

Linear and planar densities are important considerations relative to the process of slip—that is, the mechanism by which metals plastically deform (Section 7.4). Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing.

3.11 CLOSE-PACKED CRYSTAL STRUCTURES

It may be remembered from the discussion on metallic crystal structures that both face-centered cubic and hexagonal close-packed crystal structures have atomic packing factors of 0.74, which is the most efficient packing of equal-sized spheres or atoms. In addition to unit cell representations, these two crystal structures may be described in terms of close-packed planes of atoms (i.e., planes having a maximum atom or sphere-packing density); a portion of one such plane is illustrated in Figure 3.12*a*. Both crystal structures may be generated by the stacking of these close-packed planes on top of one another; the difference between the two structures lies in the stacking sequence.

Let the centers of all the atoms in one close-packed plane be labeled *A*. Associated with this plane are two sets of equivalent triangular depressions formed by three adjacent atoms, into which the next close-packed plane of atoms may rest. Those having the triangle vertex pointing up are arbitrarily designated as *B* positions, while the remaining depressions are those with the down vertices, which are marked *C* in Figure 3.12*a*.

A second close-packed plane may be positioned with the centers of its atoms over either *B* or *C* sites; at this point both are equivalent. Suppose that the *B* positions are arbitrarily chosen; the stacking sequence is termed *AB*, which is illustrated in Figure 3.12*b*. The real distinction between FCC and HCP lies in where the third close-packed layer is positioned. For HCP, the centers of this layer are aligned directly above the original *A* positions. This stacking sequence, *ABABAB* . . . , is repeated over and over. Of course, the *ACACAC* . . . arrangement would

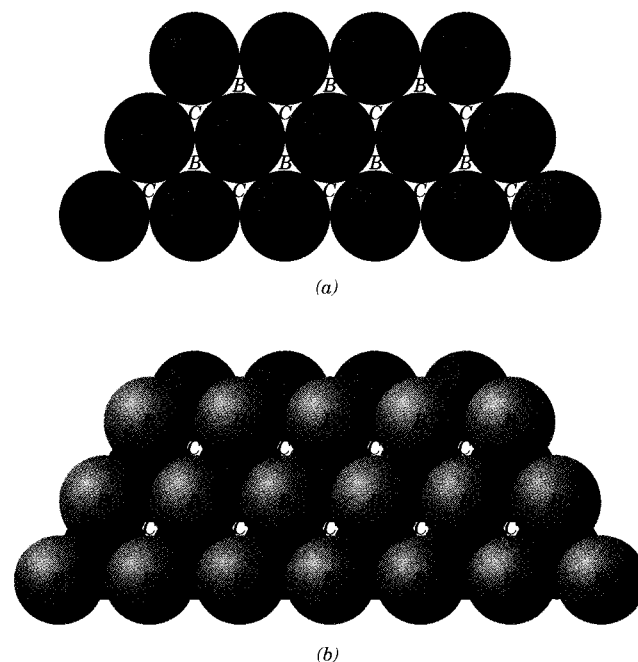


FIGURE 3.12 (a) A portion of a close-packed plane of atoms; *A*, *B*, and *C* positions are indicated. (b) The *AB* stacking sequence for close-packed atomic planes. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 50. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

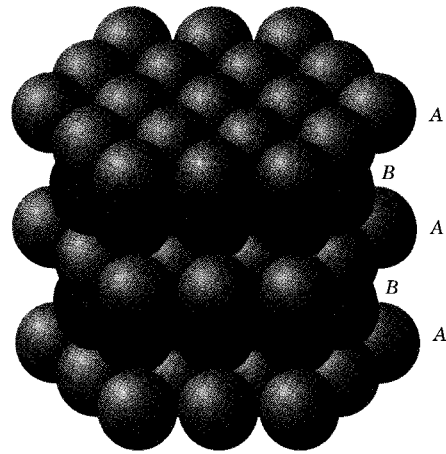


FIGURE 3.13 Close-packed plane stacking sequence for hexagonal close-packed. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

be equivalent. These close-packed planes for HCP are (0001)-type planes, and the correspondence between this and the unit cell representation is shown in Figure 3.13.

