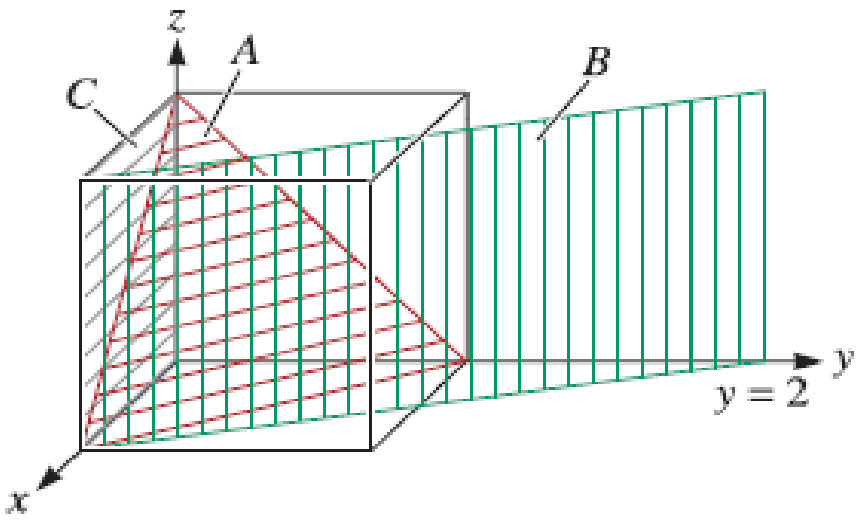


Figure 3-18
Crystallographic planes and intercepts (for Example 3-8).

Plane *B*

1. The plane never intercepts the z axis, so $x = 1$, $y = 2$, and $z = \infty$
2. $\frac{1}{x} = 1, \frac{1}{y} = \frac{1}{2}, \frac{1}{z} = 0$
3. Clear fractions: $\frac{1}{x} = 2, \frac{1}{y} = 1, \frac{1}{z} = 0$
4. (210)

Plane *C*

1. We must move the origin, since the plane passes through 0, 0, 0. Let's move the origin one lattice parameter in the y-direction. Then, $x = \infty$, $y = -1$, and $z = \infty$.
2. $\frac{1}{x} = 0, \frac{1}{y} = -1, \frac{1}{z} = 0$
3. No fractions to clear.
4. $(0\bar{1}0)$

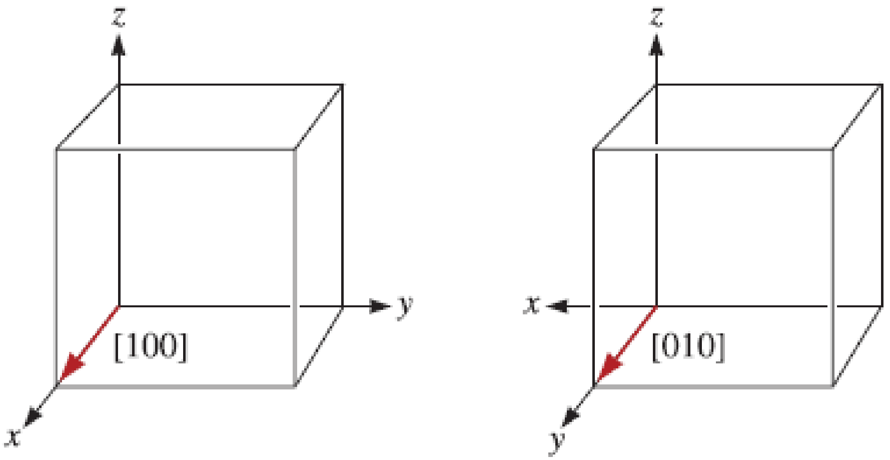
Several important aspects of the Miller indices for planes should be noted:

1. Planes and their negatives are identical (this was not the case for directions) because they are parallel. Therefore, $(020) = (0\bar{2}0)$.
2. Planes and their multiples are not identical (again, this is the opposite of what we found for directions). We can show this by defining planar densities and planar packing fractions. The **planar density** is the number of atoms per unit area with centers that lie on the plane; the packing fraction is the fraction of the area of that plane actually covered by these atoms. Example 3-9 shows how these can be calculated.
3. In each unit cell, **planes of a form** or **family** represent groups of equivalent planes that have their particular indices because of the orientation of the coordinates. We represent these groups of similar planes with the notation {}. The planes of the form {110} in cubic systems are shown in Table 3-4.
4. In cubic systems, a direction that has the same indices as a plane is perpendicular to that plane.

TABLE 3-4 ■ *Planes of the form {110} in cubic systems*

$$\{110\}\left\{\begin{array}{l}(110)\\(101)\\(011)\\(1\bar{1}0)\\(10\bar{1})\\(01\bar{1})\end{array}\right.$$

Note: The negatives of the planes are not unique planes.



Example 3-9 *Calculating the Planar Density and Packing Fraction*

Calculate the planar density and planar packing fraction for the (010) and (020) planes in simple cubic polonium, which has a lattice parameter of 0.334 nm.

SOLUTION

The two planes are drawn in Figure 3-19. On the (010) plane, the atoms are centered at each corner of the cube face, with 1/4 of each atom actually in the face of the unit cell. Thus, the total atoms on each face is one. The planar density is

$$\text{Planar density (010)} = \frac{\text{atoms per face}}{\text{area of face}} = \frac{1 \text{ atom per face}}{(0.334)^2}$$

$$= 8.96 \text{ atoms/nm}^2 = 8.96 \times 10^{14} \text{ atoms/cm}^2$$

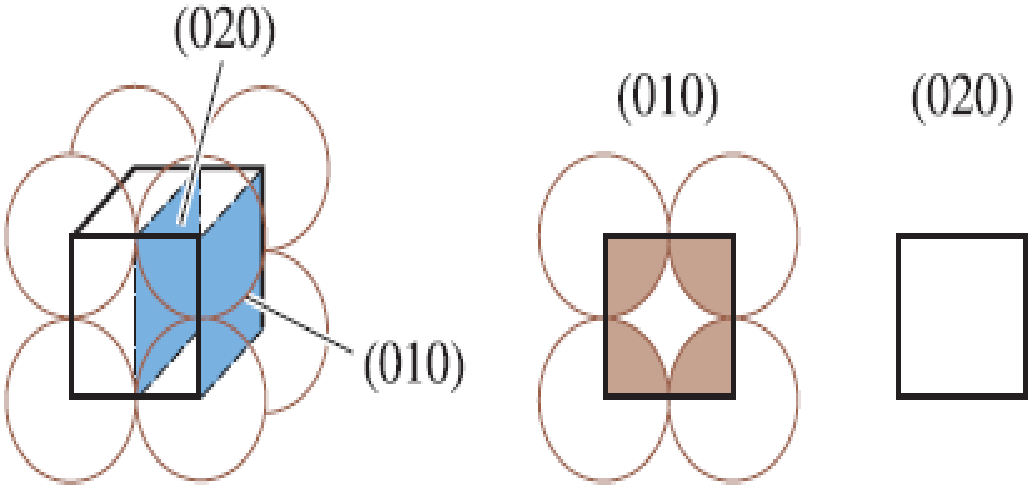


Figure 3-19 The planar densities of the (010) and (020) planes in SC unit cells are not identical (for Example 3-9).

