

X-Rays and Diffraction

1.1. X-RAYS

X-rays are high-energy electromagnetic radiation. They have energies ranging from about 200 eV to 1 MeV, which puts them between γ -rays and ultraviolet (UV) radiation in the electromagnetic spectrum. It is important to realize that there are no sharp boundaries between different regions of the electromagnetic spectrum and that the assigned boundaries between regions are arbitrary. Gamma rays and x-rays are essentially

The Electron Volt

Materials scientists and physicists often use the electron volt (eV) as the unit of energy. An electron volt is the amount of energy an electron picks up when it moves between a potential (voltage) difference of 1 volt. Thus,

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \quad (\text{the charge on an electron}) \times 1 \text{ V} = 1.602 \times 10^{-19} \text{ J}$$

Although the eV has been superseded by the joule (J)—the SI unit of energy—the eV is a very convenient unit when atomic-level processes are being represented. For example, the ground-state energy of an electron in a hydrogen atom is -13.6 eV ; to form a vacancy in an aluminum crystal requires 0.76 eV . The eV is used almost exclusively to represent electron energies in electron microscopy. The conversion factor between eV and J is $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$. Most texts on materials characterization techniques use the electron volt, so you should familiarize yourself with this unit.

The Ångström

The ångström (Å) is a unit of length equal to 10^{-10} m. The ångström was widely used as a unit of wavelength for electromagnetic radiation covering the visible part of the electromagnetic spectrum and x-rays. This unit is also used for interatomic spacings, since these distances then have single-digit values. Although the ångström has been superseded in SI units by the nanometer ($1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{ Å}$), many crystallographers and microscopists still prefer the older unit. Once again, it is necessary for you to become familiar with both units. Throughout this text (except in Experimental Module 8) we use the nanometer.

identical, γ -rays being somewhat more energetic and shorter in wavelength than x-rays. Gamma-rays and x-rays differ mainly in how they are produced in the atom. As we shall see presently, x-rays are produced by interactions between an external beam of electrons and the electrons in

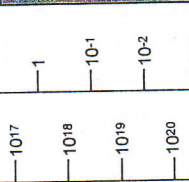
$h\nu$ [eV]	ν [Hz]	λ [nm]	Radiation
1	10^{14}	10^3	infrared
10	10^{15}	10^2	visible
102	10^{16}	10	ultraviolet
103	10^{17}	1	
104	10^{18}	10^{-1}	
105	10^{19}	10^{-2}	
106	10^{20}	10^{-3}	
107	10^{21}	10^{-4}	
108	10^{22}	10^{-5}	

FIG. 1. Part of the electromagnetic spectrum. Note that the boundaries between regions are arbitrary. The usable range of x-ray wavelengths for x-ray diffraction studies is between 0.05 and 0.25 nm (only a small part of the total range of x-ray wavelengths).

the shells of an atom. On the other hand, γ -rays are produced by changes within the nucleus of the atom. A part of the electromagnetic spectrum is shown in Fig. 1.

Each quantum of electromagnetic radiation, or *photon*, has an energy, E , which is proportional to its frequency, ν :

$$E = h\nu \quad (1)$$

The constant of proportionality is Planck's constant h , which has a value of $4.136 \times 10^{-15} \text{ eV}\cdot\text{s}$ (or $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$). Since the frequency is related to the wavelength, λ , through the speed of light, c , the wavelength of the x-rays can be written as

$$\lambda = \frac{hc}{E} \quad (2)$$

where c is $2.998 \times 10^8 \text{ m/s}$. So, using the energies given at the beginning of this section, we can see that x-ray wavelengths vary from about 10 nm to 1 pm. Notice that the wavelength is shorter for higher energies. The useful range of wavelengths for x-ray diffraction studies is between 0.05 and 0.25 nm. You may recall that interatomic spacings in crystals are typically about 0.2 nm (2 Å).

1.2. THE PRODUCTION OF X-RAYS

X-rays are produced in an x-ray tube consisting of two metal electrodes enclosed in a vacuum chamber, as shown in cross section in Fig. 2. Electrons are produced by heating a tungsten filament cathode. The cathode is at a high negative potential, and the electrons are accelerated toward the anode, which is normally at ground potential. The electrons, which have a very high velocity, collide with the water-cooled anode. The loss of energy of the electrons due to the impact with the metal anode is manifested as x-rays. Actually only a small percentage (less than 1%) of the electron beam is converted to x-rays; the majority is dissipated as heat in the water-cooled metal anode.

A typical x-ray spectrum, in this case for molybdenum, is shown in Fig. 3. As you can see, the spectrum consists of a range of wavelengths. For each accelerating potential a continuous x-ray spectrum (also known as the white spectrum), made up of many different wavelengths, is obtained. The continuous spectrum is due to electrons losing their energy in a series of collisions with the atoms that make up the target, as shown in Fig. 4. Because each electron loses its energy in a different way, a continuous spectrum of energies and, hence, x-ray wavelengths is pro-

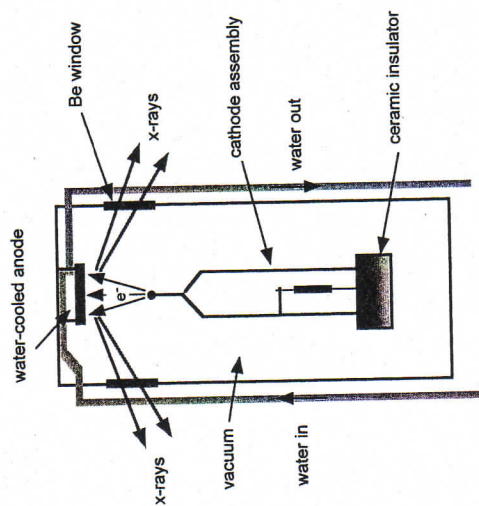


FIG. 2. Schematic showing the essential components of a modern x-ray tube. Beryllium is used for the window because it is highly transparent to x-rays.

duced. We don't normally use the continuous part of the x-ray spectrum unless we require a number of different wavelengths in an experiment, for example in the Laue method (which we will not describe).

If an electron loses all its energy in a single collision with a target atom, an x-ray photon with the maximum energy or the shortest wavelength is produced. This wavelength is known as the short-wavelength limit (λ_{SWL}) and is indicated in Fig. 3 for a molybdenum target irradiated with 25-keV electrons. [Note: When referring to electron energies, we use either eV or keV, but when referring to the accelerating potential applied to the electron, we use V or kV.]

If the incident electron has sufficient energy to eject an inner-shell electron, the atom will be left in an excited state with a hole in the electron shell. This process is illustrated in Fig. 5. When this hole is filled by an electron from an outer shell, an x-ray photon with an energy equal to the difference in the electron energy levels is produced. The energy of the x-ray photon is characteristic of the target metal. The sharp peaks, called *characteristic lines*, are superimposed on the continuous spectrum, as shown in Fig. 3. It is these characteristic lines that are most useful in x-ray diffraction work, and we deal with these later in the book.

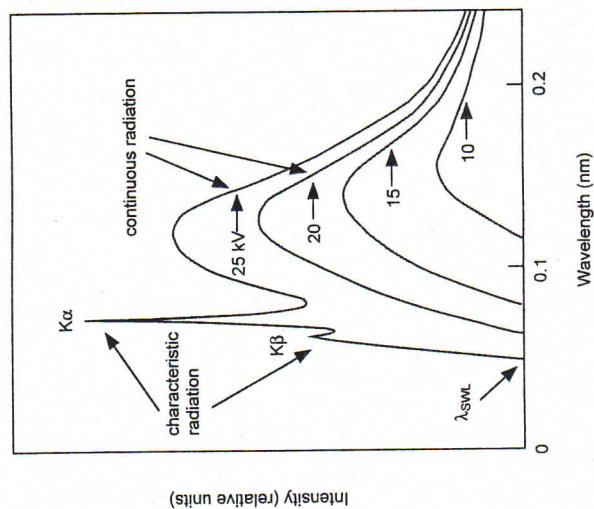


FIG. 3. X-ray spectrum of molybdenum at different potentials. The potentials refer to those applied between the anode and cathode. (The linewidths of the characteristic radiation are not to scale.)

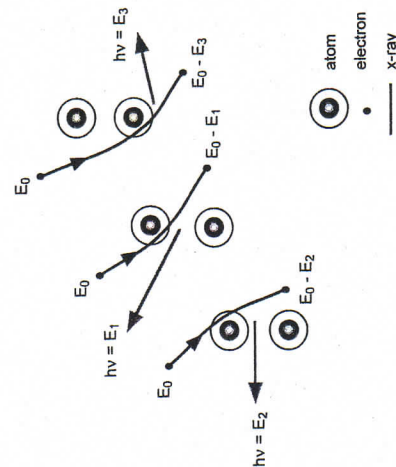


FIG. 4. Illustration of the origin of continuous radiation in the x-ray spectrum. Each electron, with initial energy E_0 , loses some, or all, of its energy through collisions with atoms in the target. The energy of the emitted photon is equal to the energy lost in the collision.

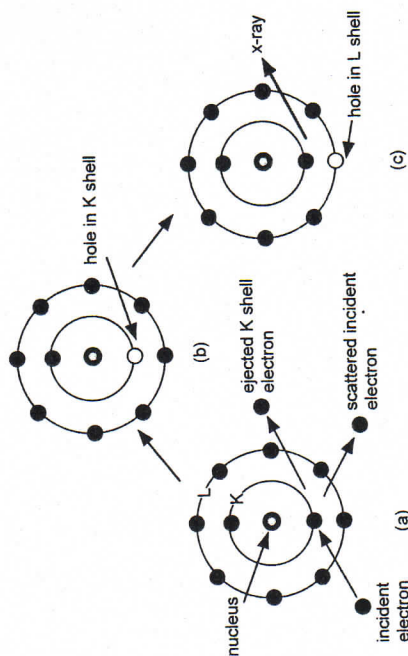


FIG. 5. Illustration of the process of inner-shell ionization and the subsequent emission of a characteristic x-ray: (a) an incident electron ejects a K shell electron from an atom, (b) leaving a hole in the K shell; (c) electron rearrangement occurs, resulting in the emission of an x-ray photon.

If the entire electron energy is converted to that of the x-ray photon, the energy of the x-ray photon is related to the excitation potential V experienced by the electron:

$$E = \frac{hc}{\lambda} = eV \quad (3)$$

where e is the electron charge (1.602×10^{-19} C). The x-ray wavelength is thus

$$\lambda = \frac{hc}{eV} \quad (4)$$

Inserting the values of the constants h , c , and e , we have

$$\lambda \text{ [nm]} = \frac{1.243}{V} \quad (5)$$

when the potential V is expressed in kV. This wavelength corresponds to λ_{swt} ; the characteristic lines will have wavelengths longer than λ_{swt} . The accelerating potentials necessary to produce x-rays having wavelengths comparable to interatomic spacings are therefore about 10 kV. Higher accelerating potentials are normally used to produce a higher-intensity line spectrum characteristic of the target metal. The use of higher accelerating potentials changes the value of λ_{swt} , but not the characteristic wavelengths. The intensity of a characteristic line depends on

both the applied potential and the tube current i (the number of electrons per second striking the target). For an applied potential V , the intensity of the K lines shown in Fig. 3 is approximately

$$I = Bi(V - V_K)^n \quad (6)$$

where B is a proportionality constant, V_K is the potential required to eject an electron from the K shell, and n is a constant, for a particular value of V , which has a value between 1 and 2.

As you can see in Fig. 3, there is more than one characteristic line. The different characteristic lines correspond to electron transitions between different energy levels. The characteristic lines are classified as K, L, M, etc. This terminology is related to the Bohr model of the atom in which the electrons are pictured as orbiting the nucleus in specific shells. For historical reasons, the innermost shell of electrons is called the K shell, the next innermost one the L shell, the next one the M shell, and so on.