For the face-centered crystal structure, the centers of the third plane are situated over the *C* sites of the first plane (Figure 3.14*a*). This yields an *ABCABCABC* . . . stacking sequence; that is, the atomic alignment repeats every third plane. It is more difficult to correlate the stacking of close-packed planes to the FCC unit cell. However, this relationship is demonstrated in Figure 3.14*b*; these planes are of the (111) type. The significance of these FCC and HCP close-packed planes will become apparent in Chapter 7.

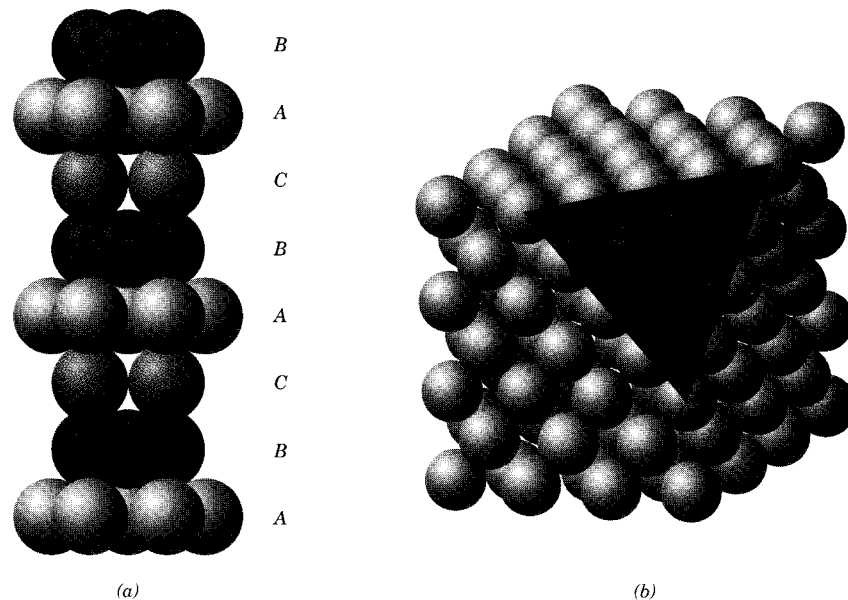


FIGURE 3.14 (a) Close-packed stacking sequence for face-centered cubic. (b) A corner has been removed to show the relation between the stacking of close-packed planes of atoms and the FCC crystal structure; the heavy triangle outlines a (111) plane. (Figure (b) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

The concepts detailed in the previous four sections also relate to crystalline ceramic and polymeric materials, which are discussed in Chapters 13 and 15. That is to say that we may specify crystallographic planes and directions in terms of directional and Miller indices; furthermore, on occasion it is important to ascertain the atomic and ionic arrangements of particular crystallographic planes. Also, the crystal structures of a number of ceramic materials may be generated by the stacking of close-packed planes of ions (Section 13.2).

CRYSTALLINE AND NONCRYSTALLINE MATERIALS

3.12 SINGLE CRYSTALS

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal**. All unit cells interlock in the same way and have the same orientation. Single crystals exist in nature, but they may also be produced artificially. They are ordinarily difficult to grow, because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces, as with some of the gem stones; the shape is indicative of the crystal structure. A photograph of several single crystals is shown in Figure 3.15. Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

3.13 POLYCRYSTALLINE MATERIALS

Most crystalline solids are composed of a collection of many small crystals or **grains**; such materials are termed **polycrystalline**. Various stages in the solidification of a polycrystalline specimen are represented schematically in Figure 3.16. Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremi-



FIGURE 3.15 Photograph showing several single crystals of fluorite, CaF_2 . (Smithsonian Institution photograph number 38181P.)