The planar packing fraction is given by

$$\text{Packing fraction (010)} = \frac{\text{area of atoms per face}}{\text{area of face}} = \frac{(1\ \text{atom})(\pi r^2)}{(a_0)^2}$$

$$= \frac{\pi r^2}{(2r)^2} = 0.79$$

No atoms are centered on the (020) planes. Therefore, the planar density and the planar packing fraction are both zero. The (010) and (020) planes are not equivalent!

Construction of Directions and Planes To construct a direction or plane in the unit cell, we simply work backwards. Example 3-10 shows how we might do this.

Example 3-10 *Drawing a Direction and Plane*

Draw (a) the $[1\bar{2}1]$ direction and (b) the $(\bar{2}10)$ plane in a cubic unit cell.

SOLUTION

a. Because we know that we will need to move in the negative *y*-direction, let's locate the origin at 0, +1, 0. The "tail" of the direction will be located at this new origin. A second point on the direction can be determined by moving +1 in the *x*-direction, −2 in the *y*-direction, and +1 in the *z*-direction [Figure 3-20(a)].

b. To draw in the $(\bar{2}10)$ plane, first take reciprocals of the indices to obtain the intercepts, that is

$$x = \frac{1}{-2} = -\frac{1}{2};\ y = \frac{1}{1} = 1;\ z = \frac{1}{0} = \infty$$

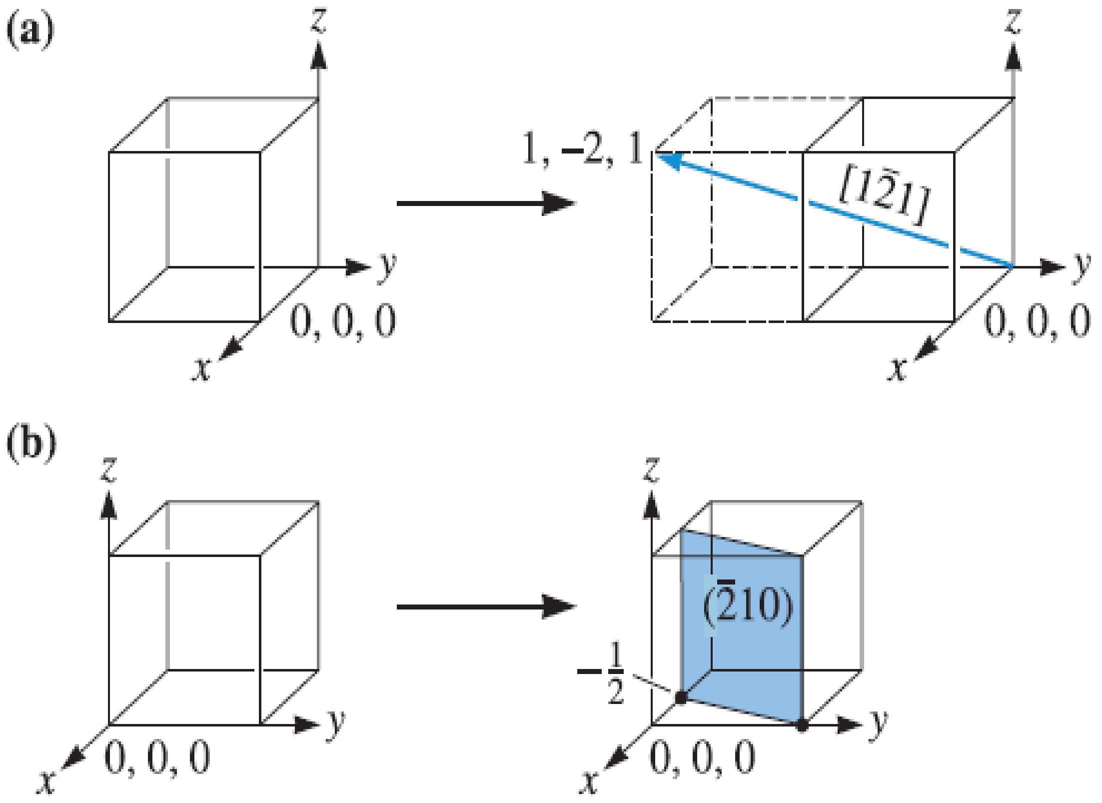


Figure 3-20 Construction of a (a) direction and (b) plane within a unit cell (for Example 3-10).

Since the *x*-intercept is in a negative direction, and we wish to draw the plane within the unit cell, let's move the origin +1 in the *x*-direction to 1, 0, 0.

Then we can locate the *x*-intercept at −1/2 and the *y*-intercept at +1. The plane will be parallel to the z-axis [Figure 3-20(b)].

Miller Indices for Hexagonal Unit Cells A special set of **Miller-Bravais indices** has been devised for hexagonal unit cells because of the unique symmetry of the system (Figure 3-21). The coordinate system uses four axes instead of three, with the a_3 axis being redundant. The axes a_1, a_2, and a_3 lie in a plane that is perpendicular to the fourth axis. The procedure for finding the indices of planes is exactly the same as before, but four intercepts are required, giving indices of the form $(hkil)$. Because of the redundancy of the a_3 axis and the special geometry of the system, the first three integers in the designation, corresponding to the a_1, a_2, and a_3 intercepts, are related by $h + k = -i$.