If we fill a hole in the K shell with an electron from the L shell, we get a $K\alpha$ x-ray, but if we fill the hole with an electron from the M shell, we get a $K\beta$ x-ray. If the hole is in the L shell and we fill it with an electron from the M shell we get an $L\alpha$ x-ray. Figure 6 shows schematically the origin of these three different characteristic lines.

The situation is complicated by the presence of subshells. For example, we differentiate the $K\alpha$ x-rays as $K\alpha_1$ and $K\alpha_2$. The reason for this differentiation is that the L shell consists of three subshells, L_I , L_{II} , and L_{III} ; a transition from L_{III} to K results in emission of the $K\alpha_1$ x-ray and a

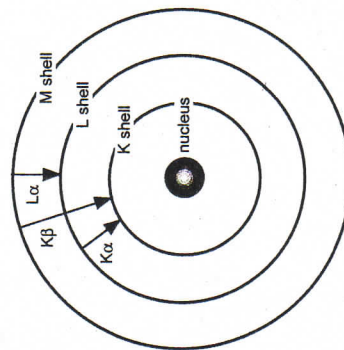


FIG. 6. Electron transitions in an atom, which produce the $K\alpha$, $K\beta$, and $L\alpha$ characteristic x-rays.

Quantum Numbers

You are probably familiar with assigning quantum numbers to the electrons in an atom and writing down the electron configuration of an atom based on these quantum numbers. For example, the electron configuration of silicon (Si), atomic number 14, is $1s^2 2s^2 2p^6 3s^2 3p^2$. The first number is the value of the principal quantum number n . For the K shell, $n = 1$, for the L shell $n = 2$, for the M shell $n = 3$, and so on. The letter (s, p , etc.) represents the value of the orbital-shape quantum number, l . For the K shell there are no subshells because there is only one value of l ; $l = 0$. For the L shell there are subshells because there are two values of l : $l = 0$ and $l = 1$. These values of l correspond to the $2s$ and the $2p$ levels, respectively.

transition from L_{II} to K results in emission of the $K\alpha_2$ x-ray. All the shells except the K shell have subshells.

Let's do an example to illustrate these different transitions for molybdenum. The energies of the K, L_{IV} , and L_{III} levels are given in Table 1. The wavelength of the emitted x-rays is related to the energy difference between any two levels by Eq. (2). The energy difference between the L_{III} and K levels is 17.48 keV. Using this energy in Eq. (2) and substituting in

Designation of Subshells and Angular Momentum

We now introduce a new quantum number, j , which represents the total angular momentum of an electron:

$$j = l + m_s$$

where m_s is the spin quantum number, which, you may remember, can have values of $\pm 1/2$. The values of j can only be positive numbers, so for the L shell we obtain

Subshell notation	n	l	m_s	j
L_I	2	0	$+\frac{1}{2}$	$\frac{1}{2}$
L_{II}	2	1	$-\frac{1}{2}$	$\frac{1}{2}$
L_{III}	2	1	$+\frac{1}{2}$	$\frac{3}{2}$

It is the presence of these subshells that gives rise to splitting of the characteristic lines in the x-ray spectrum.

TABLE 1. Energies of the K, L_{IV} , and L_{III} Levels of Molybdenum

Level	Energy (keV)
K	-20.00
L_{IV}	-2.63
L_{III}	-2.52

the constants, we obtain a wavelength of $\lambda = 0.0709$ nm. This is the wavelength of the $K\alpha_1$ x-rays of Mo. The energy difference between the L_{III} and K levels is 17.37 keV. Using Eq. (2) again, we obtain the wavelength $\lambda = 0.0714$ nm. This is the wavelength of the $K\alpha_2$ x-rays of Mo.

Figure 7 shows the x-ray spectrum for Mo at 35 kV. The right-hand-side figure shows the well-resolved $K\alpha$ doublet on an expanded energy (wavelength) scale. However, it is not always possible to resolve (separate) the $K\alpha_1$ and $K\alpha_2$ lines in the x-ray spectrum because their wavelengths are so close. If the $K\alpha_1$ and $K\alpha_2$ lines cannot be resolved, the characteristic line is simply called the $K\alpha$ line and the wavelength is given by the weighted average of the $K\alpha_1$ and $K\alpha_2$ lines.

Figure 8 shows the complete range of allowed electron transitions in a molybdenum atom. Not all the electron transitions are equally probable. For example, the $K\alpha$ transition (i.e., an electron from the L shell filling a hole in the K shell) is 10 times more likely than the $K\beta$ transition (i.e., an electron from the M shell filling a hole in the K shell).

Weighted Average

Sometimes it is not possible to resolve the $K\alpha_1$ and $K\alpha_2$ lines in the x-ray spectrum. In these cases we take the wavelength of the unresolved $K\alpha$ line as the weighted average of the wavelengths of its components. To determine the weighted average, we need to know not only the wavelengths of the resolved lines but also their relative intensities. The $K\alpha_1$ line is twice as strong (intense) as the $K\alpha_2$ line, so it is given twice the weight. The wavelength of the unresolved Mo $K\alpha$ line is thus

$$\frac{1}{3}(2 \times 0.0709 + 0.0714) = 0.0711 \text{ nm}$$

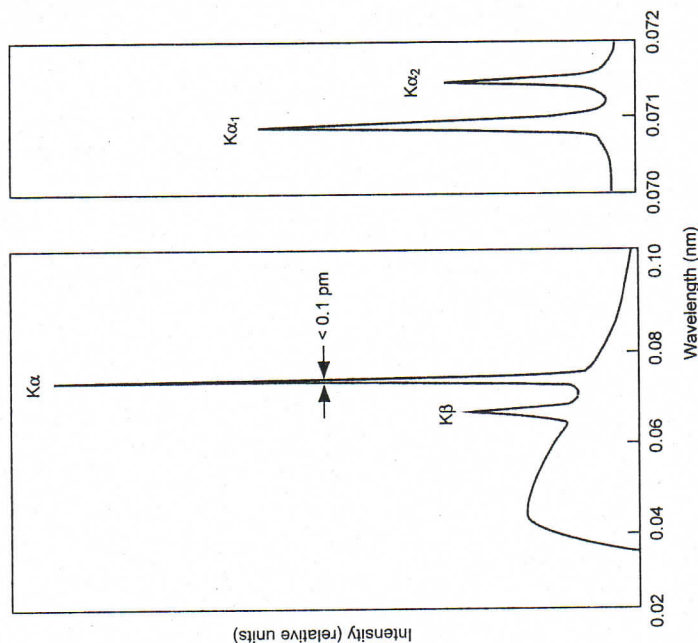


FIG. 7. X-ray spectrum of molybdenum at 35 kV. The expanded scale on the right shows the resolved $K\alpha_1$ and $K\alpha_2$ lines.

The important radiations in diffraction work are those corresponding to the filling of the innermost K shell from adjacent shells giving the so-called $K\alpha_1$, $K\alpha_2$, and $K\beta$ lines. For copper, molybdenum, and some other commonly used x-ray sources, the characteristic wavelengths to six decimal places are given in Table 2.

For most x-ray diffraction studies we want to use a *monochromatic* beam (x-rays of a single wavelength). The simplest way to obtain this is to filter out the unwanted x-ray lines by using a foil of a suitable metal whose absorption edge for x-rays lies between the $K\alpha$ and $K\beta$ components of the spectrum. The absorption edge, or, as it is also known, critical absorption wavelength represents an abrupt change in the absorption characteristics of x-rays of a particular wavelength by a material. For example, a nickel

Selection Rules Governing Electron Transitions

In Fig. 8 and in the preceding discussion you may have noticed that there is no electron transition between the L_1 subshell and the K shell. The reason for this, and the absence of other transitions, is based on a series of selection rules governing electron transitions. A detailed description of why these transitions are absent would require us to discuss the Schrödinger wave equation (the famous equation that relates the wavelike properties of an electron to its energy), which is beyond the scope of this book. But we can use the results that come from the Schrödinger equation, which show that the selection rules for electron transitions are

$$\Delta n = \text{anything}$$

$$\Delta l = \pm 1$$

$$\Delta j = 0 \text{ or } \pm 1$$

where Δn is the change in the principal quantum number, Δl is the change in the orbital-shape quantum number, and Δj is the change in the angular-momentum quantum number. Transitions between any shell (principal quantum number) are allowed (e.g., $2p \rightarrow 1s$), but transitions where the change in l is zero are not allowed (e.g., $2s \rightarrow 1s$). Therefore the L_1 to K transition is not allowed.

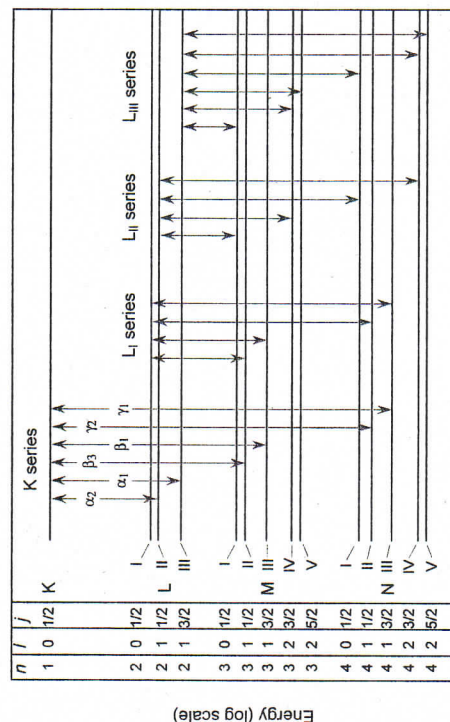


FIG. 8. Energy-level diagram showing all the allowed electron transitions in a molybdenum atom.

TABLE 2. Some Commonly Used X-Ray K Wavelengths (in nm)

Element	K α (weighted average)	K α_2 (strong)	K α_1 (very strong)	K β (weak)
Cr	0.229100	0.229361	0.228970	0.208487
Fe	0.193736	0.193998	0.193604	0.175661
Co	0.179026	0.179285	0.178897	0.162079
Cu	0.154184	0.154439	0.154056	0.139222
Mo	0.071073	0.071359	0.070930	0.063229

foil will remove Cu K β radiation, and zirconium will remove Mo K β radiation. However, in most modern x-ray diffractometers a monochromatic beam is obtained by using a crystal monochromator. A crystal monochromator consists of a crystal, graphite is often used, with a known lattice spacing oriented in such a way that it only diffracts the K α radiation, and not the K β radiation. The beam is still made up of the K α_1 and K α_2 wavelengths.

For x-ray diffraction studies there is a wide choice of characteristic K α lines obtained by using different target metals, as shown in Table 2, but, Cu K α is the most common radiation used. The K α lines are used because they are more energetic than L α and therefore less strongly absorbed by the material we want to examine. The wavelength spread of each line is extremely narrow, and each wavelength is known with very high precision.

1.3. DIFFRACTION

Diffraction is a general characteristic of all waves and can be defined as the modification of the behavior of light or other waves by its interaction with an object. You should already be familiar with the term "diffraction" from introductory physics classes. In this section we review some fundamental features of diffraction, particularly as they apply to the use of x-rays for determining crystal structures.

First let's consider an individual isolated atom. If a beam of x-rays is incident on the atom, the electrons in the atom then oscillate about their mean positions. Recall from Section 1.2 that when an electron decelerates (loses energy) it emits x-rays. This process of absorption and reemission of electromagnetic radiation is known as *scattering*. Using the concept of a photon, we can say that an x-ray photon is absorbed by the atom and another photon of the same energy is emitted. When there is no change

in energy between the incident photon and the emitted photon, we say that the radiation has been *elastically* scattered. On the other hand, inelastic scattering involves photon energy loss.

