Lecture 5

Atomic And Ionic Arrangements

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Close-Packed Planes and Directions In examining the relationship between atomic radius and lattice parameter, we looked for close-packed directions, where atoms are in continuous contact. We can now assign Miller indices to these close-packed directions, as shown in Table 3-5.

We can also examine FCC and HCP unit cells more closely and discover that there is at least one set of close-packed planes in each. Close-packed planes are shown in Figure 3-23. Notice that a hexagonal arrangement of atoms is produced in two dimensions.

The close-packed planes are easy to find in the HCP unit cell; they are the (0001) and (0002) planes of the HCP structure and are given the special name **basal planes. In fact, we can build up an HCP unit cell by stacking together close-packed planes** in an . . . *ABABAB . . .* ***stacking sequence (Figure 3-23). Atoms on plane B, the (0002)*** plane, fit into the valleys between atoms on plane *A, the bottom (0001) plane. If another* plane identical in orientation to plane *A is placed in the valleys of plane B directly above* plane *A, the HCP structure is created. Notice that all of the possible close-packed planes* are parallel to one another. Only the basal planes—(0001) and (0002)—are close-packed.

TABLE 3-5 ■ ***Close-packed planes and directions***

Structure	Directions	Planes
SC	⟨100⟩	None
BCC	⟨111⟩	None
FCC	⟨110⟩	{111}
HCP	⟨100⟩, ⟨110⟩ or ⟨11$\bar{2}$0⟩	(0001), (0002)

From Figure 3-23, we find the coordination number of the atoms in the HCP structure. The center atom in a basal plane touches six other atoms in the same plane. Three atoms in a lower plane and three atoms in an upper plane also touch the same atom. The coordination number is twelve.

In the FCC structure, close-packed planes are of the form {111} (Figure 3-24). When parallel (111) planes are stacked, atoms in plane *B* fit over valleys in plane *A* and atoms in plane *C* fit over valleys in both planes *A* and *B*. The fourth plane fits directly over atoms in plane *A*. Consequently, a stacking sequence . . . *ABCABCABC* . . . is produced using the (111) plane. Again, we find that each atom has a coordination number of twelve.

Unlike the HCP unit cell, there are four sets of nonparallel close-packed planes—(111), $(11\bar{1})$, $(1\bar{1}1)$, and $(\bar{1}11)$—in the FCC cell. This difference between the FCC and HCP unit cells—the presence or absence of intersecting close-packed planes—affects the mechanical behavior of metals with these structures.

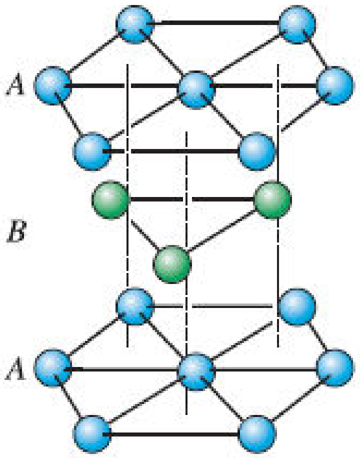

Figure 3-23
The *ABABAB* stacking sequence of close-packed planes produces the HCP structure.

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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

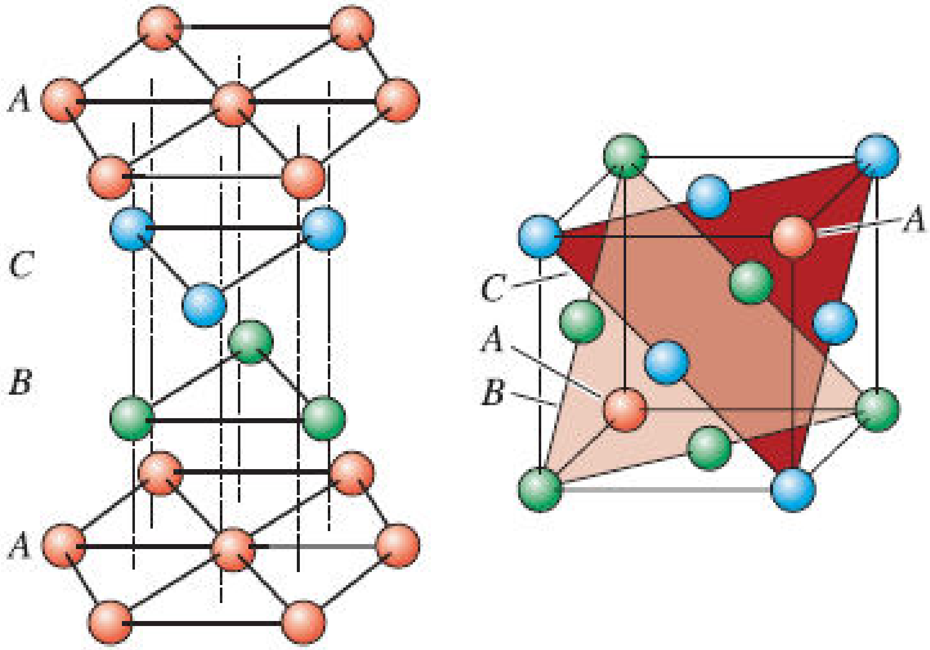


Figure 3-24
The *ABCABCABC* stacking sequence of close-packed planes produces the FCC structure.