Directions in HCP cells are denoted with either the three-axis or four-axis system. With the three-axis system, the procedure is the same as for conventional Miller indices; examples of this procedure are shown in Example 3-11. A more complicated procedure,

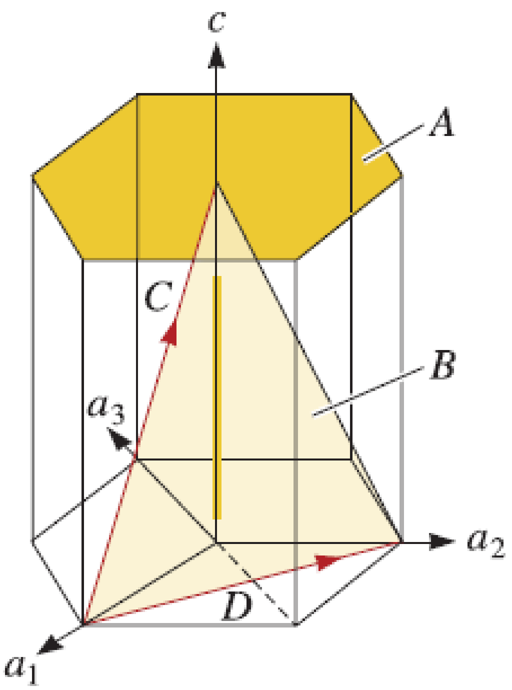


Figure 3-21
Miller-Bravais indices are obtained for crystallographic planes in HCP unit cells by using a four-axis coordinate system. The planes labeled *A* and *B* and the directions labeled *C* and *D* are those discussed in Example 3-11.

by which the direction is broken up into four vectors, is needed for the four-axis system. We determine the number of lattice parameters we must move in each direction to get from the "tail" to the "head" of the direction, while for consistency still making sure that $h + k = -i$. This is illustrated in Figure 3-22, showing that the [010] direction is the same as the $[\bar{1}2\bar{1}0]$ direction.

We can also convert the three-axis notation to the four-axis notation for directions by the following relationships, where h', k', and l' are the indices in the three-axis system:

$$\left.\begin{aligned} h &= \frac{1}{3}(2h' - k') \\ k &= \frac{1}{3}(2k' - h') \\ i &= -\frac{1}{3}(h' + k') \\ l &= l' \end{aligned}\right\} \tag{3-6}$$

After conversion, the values of h, k, i, and l may require clearing of fractions or reducing to lowest integers.

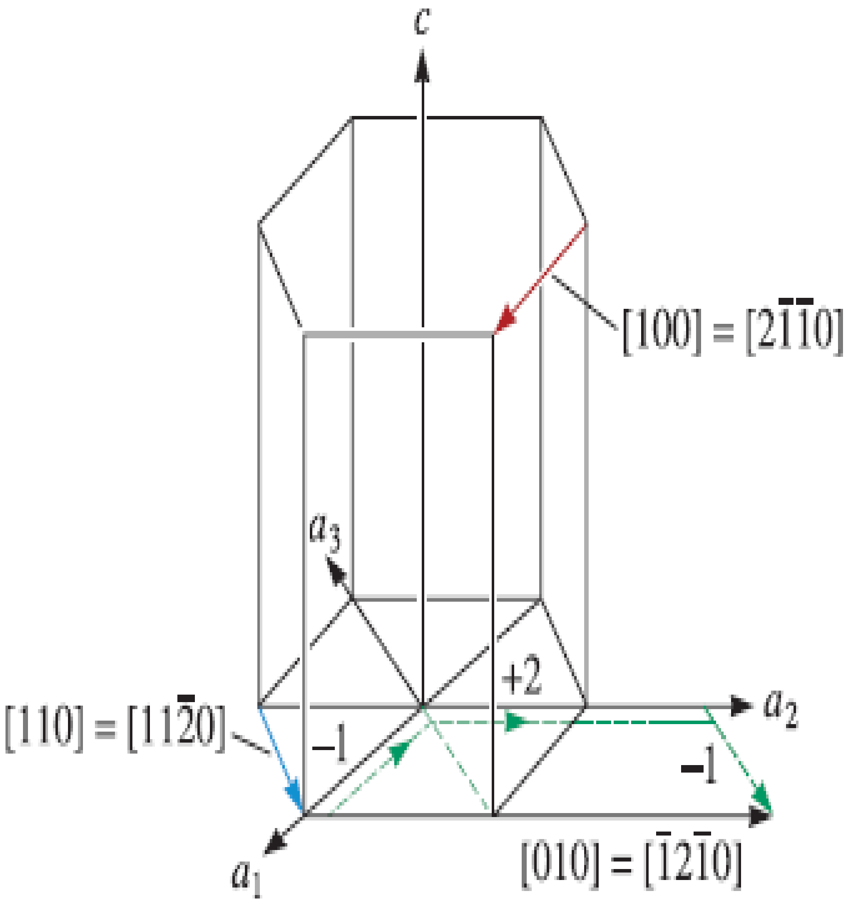


Figure 3-22
Typical directions in the HCP unit cell, using both three- and four-axis systems. The dashed lines show that the $[\bar{1}2\bar{1}0]$ direction is equivalent to a [010] direction.

$$h = \frac{1}{3}(2h' - k')$$

$$k = \frac{1}{3}(2k' - h')$$

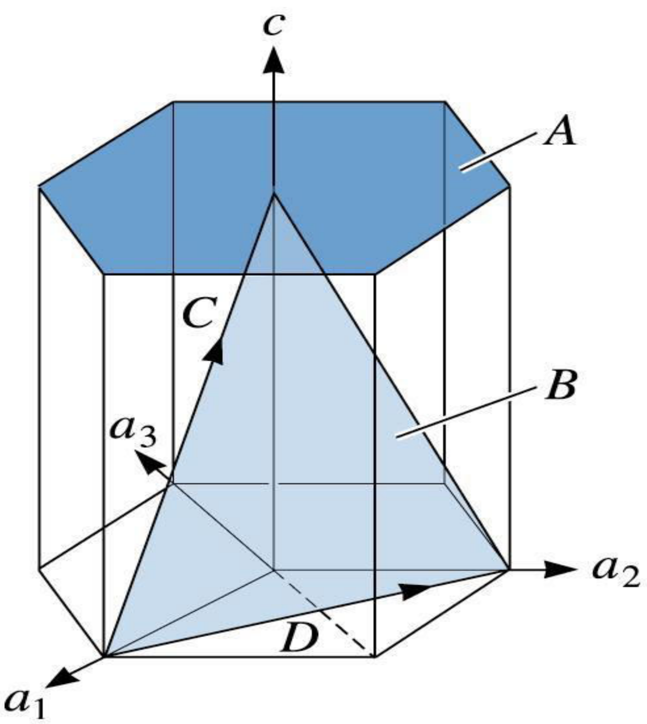
$$i = -\frac{1}{3}(h' + k')$$

$$l = l'$$

Example 3-11 Determining the Miller-Bravais Indices for Planes and Directions

Determine the Miller-Bravais indices for planes *A* and *B* and directions *C* and *D* in Figure 3-21.