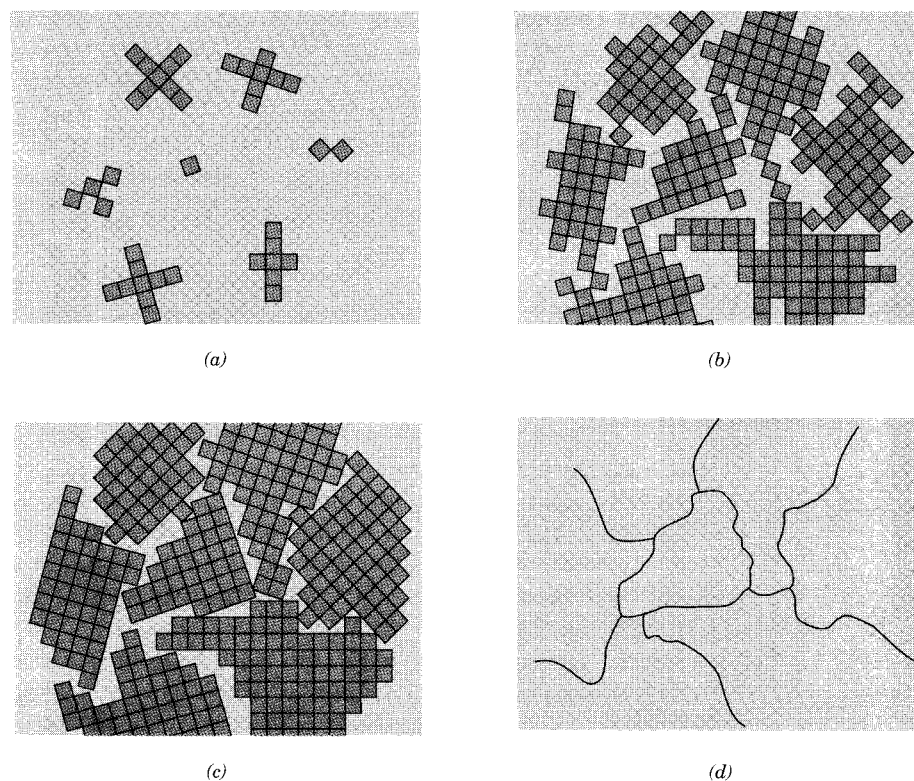


FIGURE 3.16 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (a) Small crystallite nuclei. (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed. (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy*, 2nd edition, Constable & Company Ltd., London, 1915.)

ties of adjacent grains impinge on one another as the solidification process approaches completion. As indicated in Figure 3.16, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary**, is discussed in more detail in Section 4.5.

3.14 ANISOTROPY

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed **anisotropy**, and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are **isotropic**. The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic. The modulus of elasticity

Table 3.3 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

<i>Metal</i>	<i>Modulus of Elasticity (GPa)</i>		
	<i>[100]</i>	<i>[110]</i>	<i>[111]</i>
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

values at [100], [110], and [111] orientations for several materials are presented in Table 3.3.

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random. Under these circumstances, even though each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically. Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a “texture.”