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

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.

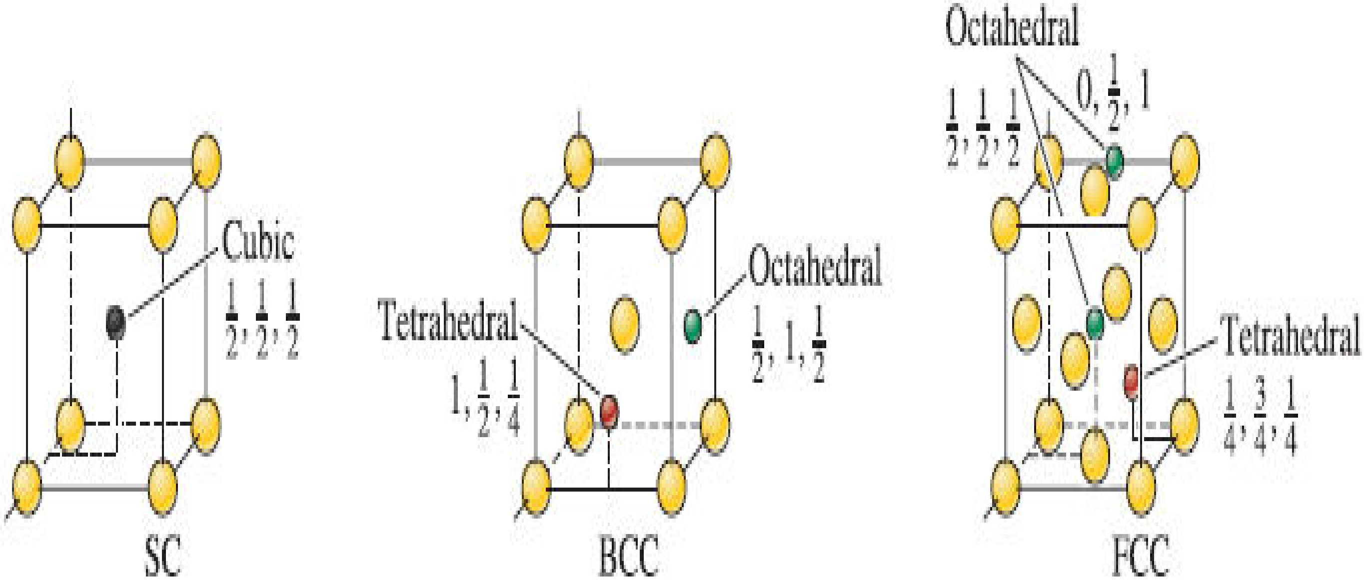


Figure 3-25 The location of the interstitial sites in cubic unit cells. Only representative sites are shown.

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

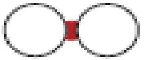
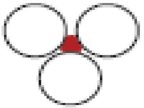
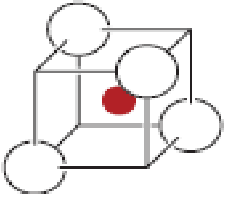
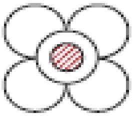
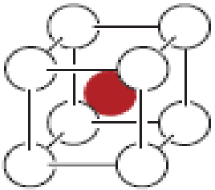
$$\begin{array}{cccc}
\tfrac{1}{2},0,0 & \tfrac{1}{2},1,0 & \tfrac{1}{2},0,1 & \tfrac{1}{2},1,1 \\
0,\tfrac{1}{2},0 & 1,\tfrac{1}{2},0 & 1,\tfrac{1}{2},1 & 0,\tfrac{1}{2},1 \\
0,0,\tfrac{1}{2} & 1,0,\tfrac{1}{2} & 1,1,\tfrac{1}{2} & 0,1,\tfrac{1}{2}
\end{array}$$

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

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

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 $r_{Na^+}/r_{Cl^-} = 0.097 \text{ nm}/0.181 \text{ nm} = 0.536$; 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.