SOLUTION



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Plane *A*

1. $a_1 = a_2 = a_3 = \infty, c = 1$
2. $\frac{1}{a_1} = \frac{1}{a_2} = \frac{1}{a_3} = 0, \frac{1}{c} = 1$
3. No fractions to clear
4. (0001)

Plane B

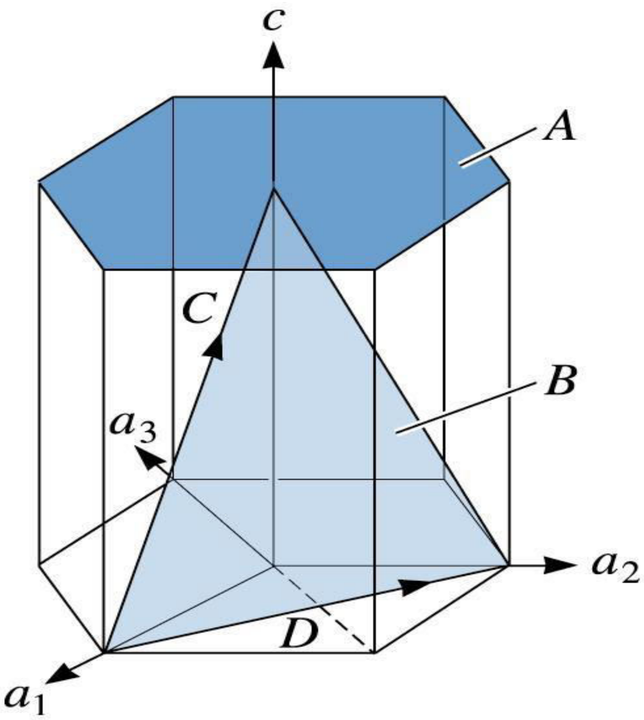
1. $a_1 = 1, a_2 = 1, a_3 = -\frac{1}{2}, c = 1$
2. $\frac{1}{a_1} = 1, \frac{1}{a_2} = 1, \frac{1}{a_3} = -2, \frac{1}{c} = 1$
3. No fractions to clear.
4. $(11\bar{2}1)$

Direction C

1. Two points are 0, 0, 1 and 1, 0, 0.
2. 0, 0, 1 – 1, 0, 0 = –1, 0, 1
3. No fractions to clear or integers to reduce.
4. $[\bar{1}01]$ or $[\bar{2}113]$

Direction D

1. Two points are 0, 1, 0 and 1, 0, 0.
2. 0, 1, 0 – 1, 0, 0 = –1, 1, 0
3. No fractions to clear or integers to reduce.
4. $[\bar{1}10]$ or $[\bar{1}100]$



Isotropic and Anisotropic Behavior Because of differences in atomic arrangement in the planes and directions within a crystal, some properties also vary with direction. A material is crystallographically **anisotropic** if its properties depend on the crystallographic direction along which the property is measured. For example, the modulus of elasticity of aluminum is 75.9 GPa (11×10^6 psi) in $\langle 111 \rangle$ directions, but only 63.4 GPa (9.2×10^6 psi) in $\langle 100 \rangle$ directions. If the properties are

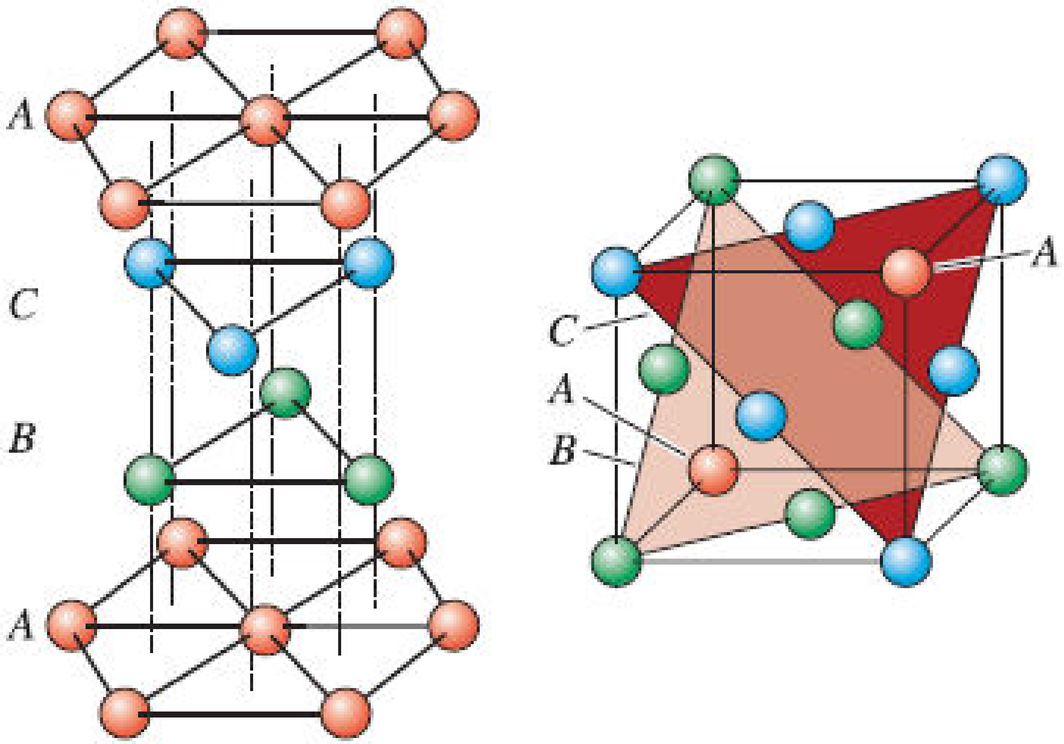


Figure 3-24
The *ABCABCABC* stacking sequence of close-packed planes produces the FCC structure.

identical in all directions, the material is crystallographically **isotropic**. Note that a material such as aluminum, which is crystallographically anisotropic, may behave as an isotropic material if it is in a polycrystalline form. This is because the random orientations of different crystals in a polycrystalline material will mostly cancel out any effect of the anisotropy as a result of crystal structure. In general, most polycrystalline materials will exhibit isotropic properties. Materials that are single crystals or in which many grains are oriented along certain directions (naturally or deliberately obtained by processing) will typically have anisotropic mechanical, optical, magnetic, and dielectric properties.

Interplanar Spacing The distance between two adjacent parallel planes of atoms with the same Miller indices is called the **interplanar spacing** (d_{hkl}). The interplanar spacing in *cubic* materials is given by the general equation

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}, \tag{3-7}$$

where a_0 is the lattice parameter and h, k, and l represent the Miller indices of the adjacent planes being considered. The interplanar spacings for non-cubic materials are given by more complex expressions.