If the atom we choose to consider is anything other than hydrogen, we would have to consider scattering from more than one electron. Figure 9 shows an atom containing several electrons arranged as points around the nucleus. Although you know from quantum mechanics that this is not a correct representation of atomic structure, it helps our explanation. We are concerned with what happens to two waves that are incident on the atom. The upper wave is scattered by electron A in the forward direction. The lower wave is scattered in the forward direction by electron B. The two waves scattered in the forward direction are said to be in phase (in step or coherent are other terms we use) across wavefront XX' since these waves have traveled the same total distance before and after scattering; in other words, there is no path (or phase) difference. (A wavefront is simply a surface perpendicular to the direction of propagation of the wave.) If the two waves are in phase, then the maximum in one wave is aligned with the maximum in the other wave. If we add these two waves across wavefront XX' (i.e., we sum their amplitudes), we obtain a wave with the same wavelength but twice the amplitude.

The other scattered waves in Fig. 9 will not be in phase across wavefront YY' when the path difference (CB - AD) is not an integral number of wavelengths. If we add these two waves across wavefront YY', we find that the amplitude of the scattered wave is less than the amplitude of the wave scattered by the same electrons in the forward direction.

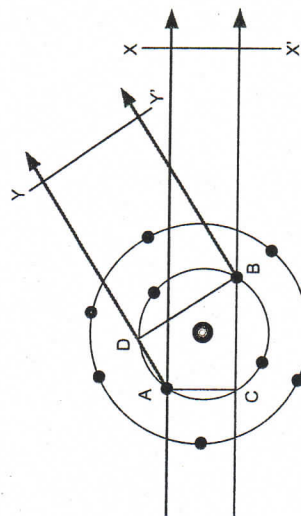


FIG. 9. Scattering of x-rays by an atom.

The Superposition of Waves

When two waves are moving through the same region of space they will superimpose (overlap). The resultant wave is the algebraic sum of the various amplitudes at each point. This is known as the superposition principle. Figure 10 shows three examples of the superposition of two waves: (a) when the component waves are in phase, we have constructive interference and the resultant wave amplitude is large; (b) when the phase difference increases, the amplitude of the resultant wave decreases; and (c) when the component waves are 180° out of phase, the resultant wave has its smallest amplitude and we have destructive interference. Since the amplitudes of wave 1 and wave 2 are different, there is some resultant amplitude. If the amplitudes of waves 1 and 2 are equal, then the resultant amplitude is zero and there is no intensity.

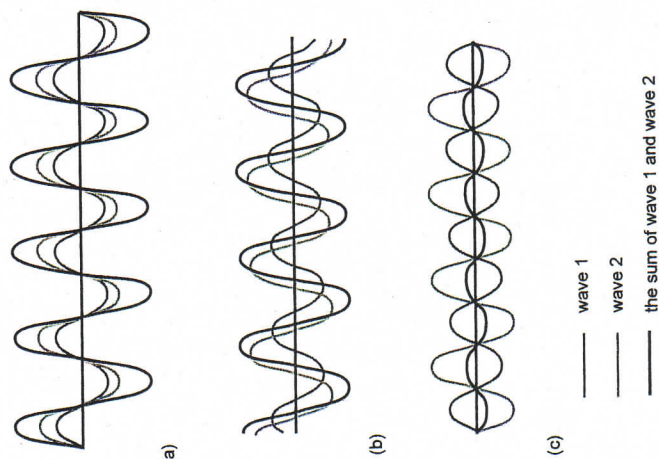


FIG. 10. Illustration of the superposition of waves.

We define a quantity called the *atomic scattering factor*, f , to explain how efficient an atom is scattering in a given direction:

$$f = \frac{\text{Amplitude of wave scattered by an atom}}{\text{Amplitude of wave scattered by one electron}} \quad (7)$$

When scattering is in the forward direction (i.e., the scattering angle, $\theta = 0^\circ$) $f = Z$ (the atomic number—i.e., the total number of electrons) since the waves scattered by all the electrons in the atom are in phase and the amplitudes sum up. But as θ increases, the waves become more and more out of phase because they travel different path lengths and, therefore, the amplitude, or f , decreases. The atomic scattering factor also depends on the wavelength of the incident x-rays. For a fixed value of θ , f is smaller for shorter-wavelength radiation. The variation of atomic scattering factor with scattering angle for copper, aluminum, and oxygen, is shown in Fig. 11. The curves begin at the atomic number (Z), which for copper is 29, and decrease with increasing values of θ or decreasing values of λ . In fact, f is generally plotted against $(\sin \theta)/\lambda$ to take into account the variation of f with both θ and λ . The rate of decrease of f with

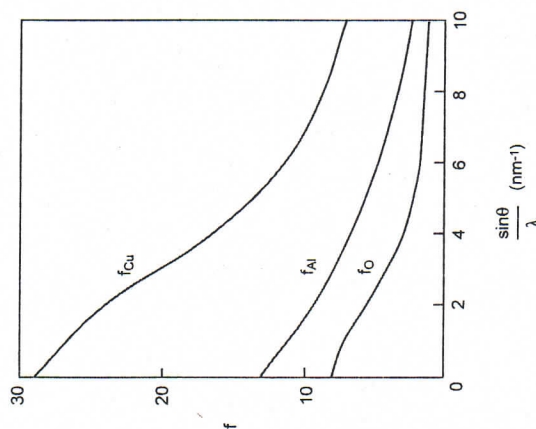


FIG. 11. Variation of the atomic scattering factor of copper, aluminum, and oxygen with $(\sin \theta)/\lambda$.

increasing values of $(\sin \theta)/\lambda$ is different for different elements, as you can see in Fig. 11. Note that most of the scattering occurs in the forward direction, when $\theta \approx 0^\circ$.

Let's now consider some closely spaced atoms each of which contributes many scattered x-rays. The scattered waves from each atom interfere. If the waves are in phase, then *constructive interference* occurs. If the waves are 180° out of phase, then *destructive interference* occurs. A diffracted beam may be defined as a beam composed of a large number of superimposed scattered waves. For a measurable diffracted beam complete destructive interference does not occur.

To describe diffraction we have introduced three terms:

- Scattering
- Interference
- Diffraction

What is the difference among these terms? Scattering is the process whereby the incident radiation is absorbed and then reemitted in different directions. Interference is the superposition of two or more of these scattered waves, producing a resultant wave that is the sum of the overlapping wave contributions. Diffraction is constructive interference of more than one scattered wave. There is no real physical difference between constructive interference and diffraction.

1.4. A VERY BRIEF HISTORICAL PERSPECTIVE

If we look back into history (hindsight is a great thing!), the first inkling that diffraction may be useful for studying crystal structure came from the classic double-slit experiment performed by Thomas Young over 200 years ago. At the time Young may well not have realized that the phenomenon he observed would have application to other forms of electromagnetic radiation, and certainly he was not aware of x-rays. Young died in 1829, sixty-six years before the discovery of x-rays by Wilhelm Röntgen in 1895.

In Young's double-slit experiment two coherent (i.e., in phase) beams of light obtained by passing light through two parallel slits were allowed to interfere. The pattern produced on a screen placed beyond the slits consisted of a series of bright and dark lines, as shown schematically in Fig. 12. If we replace the double slits with a grid consisting of many parallel slits, called a diffraction grating, and shine a line source of electromagnetic radiation on the grid, we also observe a pattern consisting of a series of bright and dark lines. The separation of the lines depends on the wavelength (λ) of the radiation and the spacing (d) between the slits in the



FIG. 12. The fringe pattern produced on a screen in Young's experiment. Waves passing through two slits interfere, and the pattern observed on the screen consists of a series of white (max) and dark (min) lines (not drawn to scale.)

grating. If two diffraction gratings are now superimposed with their lines intersecting at right angles (like a possible arrangement of the lattice planes in a crystal), a spot pattern is produced in which the distance between the spots is a function of the spacing in the gratings and the wavelength of the radiation for a given pair of diffraction gratings. For the experiment to work, the dimensions of the slits in the grating must be comparable to the wavelength of the radiation used.

Max von Laue, in 1912, realized that if x-rays had a wavelength similar to the spacing of atomic planes in a crystal, then it should be possible to diffract x-rays by a crystal and, hence, to obtain information about the arrangement of atoms in crystals.

Lattices and Crystal Structures

2.1. TYPES OF SOLID AND ORDER

We can classify solids into three general categories:

1. Single crystal
2. Polycrystalline
3. Amorphous

Simple schematics representing these three categories are shown in Fig. 13.

A crystal is said to possess long-range order because it is composed of atoms arranged in a regular ordered pattern in three dimensions. This periodic arrangement, known as the *crystal structure*, extends over dis-

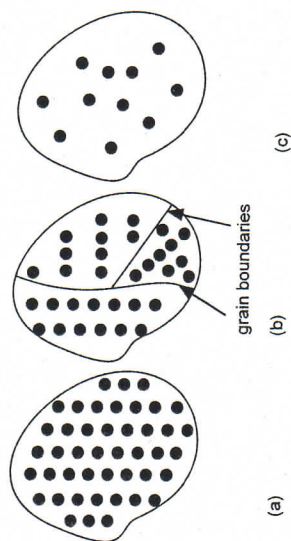


FIG. 13. Illustration of the difference between (a) single crystal, (b) polycrystalline, and (c) amorphous materials.

Grain Boundaries

Grains in a polycrystalline material are generally in many different orientations. The boundary between the grains—the grain boundary—depends on the misorientation of the two grains and the rotation axis about which the misorientation has occurred. There are two special types of grain boundary, illustrated in Fig. 14, which are relatively simple to visualize: the pure tilt boundary and the pure twist boundary. In a tilt boundary the axis of rotation is parallel to the grain-boundary plane. In a twist boundary, the rotation axis is perpendicular to the grain-boundary plane. In general, the axis of rotation will not be simply oriented with respect to either the grain or the grain-boundary plane.

tances much larger than the interatomic separation. (Remember, interatomic separations are about 0.2 nm.) In a single crystal this order extends throughout the entire volume of the material.

A polycrystalline material consists of many small single-crystal regions (called grains) separated by grain boundaries. The grains on either side of the grain boundary are misoriented with respect to each other. The grains in a polycrystalline material can have different shapes and sizes.

In amorphous materials, such as glasses and many polymers, the atoms are not arranged in a regular periodic manner. *Amorphous* is a Greek word meaning “without definite form.” Amorphous materials possess only short-range order. The order only extends to a few of the nearest neighbors—distances of less than a nanometer. (A glass is not really a solid; it is actually a supercooled liquid with a very high viscosity—about 15 orders

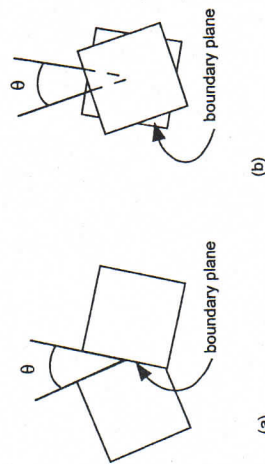


FIG. 14. Illustration of (a) a tilt grain boundary and (b) a twist grain boundary.

of magnitude greater than water at room temperature—so that in many respects it behaves like a solid.)

2.2. POINT LATTICES AND THE UNIT CELL

Let's consider the three-dimensional arrangement of points in Fig. 15. This arrangement is called a *point lattice*. If we take any point in the point lattice it has exactly the same number and arrangement of neighbors (i.e., identical surroundings) as any other point in the lattice. This condition should be fairly obvious considering our description of long-range order in Sec. 2.1. We can also see from Fig. 15 that it is possible to divide the point lattice into much smaller units such that when these units are stacked in three dimensions they reproduce the point lattice. This small repeating unit is known as the *unit cell* of the lattice and is shown in Fig. 16.