3.15 X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

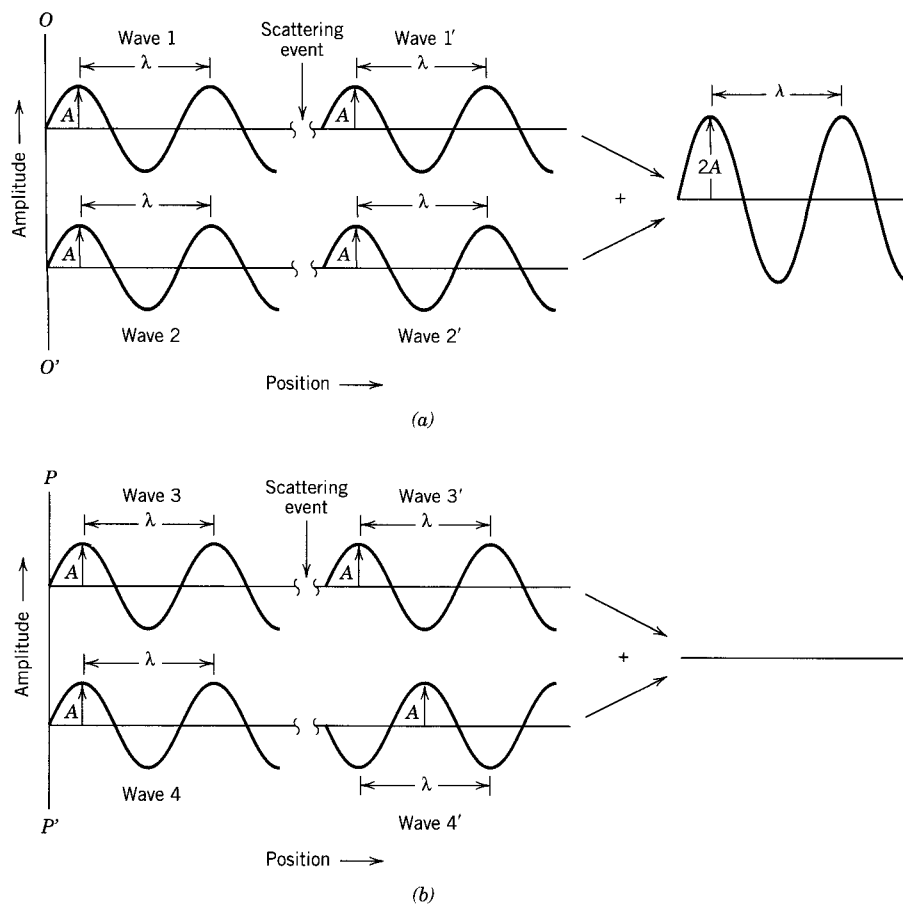
Historically much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials. A brief overview of the diffraction phenomenon and how, using x-rays, atomic interplanar distances and crystal structures are deduced will now be given.

THE DIFFRACTION PHENOMENON

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave, and (2) have spacings that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships that are established between two or more waves that have been scattered by the obstacles.

Consider waves 1 and 2 in Figure 3.17a, which have the same wavelength (λ) and are in phase at point $O-O'$. Now let us suppose that both waves are scattered in such a way that they traverse different paths. The phase relationship between the scattered waves, which will depend upon the difference in path length, is important. One possibility results when this path length difference is an integral number of wavelengths. As noted in Figure 3.17a, these scattered waves (now labeled 1' and 2') are still in phase. They are said to mutually reinforce (or constructively interfere with) one another; and, when amplitudes are added, the wave shown on the right side of the figure results. This is a manifestation of **diffraction**, and we refer to a diffracted beam as one composed of a large number of scattered waves that mutually reinforce one another.

FIGURE 3.17 (a) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength λ and remain in phase after a scattering event (waves 1' and 2') constructively interfere with one another. The amplitudes of the scattered waves add together in the resultant wave. (b) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3' and 4') destructively interfere with one another. The amplitudes of the two scattered waves cancel one another.



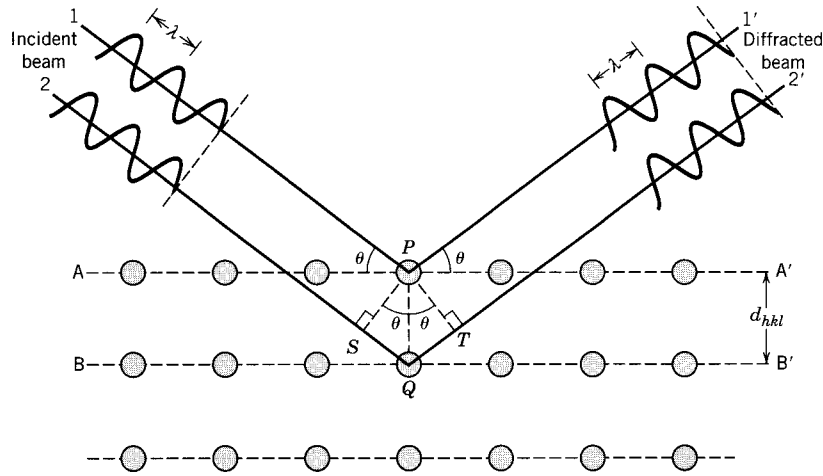
Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is that demonstrated in Figure 3.17b, wherein the path length difference after scattering is some integral number of *half* wavelengths. The scattered waves are out of phase—that is, corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the resultant wave has zero amplitude), as indicated on the extreme right side of the figure. Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