Interstitial Sites

- ☐ Interstitial sites - Locations between the ‘‘normal’’ atoms or ions in a crystal into which another - usually different - atom or ion is placed. Typically, the size of this interstitial location is smaller than the atom or ion that is to be introduced.
- ☐ Cubic site - An interstitial position that has a coordination number of eight. An atom or ion in the cubic site touches eight other atoms or ions.
- ☐ Octahedral site - An interstitial position that has a coordination number of six. An atom or ion in the octahedral site touches six other atoms or ions.
- ☐ Tetrahedral site - An interstitial position that has a coordination number of four. An atom or ion in the tetrahedral site touches four other atoms or ions.

Interstitial Sites

In all crystal structures, there are small holes between the usual atoms into which smaller atoms may be placed. These locations are called **interstitial sites.**

An atom, when placed into an interstitial site, touches two or more atoms in the lattice. This interstitial atom has a coordination number equal to the number of atoms it touches. Figure 3-25 shows interstitial locations in the SC, BCC, and FCC structures. The **cubic site**, with a coordination number of eight, occurs in the SC structure at the body-centered position. **Octahedral sites** give a coordination number of six (not eight). They are known as octahedral sites because the atoms contacting the interstitial atom form an octahedron. **Tetrahedral sites** give a coordination number of four. As an example, the octahedral sites in BCC unit cells are located at the faces of the cube; a small atom placed in the octahedral site touches the four atoms at the corners of the face, the atom at the center of the unit cell, plus another atom at the center of the adjacent unit cell, giving a coordination number of six. In FCC unit cells, octahedral sites occur at the center of each edge of the cube, as well as at the body center of the unit cell.

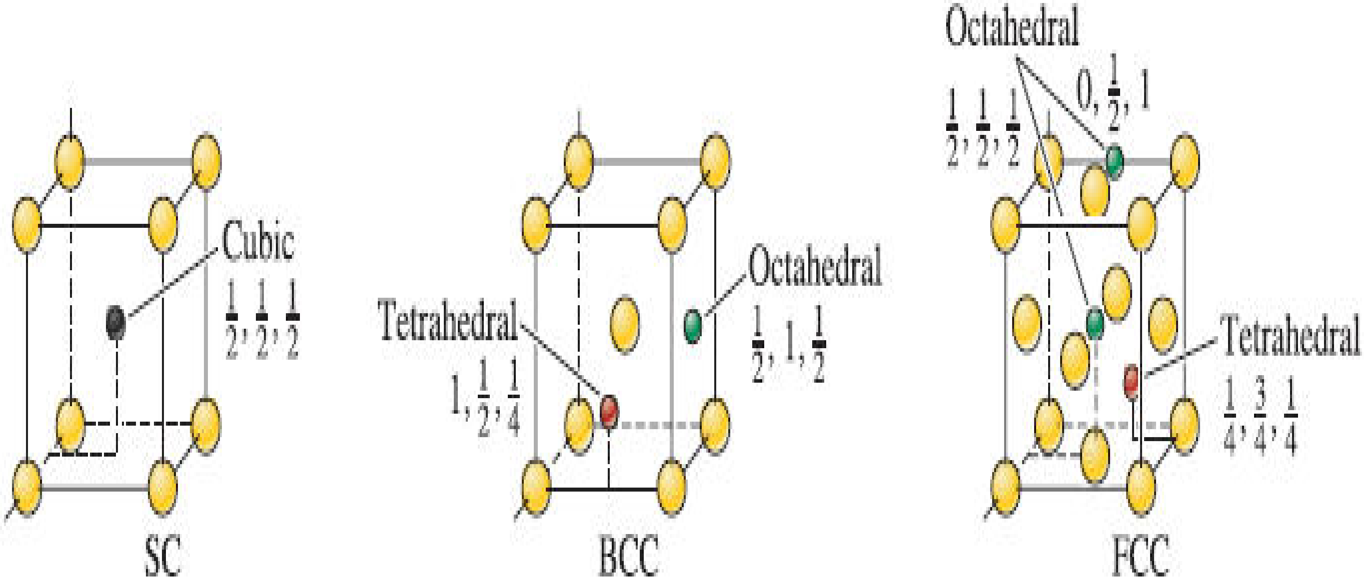


Figure 3-25 The location of the interstitial sites in cubic unit cells. Only representative sites are shown.

Example 3-12 *Calculating Octahedral Sites*

Calculate the number of octahedral sites that *uniquely* belong to one FCC unit cell.

SOLUTION

The octahedral sites include the twelve edges of the unit cell, with the coordinates

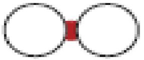
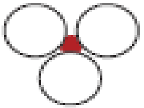
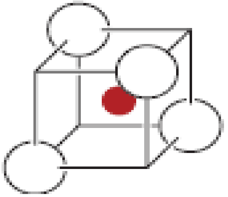
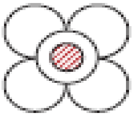
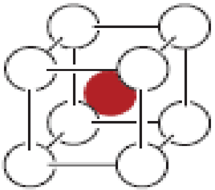
$$\begin{array}{cccc} \tfrac{1}{2},0,0 & \tfrac{1}{2},1,0 & \tfrac{1}{2},0,1 & \tfrac{1}{2},1,1 \\ 0,\tfrac{1}{2},0 & 1,\tfrac{1}{2},0 & 1,\tfrac{1}{2},1 & 0,\tfrac{1}{2},1 \\ 0,0,\tfrac{1}{2} & 1,0,\tfrac{1}{2} & 1,1,\tfrac{1}{2} & 0,1,\tfrac{1}{2} \end{array}$$

plus the center position, 1/2, 1/2, 1/2. Each of the sites on the edge of the unit cell is shared between four unit cells, so only 1/4 of each site belongs uniquely to each unit cell. Therefore, the number of sites belonging uniquely to each cell is

$$\frac{12 \text{ edges}}{\text{cell}} \cdot \frac{\frac{1}{4} \text{ site}}{\text{edge}} + \frac{1 \text{ body-center}}{\text{cell}} \cdot \frac{1 \text{ site}}{\text{body-center}} = 4 \text{ octahedral sites/cell}$$

Interstitial atoms or ions whose radii are slightly larger than the radius of the interstitial site may enter that site, pushing the surrounding atoms slightly apart. Atoms with radii smaller than the radius of the hole are not allowed to fit into the interstitial site because the ion would "rattle" around in the site. If the interstitial atom becomes too large, it prefers to enter a site having a larger coordination number (Table 3-6). Therefore,

TABLE 3-6 ■ ***The coordination number and the radius ratio***

Coordination Number	Location of Interstitial	Radius Ratio	Representation
2	Linear	0–0.155	
3	Center of triangle	0.155–0.225	
4	Center of tetrahedron	0.225–0.414	
6	Center of octahedron	0.414–0.732	
8	Center of cube	0.732–1.000	

an atom with a radius ratio between 0.225 and 0.414 enters a tetrahedral site; if its radius is somewhat larger than 0.414, it enters an octahedral site instead.