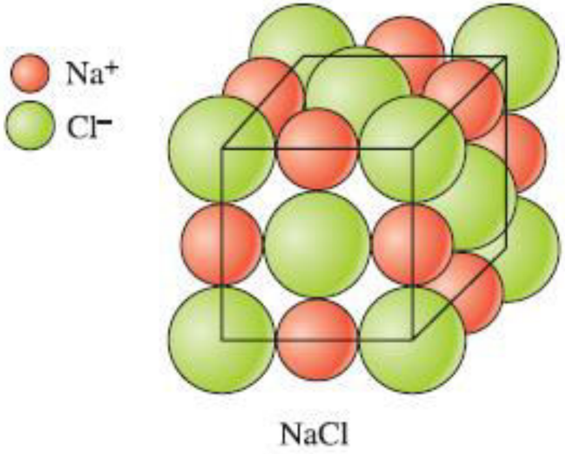


Figure 3-26
The sodium chloride structure, a FCC unit cell with two ions (Na^+ and Cl^-) per lattice point. *Note*: ion sizes not to scale.

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, $r_{Mg^{+2}} = 0.066$ nm and $r_{O^{-2}} = 0.132$ nm, so

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

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

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

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

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**,

$$\sin\theta = \frac{\lambda}{2d_{hkl}} \tag{3-8}$$

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

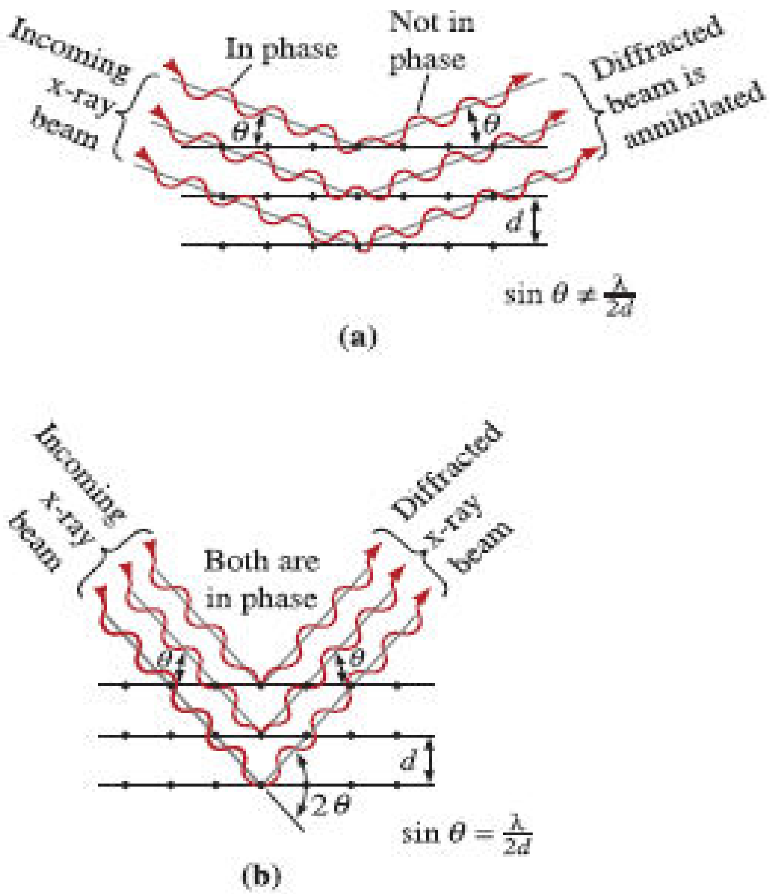


Figure 3-36
(a) Destructive and (b) reinforcing interactions between x-rays and the crystalline material. Reinforcement occurs at angles that satisfy Bragg's law.

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.