A unit cell may be described by the interrelationship between the lengths (a, b, c) of its sides and the interaxial angles (α, β, γ) between them. (α is the angle between the b and c axes, β is the angle between the a and c axes, and γ is the angle between the a and b axes.) The actual values of a, b , and c , and α, β , and γ are not important, but their interrelation is. The lengths are measured from one corner of the cell, which is taken as

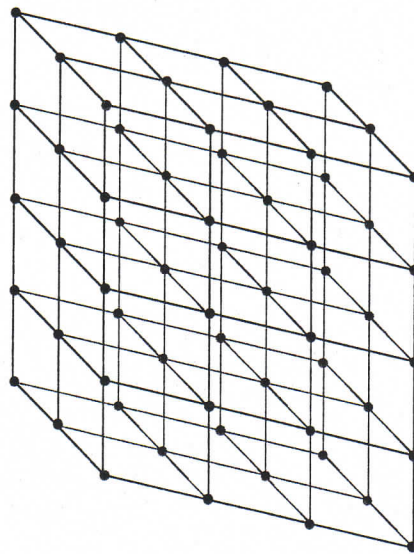


FIG. 15. A point lattice. The light lattice points are those that would not be visible when looking from the front of the lattice. But all the points are equivalent.

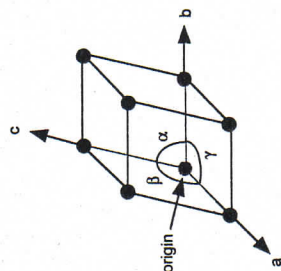


FIG. 16. A unit cell.

the origin. These lengths and angles are called the *lattice parameters* of the unit cell, or sometimes the lattice constants of the cell. But the latter term is not really appropriate because they are not necessarily constants; for example, they can vary with changes in temperature and pressure and with alloying. [Note: We use a, b, and c to indicate the axes of the unit cell; a, b, and c for the lattice parameters, and a, b, and c for the vectors lying along the unit-cell axes.]

2.3. CRYSTAL SYSTEMS AND BRAVAIS LATTICES

You can probably imagine unit cells of many different shapes. However, one of the requirements of a unit cell is that they can be stacked to fill three-dimensional space. Seven unit-cell shapes meet this requirement and are known as the seven *crystal systems*. All crystals can be classified into these seven categories. We have listed the seven crystal systems in Table 3 in order of increasing symmetry. The triclinic cell has the lowest symmetry, and the cubic cell has the highest symmetry. (*Quasicrystals* are not included in this classification. They are a relatively new form of solid matter wherein the atoms are arranged in a three-dimensional pattern that exhibits the traditionally forbidden translational symmetries, e.g., five-fold, seven-fold, etc.)

If we put a lattice point at the corner of each unit cell of the seven crystal systems, we obtain seven different point lattices. However, other arrangements of points also satisfy the requirement of a point lattice; i.e., each point has identical surroundings. Auguste Bravais, in 1848, demonstrated that there are 14 possible point lattices and no more. The 14 *Bravais*

TABLE 3. The Seven Crystal Systems

System	Relationship among Lattice Parameters
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$
Rhombohedral (or trigonal)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$

Lattice Points Per Cell

To readily calculate some of the physical characteristics of crystals, such as atomic density and density of free electrons, we must know the number of lattice points per cell. You may think that such a determination is quite trivial, but it is surprising how many people have difficulty with it! The number of lattice points per cell, N , is given by the equation

$$N = N_i + \frac{N_c}{8} \quad (8)$$

where N_i is the number of lattice points in the interior of the cell (these points "belong" only to one cell), N_i is the number of lattice points on faces (these are shared by two cells), and N_c is the number of lattice points on corners (these are shared by eight cells). For the three cubic unit cells the number of lattice points per cell is

Primitive cubic (cubic P)	1
Body-centered cubic (cubic I)	2
Face-centered cubic (cubic F)	4

All primitive cells have one lattice point per cell. All nonprimitive cells have more than one lattice point per cell.

lattices are shown in Fig. 17. These lattices are known interchangeably as Bravais lattices, point lattices, and space lattices.

The lattice symbols given to the Bravais lattices in Fig. 17 have the following meanings:

- P stands for a *primitive* or simple cell, where there is a lattice point at each corner.
- F refers to a *face-centered* cell, where a lattice point is centered on each face, in addition to the corners of the unit cell.
- I is used for *body-centered* cells, where a lattice point is in the center of the cell—in the *interior* of the cell—in addition to the corners of the unit cell.
- A, B, and C refer to *base-centered* cells where lattice points are centered on opposite faces of the cell, in addition to the corners of

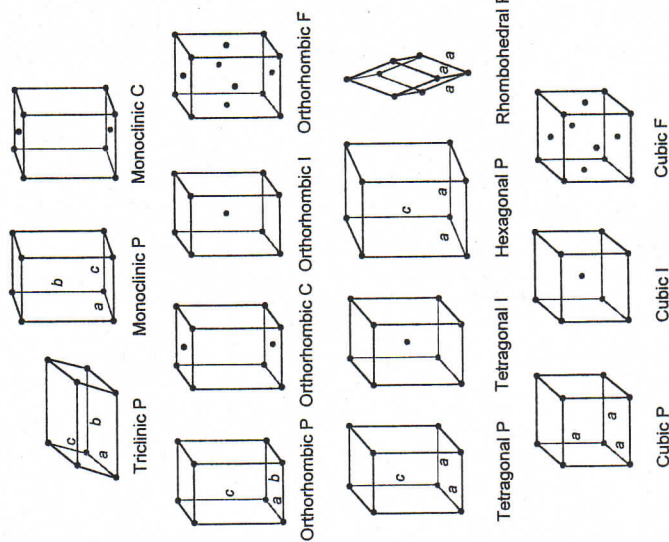


FIG. 17. The 14 Bravais lattices.

the unit cell. (The A face is the face defined by the b and c axes, the B face is defined by the a and c axes, and the C face is defined by the a and b axes. In Fig. 17 only the unit cells having lattice points centered on the C face have been shown.)

- R is used only for the *rhombohedral* system and refers to a primitive cell.

Some texts list only six crystal systems because rhombohedral crystals can always be described in terms of hexagonal axes, so the rhombohedral system is often considered to be a subdivision of the hexagonal system.

So far we have discussed only lattice points. What is the difference between a lattice point and an atom? A lattice point represents equivalent positions in a Bravais lattice. In a real crystal a lattice point may be occupied by one atom or by a group of atoms. In the latter case the atoms are in a fixed relationship with respect to each lattice point. In both cases, the number, composition, and arrangement of atoms is the same for each lattice point. This arrangement is known as the *basis*.

An important difference between lattice points and atoms is that the lattice points tell us nothing about the chemistry or bonding within the crystal; for that we need to include the identity of the atoms and their positions.

2.4. CRYSTAL STRUCTURES

Now we want to consider actual crystals and their structures. The relationship between Bravais lattices and actual crystal structures involves the basis. We can express this relationship as

$$\text{Bravais lattice} + \text{basis} \rightarrow \text{Crystal structure} \quad (9)$$

You can see that the different crystal structures are built on the framework of one of the 14 Bravais lattices and contain a basis consisting of a number of atoms. In the following sections we group crystal structures in terms of their basis. This approach may be somewhat different from that which is used to describe structures in introductory materials science classes, but it will help you when we describe the structure factor in Sec. 2.8.

2.4.1. One Atom per Lattice Point

The simplest crystal structures are those in which the basis is one atom located on each lattice point of a Bravais lattice. (Remember, each atom must be of the same kind.) Let's consider the crystal structures based on

the three cubic Bravais lattices in which each has a basis consisting of one atom. Using Eq. (9) we obtain for the primitive cubic Bravais lattice:

Primitive cubic (cubic P) lattice + one atom $\rightarrow$ Simple cubic (sc) structure

The sc structure is illustrated in Fig. 18. There is one atom per cell in the sc structure and this atom is located at the origin, i.e., its coordinates are 0,0,0. (Our choice of the origin of the unit cell is entirely arbitrary, as you will see.) The simple cubic structure is uncommon; no important metals have this structure. α -Polonium (Po) is the only element that crystallizes in the simple cubic structure, although some nonequilibrium phases obtained by rapid solidification or mechanical alloying also exhibit this structure.

Now let's consider the body-centered cubic Bravais lattice with a basis consisting of one atom. Using Eq. (9) we obtain

Body-centered cubic (cubic I) lattice + one atom $\rightarrow$
Body-centered cubic (bcc) structure

The bcc crystal structure is shown in Fig. 19. There are two atoms per cell, located at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The two atom positions are related by the body-centering translation $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (i.e., a translation of half a lattice parameter along the a axis, half a lattice parameter along the b axis, and half a lattice parameter along the c axis). If the body-centering translation is

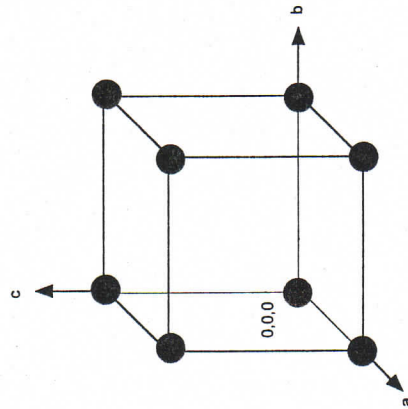


FIG. 18. Simple cubic structure.

Coordinates of Points

The location of certain points, such as the position of lattice points or atoms, in the unit cell is straightforward. It is usual to choose a right-handed coordinate system, (Fig. 16), where the origin is located at the back left-hand corner of the cell as you look at it. The distance is measured in terms of how many lattice parameters we must move along the a, b, and c axes to get from the origin to the point we are interested in. The coordinates are written as the three distances, with commas separating the numbers.

applied to the atom at 0,0,0, the body-centered atom is reproduced. If the body-centering translation is applied to the atom at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, then one of the corner atoms is reproduced. Several metals exist in the bcc structure, including sodium (Na), chromium (Cr), α -iron (α -Fe), molybdenum (Mo), and tungsten (W).

The face-centered cubic (fcc) structure in Fig. 20 is based on the face-centered cubic (cubic F) Bravais lattice with a basis of one atom:

Face-centered cubic (cubic F) lattice + one atom $\rightarrow$
Face-centered cubic (fcc) structure

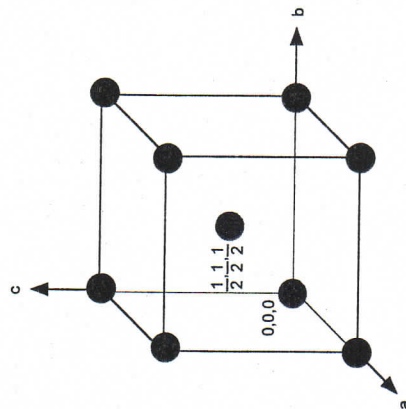


FIG. 19. Body-centered cubic structure.

Close-Packed Structures

A close-packed structure is one that has the maximum volume of the unit cell occupied by atoms. The fraction of the unit cell occupied by atoms can be determined by calculating the atomic packing factor (APF) from the following equation:

$$\text{APF} = \frac{\text{number of atoms per cell} \times \text{volume of one atom}}{\text{volume of unit cell}} \quad (10)$$

We will go through the calculation of the APF for the fcc structure; you may calculate for the other cubic structures as an exercise.

Look back at the fcc structure in Fig. 20:

- The number of atoms per cell is 4.
- The volume of each atom is $(4/3)\pi r^3$ (we assume in these calculations that the atoms are rigid spheres with a radius r).
- The unit-cell volume is a^3 .