Many ionic crystals (see Section 3-7) can be viewed as being generated by close packing of larger anions. Cations then can be viewed as smaller ions that fit into the interstitial sites of the close-packed anions. Thus, the radius ratios described in Table 3-6 also apply to the ratios of the radius of the cation to that of the anion. The packing in ionic crystals is not as tight as that in FCC or HCP metals.

Sodium Chloride Structure The radius ratio for sodium and chloride ions is $r_{\mathrm{Na}^+}/r_{\mathrm{Cl}^-} = 0.097\ \mathrm{nm}/0.181\ \mathrm{nm} = 0.536$; the sodium ion has a charge of $+1$; the chloride ion has a charge of -1. Therefore, based on the charge balance and radius ratio, each anion and cation must have a coordination number of six. The FCC structure, with Cl^{-1} ions at FCC positions and Na^+ at the four octahedral sites, satisfies these requirements (Figure 3-26). We can also consider this structure to be FCC with two ions—one Na^{+1} and one Cl^{-1}—associated with each lattice point. Many ceramics, including magnesium oxide (MgO), calcium oxide (CaO), and iron oxide (FeO) have this structure.

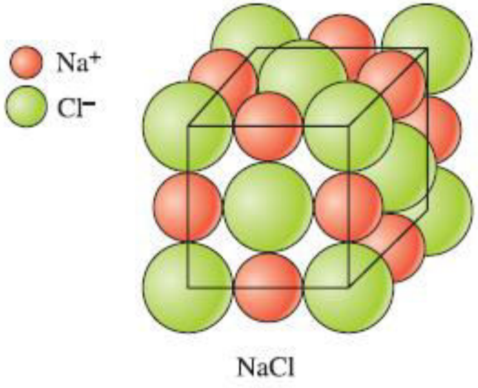


Figure 3-26
The sodium chloride structure, a FCC unit cell with two ions (Na^+ and Cl^-) per lattice point. *Note*: ion sizes not to scale.

Example 3-14 *Illustrating a Crystal Structure and Calculating Density*

Show that MgO has the sodium chloride crystal structure and calculate the density of MgO.

SOLUTION

From Appendix B, $r_{\mathrm{Mg}^{+2}} = 0.066$ nm and $r_{\mathrm{O}^{-2}} = 0.132$ nm, so

$$\frac{r_{\mathrm{Mg}^{+2}}}{r_{\mathrm{O}^{-2}}} = \frac{0.066}{0.132} = 0.50$$

Since $0.414 < 0.50 < 0.732$, the coordination number for each ion is six, and the sodium chloride structure is possible.

The atomic masses are 24.312 and 16.00 g/mol for magnesium and oxygen, respectively. The ions touch along the edge of the cube, so

$$a_0 = 2r_{\mathrm{Mg}^{+2}} + 2r_{\mathrm{O}^{-2}} = 2(0.066) + 2(0.132) = 0.396 \text{ nm} = 3.96 \times 10^{-8} \text{ cm}$$

$$\rho = \frac{(4\ \mathrm{Mg}^{+2})(24.312) + (4\ \mathrm{O}^{-2})(16.00)}{(3.96 \times 10^{-8}\ \mathrm{cm}^3)^3(6.022 \times 10^{23})} = 4.31 \text{ g/cm}^3$$

Diffraction Techniques for Crystal Structure Analysis

A crystal structure of a crystalline material can be analyzed using **x-ray diffraction (XRD)** or electron diffraction. Max von Laue (1879–1960) won the Nobel Prize in 1914 for his discovery related to the diffraction of x-rays by a crystal. William Henry Bragg (1862–1942) and his son William Lawrence Bragg (1890–1971) won the 1915 Nobel Prize for their contributions to XRD.

When a beam of x-rays having a single wavelength on the same order of magnitude as the atomic spacing in the material strikes that material, x-rays are scattered in all directions. Most of the radiation scattered from one atom cancels out radiation scattered from other atoms; however, x-rays that strike certain crystallographic planes at specific angles are reinforced rather than annihilated. This phenomenon is called **diffraction**. The x-rays are diffracted, or the beam is reinforced, when conditions satisfy **Bragg's law**,

$$\sin\theta = \frac{\lambda}{2d_{hkl}} \qquad (3\text{-}8)$$

where the angle θ is half the angle between the diffracted beam and the original beam direction, λ is the wavelength of the x-rays, and d_{hkl} is the interplanar spacing between the planes that cause constructive reinforcement of the beam (see Figure 3-36).

When the material is prepared in the form of a fine powder, there are always at least some powder particles (crystals or aggregates of crystals) with planes (hkl) oriented at the proper θ angle to satisfy Bragg's law. Therefore, a diffracted beam, making an angle of 2θ with the incident beam, is produced. In a *diffractometer*, a moving x-ray detector records the 2θ angles at which the beam is diffracted, giving a characteristic diffraction pattern (see Figure 3-37 on page 98). If we know the wavelength of the x-rays, we can determine the interplanar spacings and, eventually, the identity of the planes that cause the diffraction. In an XRD instrument, x-rays are produced by bombarding a metal target with a beam of high-energy electrons. Typically, x-rays emitted from copper have a wavelength $\lambda \cong 1.54060$ Å (K-α_1 line) and are used.

In the Laue method, which was the first diffraction method ever used, the specimen is in the form of a single crystal. A beam of "white radiation" consisting of x-rays of different wavelengths is used. Each diffracted beam has a different wavelength. In the transmission Laue method, photographic film is placed behind the crystal. In the