X-RAY DIFFRACTION AND BRAGG'S LAW

X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids. When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

Consider the two parallel planes of atoms A–A' and B–B' in Figure 3.18, which have the same h , k , and l Miller indices and are separated by the interplanar spacing d_{hkl} . Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle θ . Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q . Constructive

FIGURE 3.18
Diffraction of x-rays
by planes of atoms
(A-A' and B-B').



interference of the scattered rays 1' and 2' occurs also at an angle θ to the planes, if the path length difference between 1-P-1' and 2-Q-2' (i.e., $\overline{SQ} + \overline{QT}$) is equal to a whole number, n , of wavelengths. That is, the condition for diffraction is

$$n\lambda = \overline{SQ} + \overline{QT} \quad (3.8)$$

or

$$n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta = 2d_{hkl} \sin \theta \quad (3.9)$$

Equation 3.9 is known as **Bragg's law**; also, n is the order of reflection, which may be any integer (1, 2, 3, . . .) consistent with $\sin \theta$ not exceeding unity. Thus, we have a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg's law is not satisfied, then the interference will be nonconstructive in nature so as to yield a very low-intensity diffracted beam.

The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing d_{hkl}) is a function of the Miller indices (h , k , and l) as well as the lattice parameter(s). For example, for crystal structures having cubic symmetry,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.10)$$

in which a is the lattice parameter (unit cell edge length). Relationships similar to Equation 3.10, but more complex, exist for the other six crystal systems noted in Table 3.2.

Bragg's law, Equation 3.9, is a necessary but not sufficient condition for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams that, according to Equation 3.9, should be present. For example, for the BCC crystal structure, $h + k + l$ must be even if diffraction is to occur, whereas for FCC, h , k , and l must all be either odd or even.

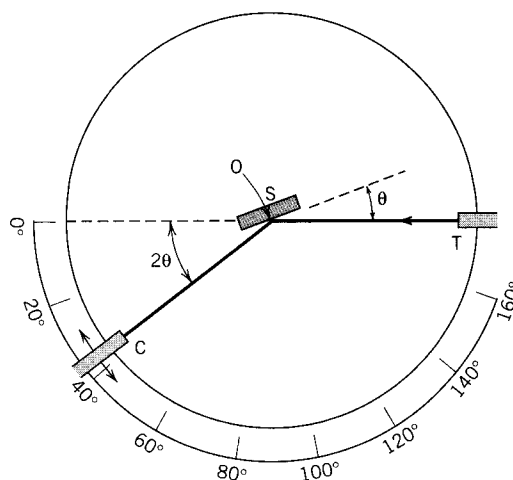


FIGURE 3.19 Schematic diagram of an x-ray diffractometer; T = x-ray source, S = specimen, C = detector, and O = the axis around which the specimen and detector rotate.

DIFFRACTION TECHNIQUES

One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation. Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

The *diffractometer* is an apparatus used to determine the angles at which diffraction occurs for powdered specimens; its features are represented schematically in Figure 3.19. A specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible; this axis is perpendicular to the plane of the page. The monochromatic x-ray beam is generated at point T, and the intensities of diffracted beams are detected with a counter labeled C in the figure. The specimen, x-ray source, and counter are all coplanar.

The counter is mounted on a movable carriage that may also be rotated about the O axis; its angular position in terms of 2θ is marked on a graduated scale.² Carriage and specimen are mechanically coupled such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter; this assures that the incident and reflection angles are maintained equal to one another (Figure 3.19). Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam.

As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of 2θ ; 2θ is termed the *diffraction angle*, which is measured experimentally. Figure 3.20 shows a diffraction pattern for a polycrystalline specimen of iron. The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes. These peaks are plane-indexed in the figure.

Other powder techniques have been devised wherein diffracted beam intensity

² It should be pointed out that the symbol θ has been used in two different contexts for this discussion. Here, θ represents the angular locations of both x-ray source and counter relative to the specimen surface. Previously (e.g., Equation 3.9), it denoted the angle at which the Bragg criterion for diffraction is satisfied.