We can rewrite the lattice parameter a in terms of r (Fig. 21), where the figure shows that the atoms touch across the face diagonal of the cell. Therefore, $\sqrt{2}a = 4r$, or $a = 2\sqrt{2}r$. Using Eq. (10) we obtain

$$\text{APF} = \frac{4\left(\frac{4}{3}\pi r^3\right)}{(2\sqrt{2}r)^3} = 0.74$$

For the fcc structure, the atomic packing factor is 0.74. This is the *maximum* possible value for packing spheres of the same size. Crystal structures with an APF of 0.74 are called close-packed structures. Of the three cubic structures only the fcc structure is close-packed.

2.4.2. Two Atoms of the Same Kind per Lattice Point

The Hexagonal Close-Packed Structure

Many metals have the hexagonal close-packed (hcp) structure, including magnesium (Mg), titanium (Ti), zinc (Zn), and cadmium (Cd). The hcp structure is built on the hexagonal Bravais lattice with a basis consisting of two identical atoms associated with each lattice point. Using the relationship in Eq. (9), we have

Hexagonal P lattice + two atoms $\rightarrow$ Hexagonal close-packed (hcp) structure

Figure 22a shows the arrangement of atoms in the hcp structure. There are two atoms per unit cell, located at $0,0,0$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$. However, in the

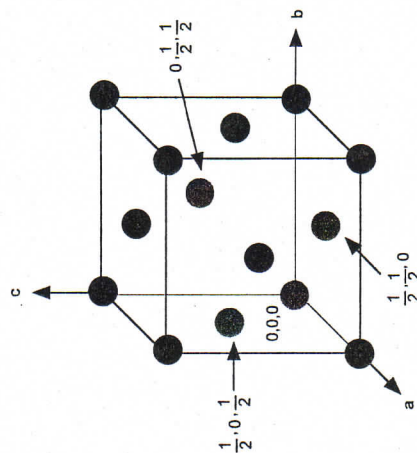


FIG. 20. Face-centered cubic structure.

The fcc structure has four atoms per cell, located at $0,0,0$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$. If the face-centering translations $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$ are repeatedly applied to any atom in the cell, the positions of all the atoms in the crystal structure will be reproduced. The fcc structure is exhibited by several metals including calcium (Ca), copper (Cu), gold (Au), nickel (Ni), and silver (Ag). [Note: When referring to the Bravais lattice we write, for example, face-centered cubic, but when referring to a crystal with the face-centered cubic structure we write fcc.]

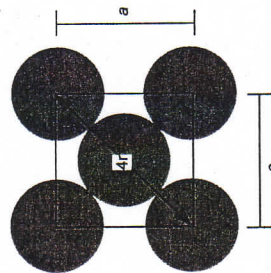


FIG. 21. Atoms touch across the face diagonal in the fcc structure.

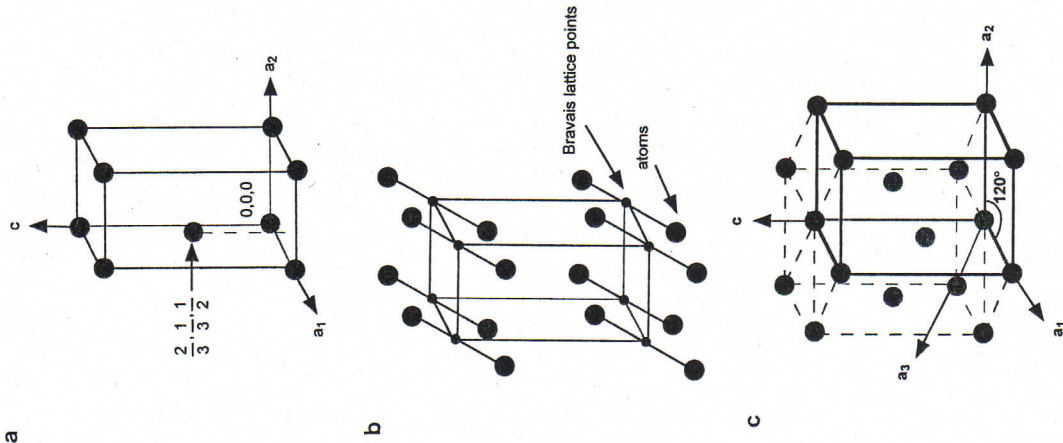


FIG. 22. Hexagonal close-packed structure.

hexagonal Bravais lattice there is only one lattice point per cell (because the cell is primitive). Figure 22b shows the hcp structure redrawn (of course, all the atoms are still in same place) with the origin of the unit cell shifted upward so that the point $1,0,0$ in the new cell is now midway between the atoms at $1,0,0$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ in the old cell. Now, if a Bravais lattice point is located on each corner of the new cell, then a pair of atoms is associated with each Bravais lattice point. To get a better idea of the hexagonal symmetry of the hcp structure, look at Fig. 22c. The hcp structure, as the name suggests, is a close-packed structure (APF = 0.74). Only the hcp and fcc structures are close-packed.

The Diamond Cubic Structure

Another important structure with two atoms per lattice point is the diamond cubic. This structure is adopted by diamond (one of the crystalline forms of carbon) and the industrially important elemental semiconductors silicon (Si) and germanium (Ge).

The diamond cubic structure (Fig. 23) is based on the face-centered cubic Bravais lattice with a basis of two atoms:

Face-centered cubic (cubic F) lattice + two atoms $\rightarrow$ Diamond cubic structure

There are eight atoms per cell in the diamond cubic structure, located at $0,0,0$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$; or, in terms of the face-centering

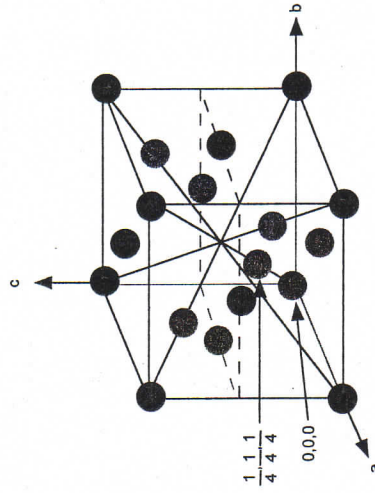


FIG. 23. Diamond cubic structure.

translations, $0,0,0 + \text{face-centering translations}$, and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4} + \text{face-centering translations}$.

Although the atoms at these two sets of positions are chemically identical (they are all carbon atoms in diamond or all silicon atoms in a crystal of silicon) the lattice positions are not equivalent. If the two lattice positions were equivalent, it would be possible to move from one to another by the same translation vector. The vector $\mathbf{v}_1$ in Fig. 24 would move the atom located at $0,0,0$ to the point $\frac{1}{2}, \frac{1}{2}, 0$, which is also a lattice position in the diamond cubic structure. The vector $\mathbf{v}_2$ in Fig. 24 would move an atom at $0,0,0$ to the point $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. However, if the point $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ is operated on by $\mathbf{v}_2$ it would translate it to the coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (a position in the body center of the diamond cubic unit cell). The point $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ is not a lattice position in the diamond cubic structure.

If we consider only the atom at $0,0,0$ and use the face-centering translations, we produce an fcc crystal structure. If we now consider only the atom at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and perform the face-centering translations, we also produce an fcc crystal structure. So we can think of the diamond cubic

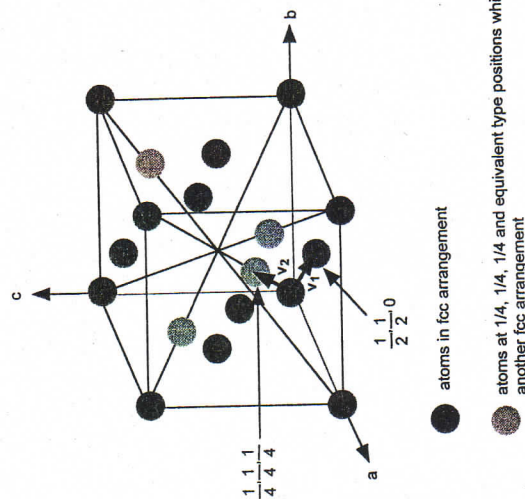


FIG. 24. Illustration of the diamond cubic structure showing the atoms which form two face-centered cubic arrangements.

Names of Crystal Structures

As we go through this chapter, and when you take other materials science classes, you will find that many crystal structures are named after a particular material (often a naturally occurring mineral) that exhibits the structure. There are no systematic names for crystal structures. In chemistry, for example, organic compounds are named with a system recommended by the International Union of Pure and Applied Chemistry (IUPAC). The IUPAC system is a systematic way of naming many organic compounds on sight, and the name indicates the structure of the compound. A similar system is not used for naming crystal structures. However, in the next section we introduce a systematic notation for crystal structures, which can be very useful. Table 4 lists the names of some common crystal structures. For example, MgO (which has a melting point of 2800°C) has the same structure as NaCl (melting point of 801°C). Even though two or more materials may share the same crystal structure they may have different properties. The properties of a material depend on the types of atoms present, the way the atoms are held together (bonding), the crystal structure, and the defects present. You can also see from the table that ZnS exists in both the zinc blende (sphalerite) and wurtzite structures. This phenomenon is known as *polymorphism* and is exhibited by many materials.

structure as consisting of two *interpenetrating* face-centered cubic lattices, the origin of one displaced by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ from the other.

It is important to realize that, although the fcc structure and the diamond cubic structure both have the same Bravais lattice, they are very different structures and, consequently, materials with a diamond cubic structure have properties significantly different from those with an fcc

TABLE 4. Names of Some Common Crystal Structures

Name of Structure	Corresponding Mineral	Other Materials with the Same Structure
Rocksalt	NaCl	KCl, LiF, MgO, NiO, CaO, TiN
Zinc blende (sphalerite)	ZnS	BeO, β -SiC, GaAs
Rutile	TiO ₂	GeO ₂ , SnO ₂
Corundum	Al ₂ O ₃	Fe ₂ O ₃ , Cr ₂ O ₃ , Ti ₂ O ₃
Wurtzite	ZnS	ZnO, α -SiC, AlN
Perovskite	CaTiO ₃	BaTiO ₃ , SrTiO ₃
Spinel	MgAl ₂ O ₄	FeAl ₂ O ₄ , ZnAl ₂ O ₄

structure. One significant difference between the two structures is the atomic packing factor. The APF is only 0.34 for the diamond cubic structure; remember it was 0.74 for the fcc structure. You will also see that the structure factors (selection rules for the observance of reflections in the x-ray diffraction pattern) are different for the two structures.

2.4.3. Two Different Atoms per Lattice Point

We describe four crystal structures in this section, known by the common names

- Cesium chloride (CsCl)
- Sodium chloride (NaCl, or rocksalt)
- Zinc blende (ZnS, or sphalerite)
- Wurtzite (ZnS)

Cesium Chloride Structure

In addition to CsCl, many other compounds have the "CsCl structure," including CsBr, NiAl, the ordered form of β -brass (CuZn), and CuPd. The CsCl structure is shown in Fig. 25. The unit cell contains two atoms. For

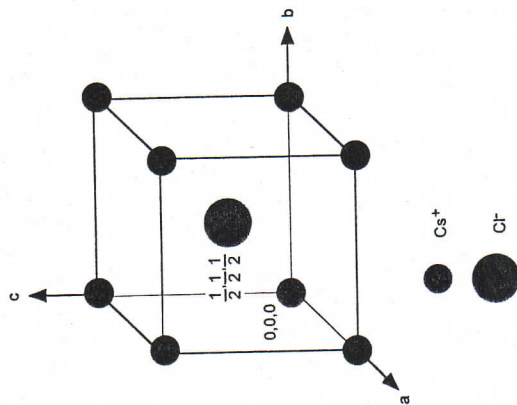


FIG. 25. Cesium chloride structure.