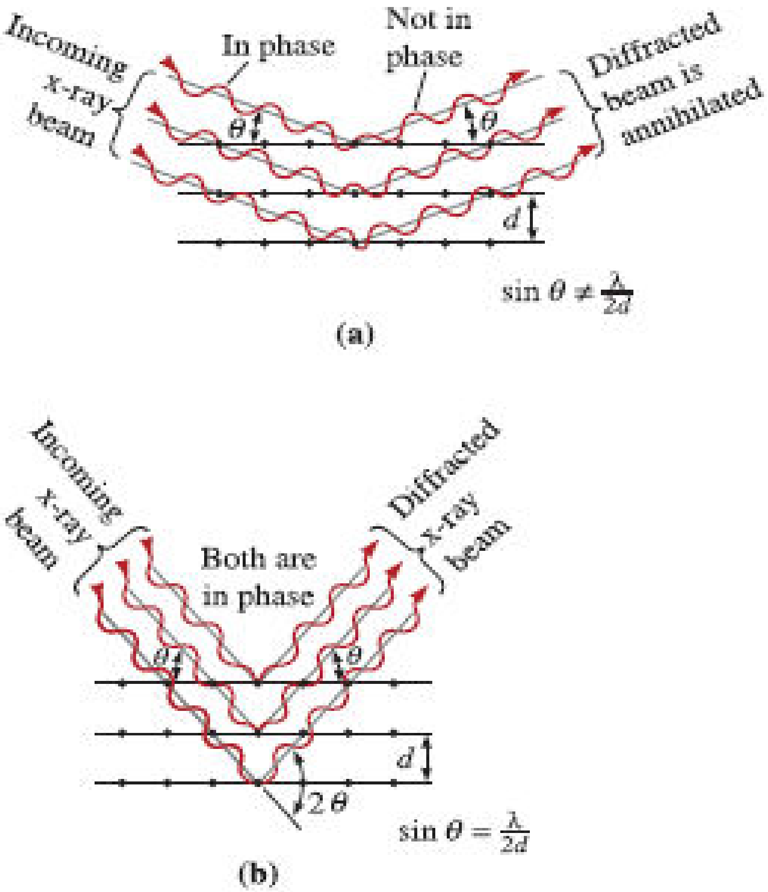


Figure 3-36
(a) Destructive and (b) reinforcing interactions between x-rays and the crystalline material. Reinforcement occurs at angles that satisfy Bragg's law.

back-reflection Laue method, the beams that are back diffracted are recorded on a film located between the source and sample. From the recorded diffraction patterns, the orientation and quality of the single crystal can be determined. It is also possible to determine the crystal structure using a rotating crystal and a fixed wavelength x-ray source.

Typically, XRD analysis can be conducted relatively rapidly (~30 minutes to 1 hour per sample), on bulk or powdered samples and without extensive sample preparation. This technique can also be used to determine whether the material consists of many grains oriented in a particular crystallographic direction (texture) in bulk materials and thin films. Typically, a well-trained technician can conduct the analysis as well as interpret the powder diffraction data rather easily. As a result, XRD is used in many industries as one tool for product quality control purposes. Analysis of single crystals and materials containing several phases can be more involved and time consuming.

To identify the crystal structure of a cubic material, we note the pattern of the diffracted lines—typically by creating a table of $\sin^2\theta$ values. By combining Equation 3-7 with Equation 3-8 for the interplanar spacing, we find that:

$$\sin^2\theta = \frac{\lambda^2}{4a_0^2}(h^2 + k^2 + l^2)$$

In simple cubic metals, all possible planes will diffract, giving an $h^2 + k^2 + l^2$ pattern of 1, 2, 3, 4, 5, 6, 8, ... In body-centered cubic metals, diffraction occurs only from planes having an even $h^2 + k^2 + l^2$ sum of 2, 4, 6, 8, 10, 12, 14, 16, ... For face-centered cubic metals, more destructive interference occurs, and planes having $h^2 + k^2 + l^2$ sums of 3, 4, 8, 11, 12, 16, . . . will diffract. By calculating the values of $\sin^2\theta$ and then finding the appropriate pattern, the crystal structure can be determined for metals having one of these simple structures, as illustrated in Example 3-20.

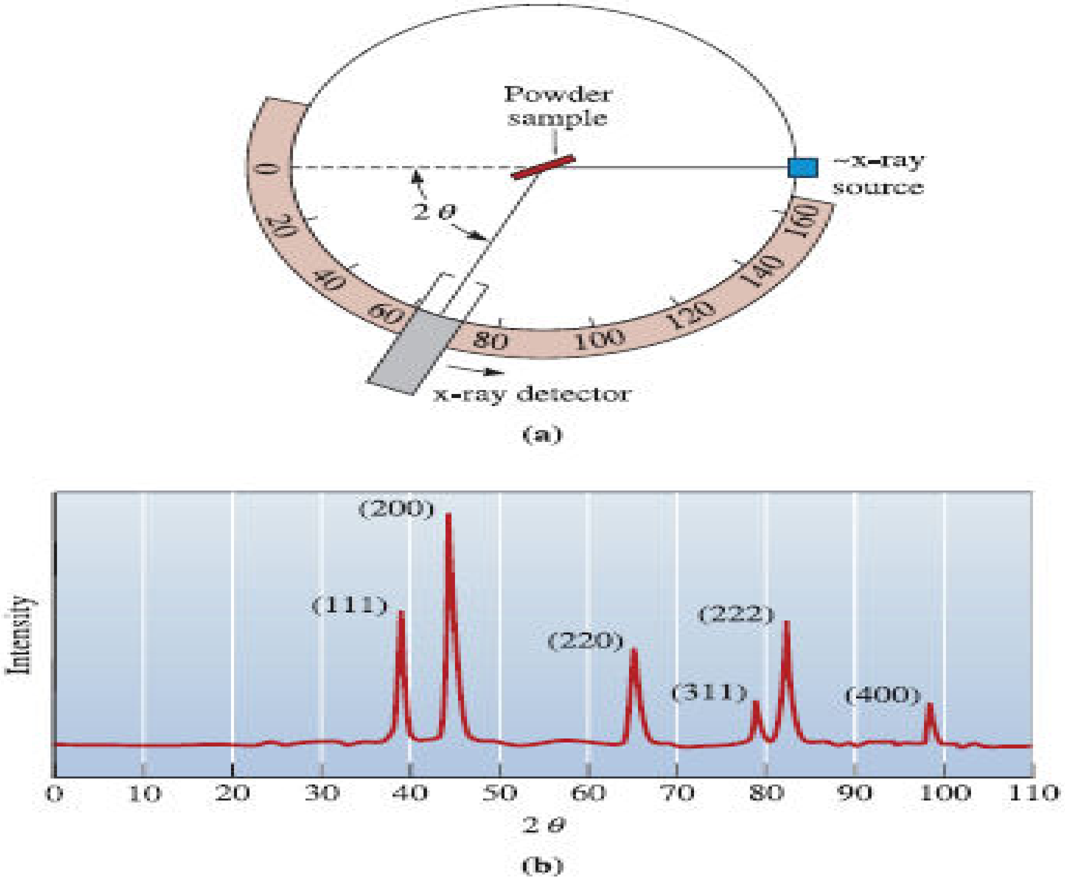


Figure 3-37 (a) Diagram of a diffractometer, showing powder sample, incident and diffracted beams. (b) The diffraction pattern obtained from a sample of gold powder.