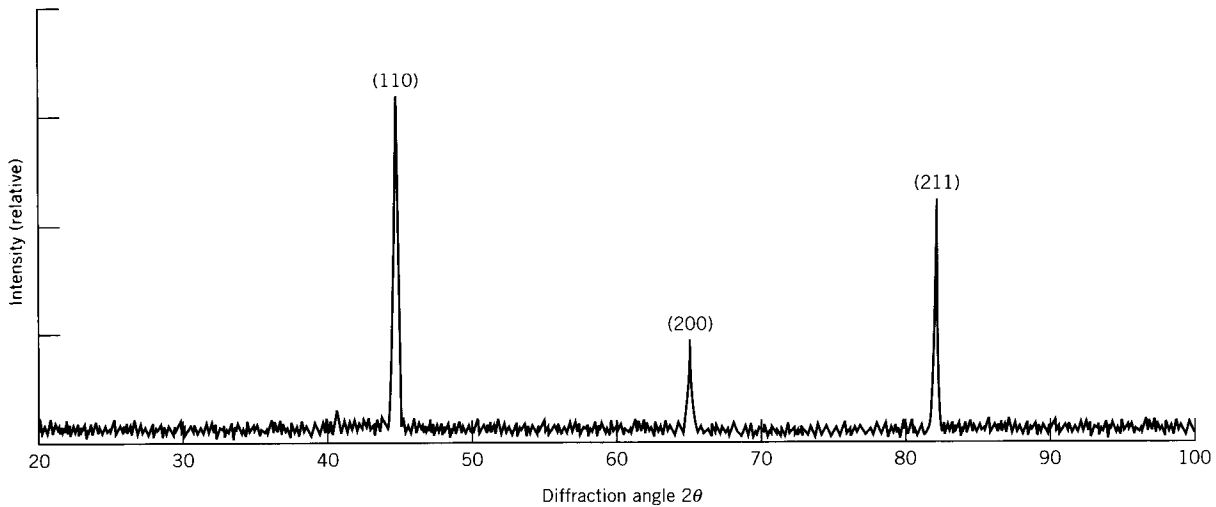


FIGURE 3.20 Diffraction pattern for polycrystalline α -iron.

and position are recorded on a photographic film instead of being measured by a counter.

One of the primary uses of x-ray diffractometry is for the determination of crystal structure. The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks, whereas arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

X-rays, as well as electron and neutron beams, are also used in other types of material investigations. For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs. On page 30 is shown a photograph that was generated using an incident electron beam that was directed on a gallium arsenide crystal; each spot (with the exception of the brightest one near the center) resulted from an electron beam that was diffracted by a specific set of crystallographic planes. Other uses of x-rays include qualitative and quantitative chemical identifications, and the determination of residual stresses and crystal size.

EXAMPLE PROBLEM 3.10

For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm (2.866 Å). Also, assume that monochromatic radiation having a wavelength of 0.1790 nm (1.790 Å) is used, and the order of reflection is 1.

SOLUTION

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.10, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$, since we are considering the (220) planes. Therefore,

$$\begin{aligned} d_{hkl} &= \frac{a}{\sqrt{h^2 + k^2 + l^2}} \\ &= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm (1.013 \AA)} \end{aligned}$$

(b) The value of θ may now be computed using Equation 3.9, with $n = 1$, since this is a first-order reflection:

$$\sin \theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790 \text{ nm})}{(2)(0.1013 \text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13^\circ$$

The diffraction angle is 2θ , or

$$2\theta = (2)(62.13^\circ) = 124.26^\circ$$

3.16 NONCRYSTALLINE SOLIDS

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally without form), or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide (SiO_2), which may exist in both states. Figures 3.21a and 3.21b present two-dimensional schematic diagrams for both structures of SiO_2 . Even though each silicon ion bonds to three oxygen ions for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Furthermore, rapidly cooling through the freezing temperature favors the formation of a noncrystalline solid, since little time is allowed for the ordering process.

Metals normally form crystalline solids; but some ceramic materials are crystalline, whereas others, the inorganic glasses, are amorphous. Polymers may be completely crystalline, entirely noncrystalline, or a mixture of the two. More about

FIGURE 3.21 Two-dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide.