CsCl, which is strongly ionic, it would be better to refer to ions rather than atoms, but remember that compounds with nonionic bonding can also have this structure. In the CsCl structure there is a cesium ion at 0,0,0 and a chlorine ion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ forming the basis. The Bravais lattice is primitive cubic (cubic P);

Primitive cubic (cubic P) lattice + two atoms $\rightarrow$ CsCl structure

A common mistake when assigning the Bravais lattice to the CsCl structure is to say that the Bravais lattice is body-centered cubic. However, in the bcc crystal structure, which we saw in Sec. 2.4.1 is built on the body-centered cubic Bravais lattice, all the atoms must be of the *same* type and the body-centering translation must join identical atoms. In CsCl if we apply the body-centering translation to the Cs^+ ion at 0,0,0 we would get to a position occupied by a Cl^- ion. So in CsCl, where there are two kinds of atoms, the Bravais lattice cannot be body-centered cubic.

We can describe the CsCl structure as two interpenetrating simple cubic structures—one of Cs^+ ions and one of Cl^- ions, one displaced by $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with respect to the other.

Sodium Chloride Structure

Many materials exist in the sodium chloride (NaCl) or rocksalt crystal structure. In addition to many of the halides, including AgCl, KBr, LiF, NaI, many ceramics, including MgO, CaO, NiO, TiN, ZrN, TiC, ZrC, and ZrB, have the NaCl structure. The NaCl structure (Fig. 26) is based on the face-centered cubic Bravais lattice with a basis of two atoms at 0,0,0 and $\frac{1}{2}, 0, 0$.

Face-centered cubic (cubic F) lattice + two atoms $\rightarrow$ NaCl structure

There are a total of eight atoms per cell, four Na and four Cl. (Strictly speaking, for the actual compound NaCl we should refer to ions, Na^+ and Cl^- , not atoms, because the compound is completely ionized.) The Na^+ ions are located at positions 0,0,0; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and the Cl^- ions are located at $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $0, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

The sodium ions are in a face-centered cubic arrangement and if we apply the face-centering translations to the chlorine ion at $\frac{1}{2}, 0, 0$ we can see that the chlorine ions are also in a face-centered cubic arrangement. So we can describe the NaCl structure as two interpenetrating face-centered cubic lattices, the origin of one displaced from the other by $\frac{1}{2}, 0, 0$.

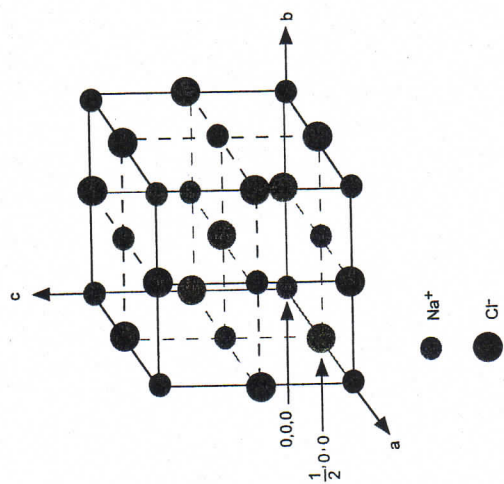


FIG. 26. Sodium chloride structure.

Zinc Blende Structure

The zinc blende, or sphalerite, structure is shown in Fig. 27. In this structure the arrangement of atoms is the same as in the diamond cubic structure in Fig. 23. But the zinc blende structure has two types of atoms in the unit cell (classically Zn and S). The structure is built on the face-centered cubic Bravais lattice with two atoms per lattice point, one at 0,0,0 and the other at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$.

Face-centered cubic (cubic F) lattice + two atoms $\rightarrow$ Zinc blende structure
There are a total of eight atoms per cell, four Zn and four S, and these are located at

S atoms at	0,0,0	$\frac{1}{2}, \frac{1}{2}, 0$	$0, \frac{1}{2}, \frac{1}{2}$
Zn atoms at	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$	$\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$

or, in terms of the face-centering translations,

S	0,0,0 + face-centering translations
Zn	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ + face-centering translation

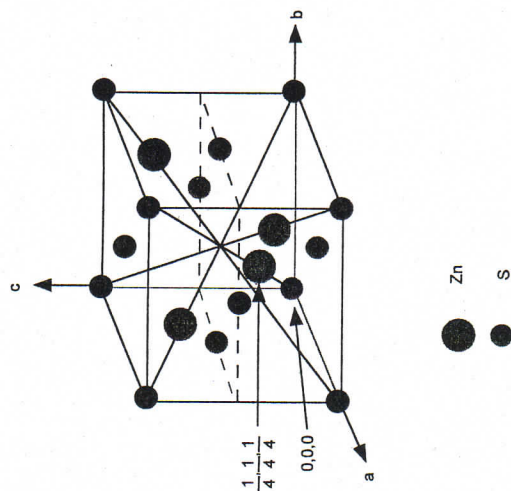


FIG. 27. Zinc blende structure.

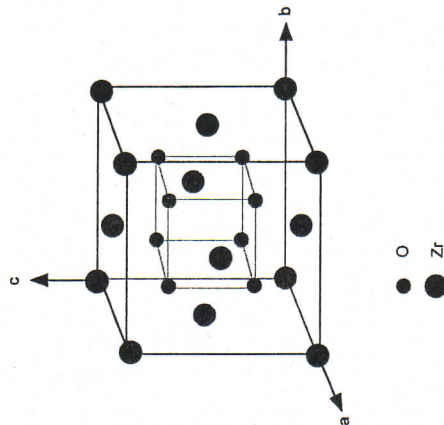


FIG. 28. Fluorite structure.

2.4.4. More than Two Atoms per Lattice Point

In the experimental modules in Part II we have concentrated on crystal structures that have either one or two atoms per lattice point. But you should be aware that there are crystal structures with more than two atoms associated with each lattice point. Of course, the structures are still based on 1 of the 14 Bravais lattices shown in Fig. 17. In this section we present just three examples of materials having crystal structures more complex than those already considered.

The first example is cubic zirconium oxide (ZrO_2), or cubic zirconia as it is commonly known. Cubic zirconia is a hard ceramic that exists in what

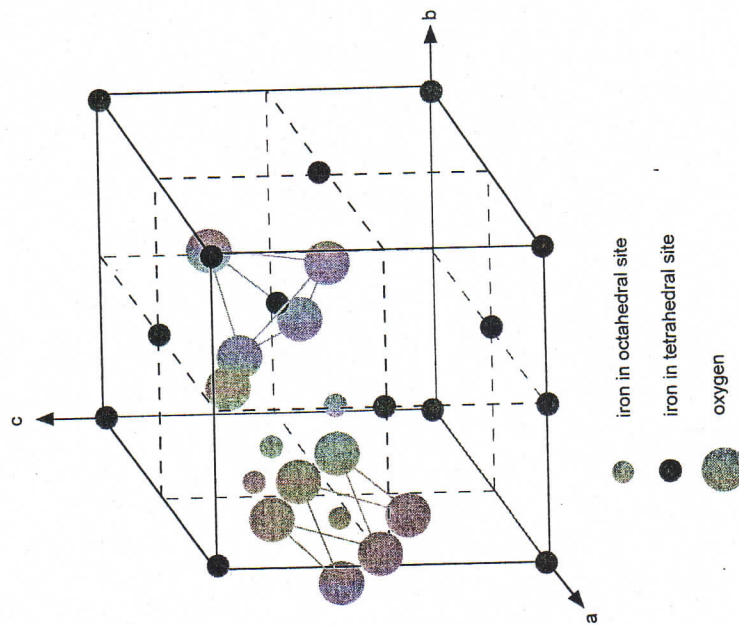


FIG. 29. Part of the spinel structure. There are 32 octahedral sites and 64 tetrahedral sites per unit cell.

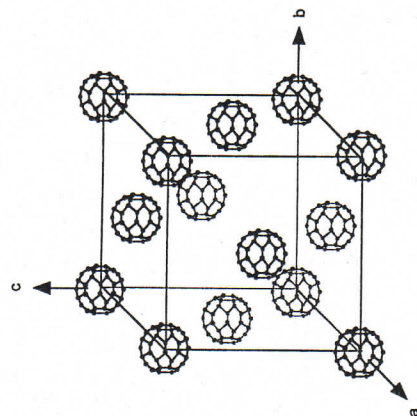


FIG. 30. Structure of solid C_{60} .

is called the fluorite structure (Fig. 28). The structure is built on the face-centered cubic Bravais lattice with a basis of three atoms (two oxygen and one zirconium).

The second example is the spinel structure. The mineral spinel is MgAl_2O_4 , but many other materials exist in its structure. One example is the magnetic oxide Fe_3O_4 (known by the common name magnetite). The structure of magnetite is shown in Fig. 29. The Bravais lattice is face-centered cubic once again, but this time there are 14 atoms associated with each lattice point. (There are 56 atoms per unit cell.)

The last example is the structure of solid C_{60} . The C_{60} molecule is quite familiar to many people, even though it was only discovered in 1985, because its shape is characteristic of a geodesic dome and is called a "buckyball." In the solid state, the C_{60} molecules form a crystalline structure in which they are arranged in a face-centered cubic array as shown in Fig. 30. At each lattice point there is one C_{60} molecule, so there are 60 atoms associated with each lattice point, or 240 atoms per unit cell!

2.5. NOTATION FOR CRYSTAL STRUCTURES

As noted, there is no systematic sequence for naming crystal structures. However, a *systematic notation* for describing crystal structures has been developed by W. B. Pearson (*The Crystal Chemistry and Physics of Metals*

can refer to the structures of sodium chloride, diamond cubic, or zinc blende, which differ from one another. However, this appears to be the best possible notation for the moment and is extensively used by the International Centre for Diffraction Data when referring to crystal structures, as you will see in Experimental Module 8.

2.6. MILLER INDICES

It is essential to have a way of uniquely describing different crystal planes in a lattice. Miller indices provide us with such a way. They are determined as follows:

1. Identify the points at which the plane intersects the a , b , and c axes. The intercept is measured in terms of fractions or multiples of the lattice parameters. If the plane moves through the origin, then the origin must be moved. We will show you how this works a little later.
2. Take reciprocals of the intercepts. This is done because if the plane never intersects one of the axes the intercept will be at ∞ . We don't want to have ∞ in the indices so we take reciprocals.
3. Clear the fractions. We only want whole numbers in the indices, but don't reduce the numbers to the lowest integers.
4. Enclose the resulting numbers in parentheses (). Negative numbers are written with a bar over the number ($\bar{1}$), and pronounced, for example, as bar one.

These steps give us the Miller indices of any plane in any crystal system, whether cubic, orthorhombic, or triclinic. Also note that the interaxial angles are not important in this case—the A face has indices (100) in all crystal systems, and the C face has indices (001) in all crystal systems. The actual values of the lattice parameters a , b , and c are also unimportant.

Let's determine the Miller indices of the planes A and B in Fig. 31.

For plane A :

	a	b	c
Intercepts	1	1	1
Reciprocals	1	1	1
Clear fractions (not necessary in this case)	1	1	1

Therefore, plane A has Miller indices (111).

TABLE 5. Symbols for the 14 Bravais Lattices

Symbol	System	Lattice Symbol
aP	Triclinic (anorthic)	P
mP	Simple monoclinic	P
mC	Base-centered monoclinic	C
oP	Simple orthorhombic	P
oC	Base-centered orthorhombic	C
oF	Face-centered orthorhombic	F
oI	Body-centered orthorhombic	I
tP	Simple tetragonal	P
tI	Body-centered tetragonal	I
hP	Hexagonal	P
hR	Rhombohedral	R
cP	Simple cubic	P
cF	Face-centered cubic	F
cI	Body-centered cubic	I

and Alloys, Wiley-Interscience, New York, 1972). This system classifies structures according to crystal system, Bravais lattice, and number of atoms per unit cell. The symbols give successively the crystal system, the Bravais lattice symbol, and the number of atoms per unit cell according to the designation in Table 5. For the crystal structures in Sec. 2.4 the Pearson symbols are given in Table 6.