Example 3-20 *Examining X-ray Diffraction Data*

The results of an x-ray diffraction experiment using x-rays with $\lambda = 0.7107$ Å (radiation obtained from a molybdenum (Mo) target) show that diffracted peaks occur at the following 2θ angles:

Peak	2θ (°)	Peak	2θ (°)
1	20.20	5	46.19
2	28.72	6	50.90
3	35.36	7	55.28
4	41.07	8	59.42

Determine the crystal structure, the indices of the plane producing each peak, and the lattice parameter of the material.

SOLUTION

We can first determine the $\sin^2\theta$ value for each peak, then divide through by the lowest denominator, 0.0308.

Peak	2θ(°)	$\sin^2\theta$	$\sin^2\theta/0.0308$	$h^2 + k^2 + l^2$	(hkl)
1	20.20	0.0308	1	2	(110)
2	28.72	0.0615	2	4	(200)
3	35.36	0.0922	3	6	(211)
4	41.07	0.1230	4	8	(220)
5	46.19	0.1539	5	10	(310)
6	50.90	0.1847	6	12	(222)
7	55.28	0.2152	7	14	(321)
8	59.42	0.2456	8	16	(400)

When we do this, we find a pattern of $\sin^2\theta/0.0308$ values of 1, 2, 3, 4, 5, 6, 7, and 8. If the material were simple cubic, the 7 would not be present, because no planes have an $h^2 + k^2 + l^2$ value of 7. Therefore, the pattern must really be 2, 4, 6, 8, 10, 12, 14, 16, . . . and the material must be body-centered cubic. The (hkl) values listed give these required $h^2 + k^2 + l^2$ values.

We could then use 2θ values for any of the peaks to calculate the interplanar spacing and thus the lattice parameter. Picking peak 8:

$$2\theta = 59.42^\circ \quad \text{or} \quad \theta = 29.71^\circ$$

$$d_{400} = \frac{\lambda}{2\sin\theta} = \frac{0.7107}{2\sin(29.71)} = 0.71699 \text{ Å}$$

$$a_0 = d_{400}\sqrt{h^2 + k^2 + l^2} = (0.71699)(4) = 2.868 \text{ Å}$$

This is the lattice parameter for body-centered cubic iron.

Electron Diffraction and Microscopy

Louis de Broglie theorized that electrons behave like waves. In electron diffraction, we make use of high-energy (~100,000 to 400,000 eV) electrons. These electrons are diffracted from electron transparent samples of materials. The electron beam that exits from the sample is also used to form an image of the sample. Thus, transmission electron microscopy and electron diffraction are used for imaging microstructural features and determining crystal structures.

A 100,000 eV electron has a wavelength of about 0.004 nm! This ultra-small wavelength of high-energy electrons allows a **transmission electron microscope** (TEM) to simultaneously image the microstructure at a very fine scale. If the sample is too thick, electrons cannot be transmitted through the sample and an image or a diffraction pattern will not be observed. Therefore, in transmission electron microscopy and electron diffraction, the sample has to be made such that portions of it are electron transparent. A transmission electron microscope is the instrument used for this purpose. Figure 3-38 shows a TEM image and an electron diffraction pattern from an area of the sample. The large bright spots correspond to the grains of the matrix. The smaller spots originate from small crystals of another phase.

Another advantage to using a TEM is the high spatial resolution. Using TEM, it is possible to determine differences between different crystalline regions and between

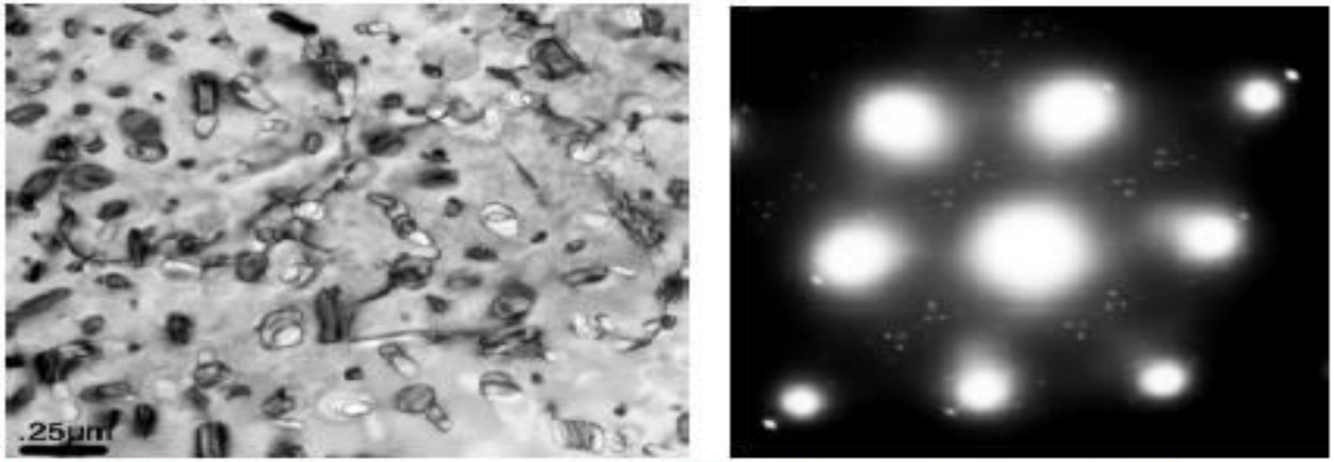


Figure 3-38 A TEM micrograph of an aluminum alloy (Al-7055) sample. The diffraction pattern at the right shows large bright spots that represent diffraction from the main aluminum matrix grains. The smaller spots originate from the nanoscale crystals of another compound that is present in the aluminum alloy. (*Courtesy of Dr. Jörg M.K. Wiezorek, University of Pittsburgh.*)

amorphous and crystalline regions at very small length scales (~1–10 nm). This analytical technique and its variations (e.g., high-resolution electron microscopy (HREM), scanning transmission electron microscopy (STEM), etc.) are also used to determine the orientation of different grains and other microstructural features discussed in later chapters. Advanced and specialized features associated with TEM also allow chemical mapping of elements in a given material. Some of the disadvantages associated with TEM include

(a) the time consuming preparation of samples that are almost transparent to the electron beam;

(b) considerable amount of time and skill are required for analysis of the data from a thin, three-dimensional sample, that is represented in a two-dimensional image and diffraction pattern;

(c) only a very small volume of the sample is examined; and

(d) the equipment is relatively expensive and requires great care in use.

In general, TEM has become a widely used and accepted research method for analysis of microstructural features at micro- and nano-length scales.