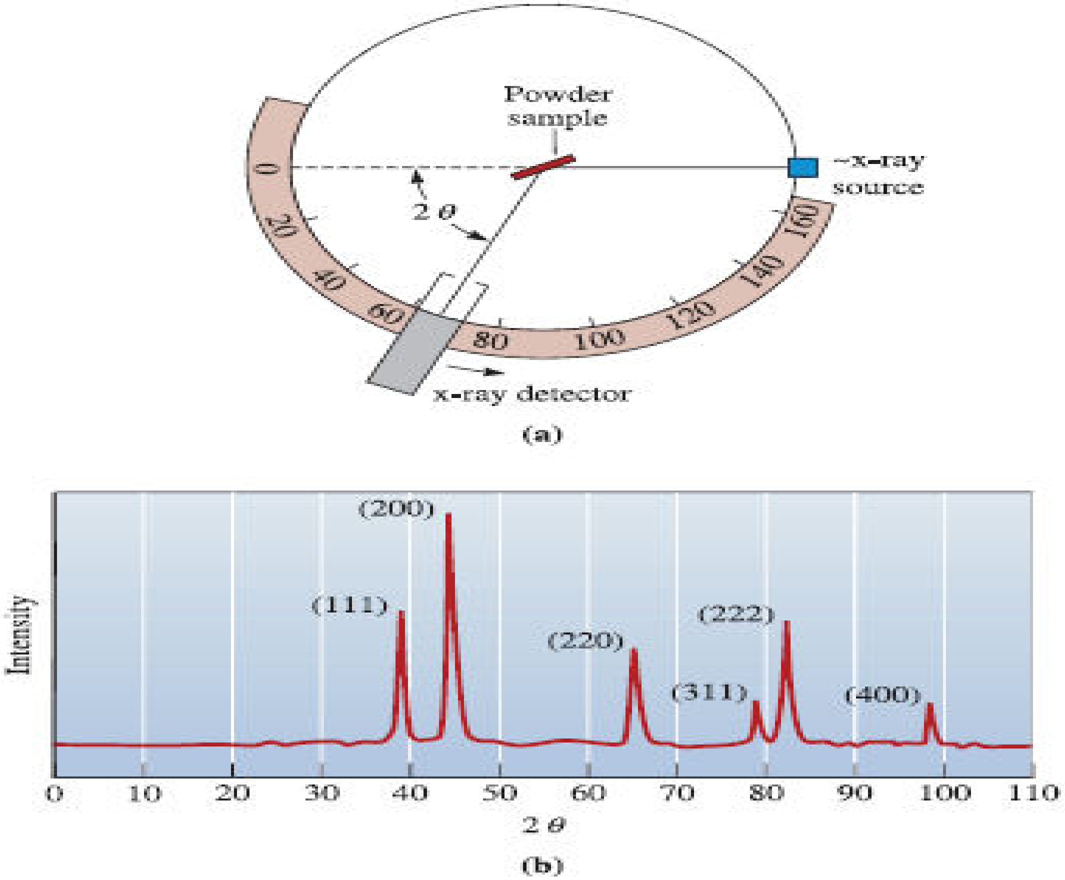


Figure 3-37 (a) Diagram of a diffractometer, showing powder sample, incident and diffracted beams. (b) The diffraction pattern obtained from a sample of gold powder.

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

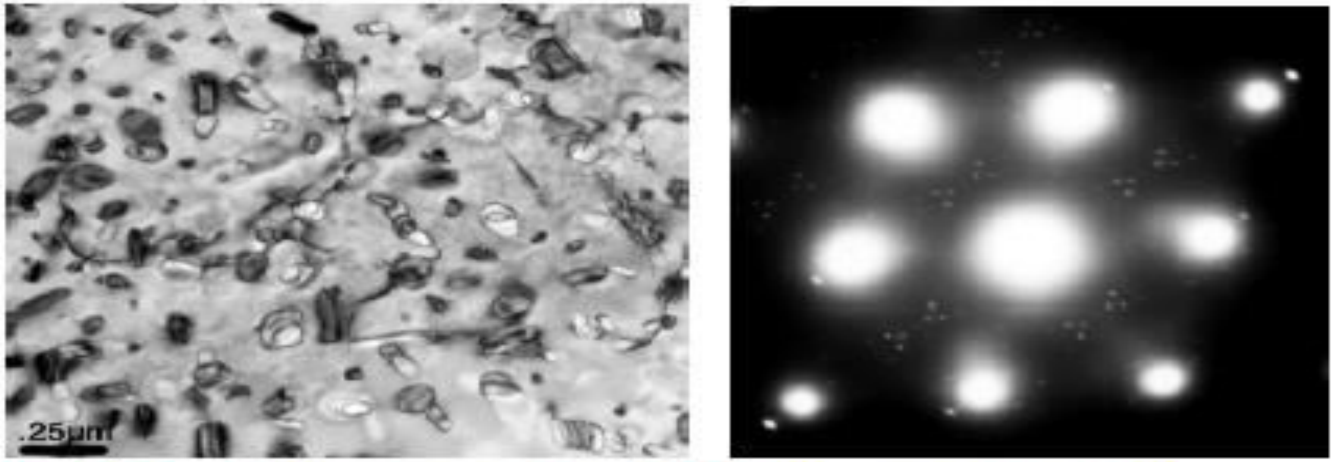


Figure 3-38 A TEM micrograph of an aluminum alloy (Al-7055) sample. The diffraction pattern at the right shows large bright spots that represent diffraction from the main aluminum matrix grains. The smaller spots originate from the nanoscale crystals of another compound that is present in the aluminum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

Thank you for your attention