Even though you can determine the crystal system, the Bravais lattice, and the number of atoms from this notation, you will not be able to differentiate different structures with the same notation. For example, cF8

TABLE 6. Pearson Symbols for Some Crystal Structures

Crystal Structure	Pearson Symbol
Simple cubic	cP1
Body-centered cubic	cI2
Face-centered cubic	cF4
Hexagonal close-packed	hP2
Cesium chloride	cP2
Sodium chloride	cF8
Diamond cubic	cF8
Zinc Blende	cF8
Fluorite	cF12
Spinel	cF56
Solid C_{60}	cF240

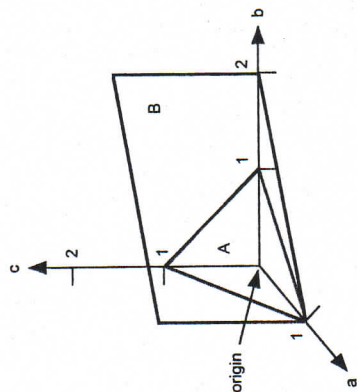


FIG. 31. Determination of Miller indices of planes.

For plane B:

	a	b	c
Intercepts	1	2	∞
Reciprocals	1	$\frac{1}{2}$	0
Clear fractions	2	1	0

Therefore, the Miller indices for plane B are (210).

Let's now look at what happens if the plane goes through the origin, as does plane C in Fig. 32. To index this plane we need to move the origin. Remember that the origin of the unit cell is arbitrarily chosen and can be taken to be any point. So let's move the origin to the point that originally had coordinates 0,1,0. Now we follow the same procedure as before, only using our new origin.

For plane C:

	a	b	c
Intercepts	∞	-1	∞
Reciprocals	0	-1	0
Clear fractions	0	-1	0

So plane C is the (0 $\bar{1}$ 0) plane.

If, however, you want to compare the Miller indices of planes in a unit cell, the origin must be the same for each plane. In such a situation, if the

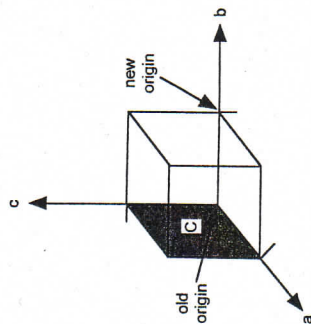


FIG. 32. Determination of Miller indices of a plane when it passes through the origin.

plane goes through the origin, instead of shifting the origin you can mentally shift the position of the plane to be parallel to the plane under consideration.

Look again at the cubic unit cell in Fig. 32. Notice that plane C is a face of the cube. If you closed your eyes and we rotated the cube 90° clockwise, when you opened your eyes you would not know that the cube had been moved. Hence, the face planes of a cube are all symmetrically related. There are six different face planes, but they are all equivalent. When a set of planes is equivalent, they are known as a *family* of planes. The faces of the cube form the family of {100} planes. Note that now we use a different

Multiplicity

As we have just seen, there are six planes in the {100} family of planes for a cubic crystal. These planes all have the same spacing. We can define the *multiplicity factor*, which is the number of planes in a family that have the same spacing. The multiplicity or multiplicity factor for the {100} family of planes of a cubic crystal is 6. The multiplicity factors are different for different planes, and these values for the cubic and hexagonal systems are listed in Appendix 6.

The multiplicity is important because in a polycrystalline or powder specimen consisting of many randomly oriented grains diffraction can occur, for example, from all the {100} planes. The intensity of a reflection therefore depends on the multiplicity. You will need to use the multiplicity factor in Experimental Module 7.

type of bracket to indicate a family of planes. Parentheses () are used for a specific plane, and braces { } are used for a family of planes. The six planes in the (100) family of planes for a cubic unit cell are (100), (010), (001), ($\bar{1}00$), (0 $\bar{1}0$), and (00 $\bar{1}$). For a tetragonal unit cell the {100} family of planes consists of four planes that have Miller indices (100), (010), ($\bar{1}00$), and (0 $\bar{1}0$), and the {001} family of planes consists of planes (001) and (00 $\bar{1}$). In the tetragonal system the {100} planes are not equivalent to the {001} planes since $a \neq c$.

When you start to work through the experimental modules you will find that there are peaks in the x-ray diffraction pattern that correspond to planes of the form ($nh\ nk\ nl$), where n is an integer. What is the relationship between the plane (hkl) and the planes ($nh\ nk\ nl$)? The two sets of planes are parallel, but the spacing of the ($nh\ nk\ nl$) planes is $1/n$ the spacing of the (hkl) plane. As shown in Fig. 33, the (100) and (200) planes are parallel, but the spacing of the (200) planes is half the spacing of the (100) planes. For example, in magnesium oxide (MgO) the spacing of the (200) planes is 0.2106 nm; the spacing of the (400) planes is 0.1053 nm.

The distance, d , between adjacent planes in the set (hkl) for a crystal in the cubic system is

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (11)$$

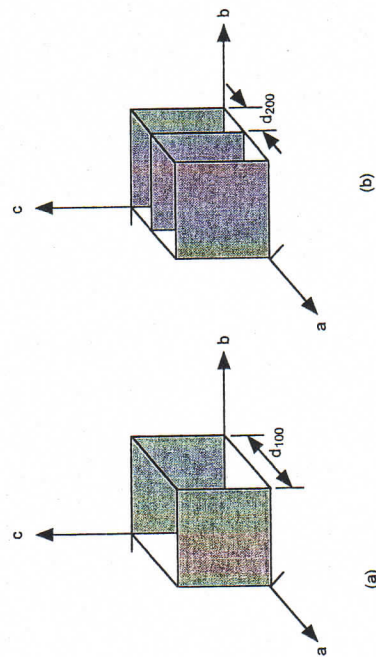


FIG. 33. Difference between the (100) and (200) planes.

This relationship, which can be derived quite simply by using analytical geometry, is very useful, and you will use it in Experimental Module 1 and others. Equation (11) applies only to cubic systems, but similar equations can be formulated for the other crystal systems and they are listed in Appendix 1.

The density of atoms on a particular plane (known as the planar density) can be determined from the equation

$$\text{Planar density} = \frac{\text{number of atoms on the plane}}{\text{area of the plane}} \quad (12)$$

For example, the planar density on the (100) plane of a material with the fcc structure, shown in Fig. 34, is

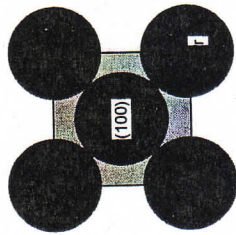
$$\text{Planar density} = \frac{2}{a^2} = \frac{2}{(2\sqrt{2}r)^2} = \frac{1}{4r^2}$$

Copper has an atomic radius of 0.128 nm, and the density of atoms on its (100) plane is 15.26 atoms/nm². Planes of the lowest indices (called low-index planes) have the largest d spacing and the greatest density of lattice points (and atoms), and, as we shall see, they produce the most intense reflections in the x-ray diffraction patterns.

A slightly different system is used for indexing planes in the hexagonal system. Although most of the important characteristics of hcp crystals can

Notation for Directions in a Crystal

Directions in a crystal can be determined in a very straightforward way if the coordinates u, v, w of two points lying along that direction are known. If a line connects two points A and B , then the direction of that line is $(u, v, w)_B - (u, v, w)_A$. For example, if a line points from the origin 0,0,0 (point A) to a point B located at 1,1,1, then the direction of that line is $[111]$. Note that for a specific direction we use brackets [] to enclose the indices (no commas between them). Keeping the same origin, the line $[\bar{1}\bar{1}\bar{1}]$ is antiparallel to the line $[111]$. In the same way that we can have a family of planes, we can also have a family of directions. The $[111]$ direction is across the body diagonal of the cube. A cube has four body diagonals, and if we count the antiparallel directions there are a total of eight body diagonal directions. The indices of these directions are $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}\bar{1}]$, $[\bar{1}11]$, $[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$, and $[1\bar{1}1]$. This family of directions is the $\langle 111 \rangle$ family. Note that we use angled brackets $\langle \rangle$ for a family of directions. In a cubic crystal the $[hkl]$ direction is perpendicular to the (hkl) plane.



$$\text{Planar density} = \frac{1}{4r^2}$$

FIG. 34. Atom arrangement on the (100) plane in an fcc crystal structure.

be described without the aid of this other system, we feel that you need to be familiar with it. (You will find it particularly useful if you do any electron diffraction of hexagonal materials in the transmission electron microscope.)

The hexagonal unit cell is described by three vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{c}$. Vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ lie at 120° to one another in the same plane, called the basal plane, and $\mathbf{c}$ is perpendicular to the basal plane, as shown in Fig. 22c. To show the symmetry of the hexagonal lattice, we often extend the unit cell, as indicated by the dashed lines in Fig. 22c. A third vector, $\mathbf{a}_3$, which also lies in the basal plane at 120° to $\mathbf{a}_1$ or $\mathbf{a}_2$, can be drawn in this extended cell. The indices of a plane in the hexagonal system, written (hki) , refer to these four axes and are known as the *Miller-Bravais* indices of the plane. To determine the Miller-Bravais indices of a plane in a hexagonal unit cell, follow exactly the same procedure for determining Miller indices in the cubic system. Figure 35 shows the Miller-Bravais indices of some of the low-index planes and directions in the hexagonal system.

Since the intercepts of a plane on the $\mathbf{a}_1$ and $\mathbf{a}_2$ axes determine its intercept on the $\mathbf{a}_3$ axis, the value of i depends on the values of both h and k . The relationship between these three indices is

$$h + k + i = 0 \quad (13)$$

Thus, it is easy to convert between the four-index Miller-Bravais system and the three-index Miller system. However, the advantage of the four-index system—and the main reason for its use—is that similar planes have similar indices (as we saw for the Miller system for a cubic

Notation for Directions in a Hexagonal Crystal

The directions in a hexagonal cell can be determined in exactly the same way as for a cubic unit cell. We use a three-index notation in which the indices refer to vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{c}$. As shown in Fig. 35, the directions in the hexagonal system can also be represented by a four-index notation, based on the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, and $\mathbf{c}$. The three-index notation is often preferred, but the four-index notation has the advantage that similar directions have similar indices. The two notations are related as follows. If $[UVW]$ are the indices of a direction referred to three axes and $[uvw]$ are the four-axis indices, then

$$\begin{aligned} U &= u - t \\ V &= v - t \\ W &= w \\ u &= (2U - V)/3 \\ v &= (2V - U)/3 \\ t &= -(u + v) = -(U + V)/3 \\ w &= W \end{aligned}$$

So the direction $[100]$ in the three-index notation becomes $[2\bar{1}\bar{1}0]$ in the four-index notation.

lattice). For example, the planes $(10\bar{1}0)$, $(01\bar{1}0)$, $(\bar{1}100)$, $(\bar{1}010)$, $(0\bar{1}10)$, $(1\bar{1}00)$ are the six side planes (called prism planes) of the hexagonal lattice; these are of similar type. In the Miller system, however, they are written (100) , (010) , $(\bar{1}10)$, $(\bar{1}00)$, $(0\bar{1}0)$, $(1\bar{1}0)$ and they definitely do not appear to be of a similar type.

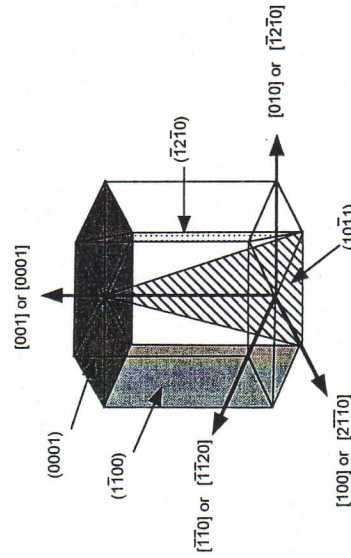


FIG. 35. Indices of planes and directions in the hexagonal system.

2.7. DIFFRACTION FROM CRYSTALLINE MATERIALS—BRAGG'S LAW

In Sec. 1.3 we said that an atom can scatter x-rays, and if many atoms are together then the scattered waves from all the atoms can interfere. If the scattered waves are in phase (coherent), they interfere in a constructive way and we get diffracted beams in specific directions. These directions are governed by the wavelength (λ) of the incident radiation and the nature of the crystalline sample. Bragg's law, formulated by W. L. Bragg in 1913, relates the wavelength of the x-rays to the spacing of the atomic planes.

To derive Bragg's law, we begin by assuming that each plane of atoms partially reflects the incident wave much like a half-silvered mirror. The

Diffraction and Reflection—What's the Difference?

In the derivation of Bragg's law we treat the planes of atoms as mirrors that can reflect the x-rays. This analogy between diffraction and reflection simplifies the derivation: we are all familiar with the reflection of visible light. The angle the incident x-ray beam makes with the lattice planes is the same as that made by the diffracted beam, so there is a qualitative similarity between diffraction of x-rays and reflection of visible light. Diffraction and reflection however, are actually different phenomena. Some important differences are listed here.

- The diffracted beam is composed of waves that have been scattered by all the atoms of the crystal lying in the path of the incident beam. Reflection of visible light is a surface phenomenon occurring in a layer about $\lambda/2$ thick.
- The diffraction of x-rays of a single wavelength takes place only at certain angles, θ (known as the Bragg angle), where there is constructive interference and Bragg's law is thus satisfied. The reflection of visible light takes place at any angle of incidence.
- The intensity of the beam of visible light reflected by a good mirror is almost the same as the intensity of the incident beam. The intensity of a diffracted beam of x-rays from a crystal is extremely small compared to that of the incident beam.
- In reflection, the angle of incidence (or reflection) is defined as the angle between the *normal* to the specimen surface and the incident (or reflected) beam. In diffraction, the angle of the incident beam (or the diffracted one) is defined as the angle between the specimen surface and the incident (or diffracted) beam.

x-rays are not really being reflected—they are being scattered—but it is very convenient to think of them as reflected, and we often call the planes the "reflecting planes" and the diffracted beams the "reflected beams," when we really mean diffracting planes and diffracted beams. Many books use these terms interchangeably, so you'll just have to get used to it. Because of this reflection analogy, the peaks that occur in an x-ray diffraction pattern are often called *reflections*.

Consider the diffracted wave in Fig. 36. It is assumed to make the same angle, θ , with the atomic planes as does the incident wave. Now the criterion for the existence of the diffracted wave is that the scattered ("reflected") x-rays should all be in phase across a wavefront such as BB'. For this to be so, the path lengths between wavefronts AA' and BB' for the rays shown must differ by exactly an integral number (n) of wavelengths λ . Therefore the path difference, δ , must be

$$\delta = n\lambda \quad (14)$$

where n is an integer. Now since lines CC' and CD in Fig. 36 are also wavefronts, we can write

$$\delta = DE + EC' = 2EC' \quad (15)$$

From elementary trigonometry,

$$\delta = 2CE \sin \theta \quad (16)$$

and because CE is the interplanar spacing d' we can write

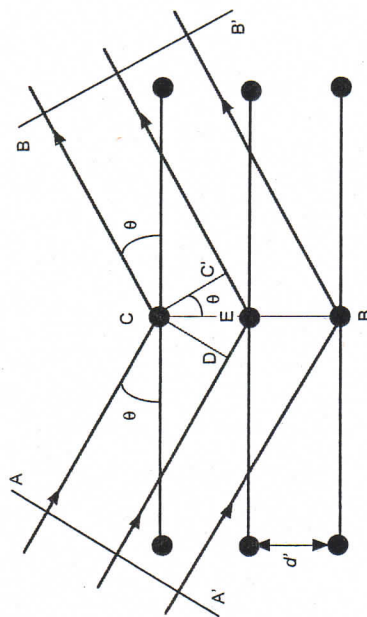


FIG. 36. Diffraction of x-rays by a crystal.

$$\delta = 2d' \sin \theta \quad (17)$$

By combining Eqs. (14) and (17), we get

$$n\lambda = 2d' \sin \theta \quad (18)$$

This equation is known as *Bragg's law* and is extremely important in indexing x-ray diffraction patterns and, hence, for determining things like the crystal structure of the material, as you will see in the experimental modules in Part II. It is well worth committing this equation to memory.

The parameter n is known as the *order of reflection* and is the path difference, in terms of number of wavelengths, between waves scattered by adjacent planes of atoms, as indicated by Eq. (14). A first-order reflection occurs when $n = 1$ and the scattered and incident waves have a path difference of one wavelength. When $n > 1$, the reflections are called higher-order.

We can rewrite Eq. (18) as

$$\lambda = 2 \frac{d'}{n} \sin \theta \quad (19)$$

where, as defined in Fig. 36, d' corresponds to the spacing between planes (hkl) and the parameter d'/n corresponds to the spacing between planes ($n h k n l$). So we can consider a higher-order reflection as a first-order reflection from planes spaced at a distance of $1/n$ of the previous spacing. By setting $d = d'/n$ and substituting into Eq. (19), we can write Bragg's law in the customary way as

$$\lambda = 2d \sin \theta \quad (20)$$

As an example, the 440 reflection can be considered a fourth-order reflection from the (110) planes of spacing d' or a second-order reflection from the (220) planes of spacing $d = d'/2$, or even as a first-order reflection from the (440) planes of spacing $d = d'/4$. This convention is consistent with our definition of Miller indices in Sec. 2.6, since the plane with Miller indices ($n h n k n l$) is parallel to the plane with Miller indices ($h k l$) but has a spacing $1/n$ times the spacing of the ($h k l$) planes. (Note: Higher-order reflections are very important for electron diffraction in the transmission electron microscope.)

2.8. THE STRUCTURE FACTOR

The *structure factor*, F , describes the effect of the crystal structure on the intensity of the diffracted beam. We start by showing the importance of

the structure factor in a qualitative way, and then we use a more quantitative approach. Consider the two orthorhombic unit cells in Fig. 37. One cell is base-centered orthorhombic, and the other is body-centered orthorhombic. Both cells have two atoms per cell. Diffraction from the (001) planes of the two cells is shown in Fig. 38. For the base-centered orthorhombic lattice in Fig. 37a, if Bragg's law is satisfied, this means that the path difference ABC between wave 1' and wave 2' is λ and diffraction will occur. In the same way for the body-centered lattice, if waves 1' and 2' are in phase, their path difference is λ . However, another plane of atoms is midway between the (001) planes in the body-centered lattice (Fig. 38b). The path difference between waves 1' and 3' is $\lambda/2$. These waves will be completely out of phase, destructive interference will occur, and we will get no diffracted beam. A wave reflected from the next plane down will cancel wave 2', and so on. The net result is that there is no 001 reflection for the body-centered lattice. [Note: The 001 reflection (without brackets) comes from diffraction of the x-ray beam by the (001) planes.] Thus, for certain structures some reflections will be absent from the diffraction pattern. They are known as *forbidden reflections*—they are forbidden by the structure factor. The intensity of the beam diffracted by all the atoms in the unit cell in a given direction predicted by Bragg's law is proportional to F^2 . The intensities of the reflections are what we see in the diffraction pattern. If $F^2 = 0$, there is no reflection.

Now we present the equation for calculating F . The derivation of this equation is beyond the scope of this book, but one of the texts in the Bibliography gives the derivation. Anyway,

$$F = \sum_i f_i e^{2\pi i(hu_i + kv_i + lw_i)} \quad (21)$$

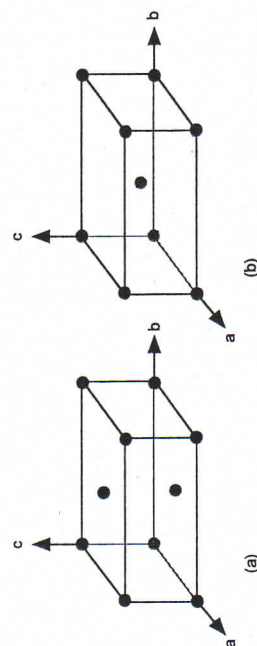


FIG. 37. (a) Base-centered and (b) body-centered orthorhombic unit cells.

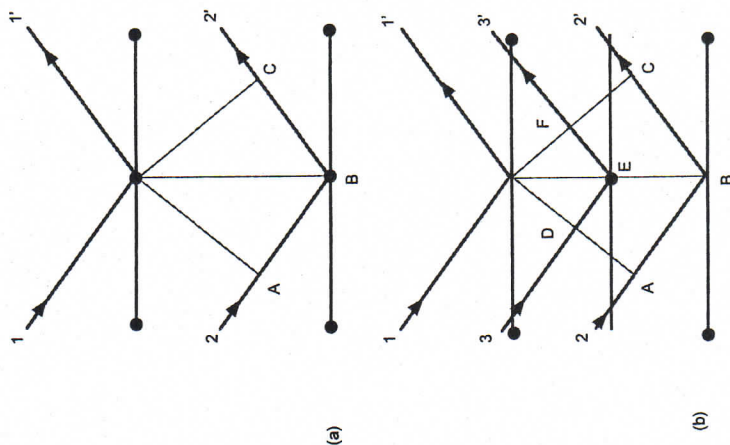


FIG. 38. Diffraction from the (001) planes of (a) base-centered and (b) body-centered orthorhombic unit cells.

where f is the atomic scattering factor, discussed in Sec. 1.3, u , v , and w are the atom positions in the unit cell, and h , k , and l are the Miller indices of the reflection. The summation is performed over all atoms in the unit cell. What does Eq. (21) tell us? Most importantly, it tells us what reflections hkl to expect in a diffraction pattern from a given crystal structure with atoms located at positions u, v, w . These are known as *selection rules*. Reflections for which $F = 0$ will have zero intensity and will not appear in the diffraction pattern; these reflections are called *forbidden*. Equation (21) is a completely general equation. It applies to *all* crystal lattices regardless of whether there are 1 or 100 atoms per unit cell and whether the structure is cubic, hexagonal, or triclinic.

Useful Relations in Evaluating Complex Exponential Functions

Calculating structure factors using Eq. (21) involves complex exponential functions. The following relations are useful:

$$\begin{aligned} e^{2\pi i} &= e^{3\pi i} = e^{5\pi i} = -1 \\ e^{4\pi i} &= e^{6\pi i} = e^{8\pi i} = 1 \\ e^{n\pi i} &= (-1)^n, \text{ where } n \text{ is any integer} \\ e^{n\pi i} &= e^{-n\pi i}, \text{ where } n \text{ is any integer} \\ e^{ix} + e^{-ix} &= 2 \cos x \end{aligned}$$

Let's do some examples to show how Eq. (21) is used. First consider a simple cubic crystal structure. We know from Sec. 2.4.1 that there is one atom per cell in the simple cubic structure located at 0,0,0. So we can insert the atomic coordinates 0,0,0 for u, v, w , respectively, in Eq. (21). Therefore the structure factor for the simple cubic structure is

$$F = f e^{2\pi i(0)} = f \quad (22)$$

For the simple cubic structure F is independent of h , k , and l , which means that *all* the reflections are allowed. In an x-ray diffraction pattern from a simple cubic material we would see reflections corresponding to beams diffracted by all the lattice planes in the material, such as (100), (110), (111), (200), (210), etc.

Now consider the fcc structure. It has four atoms, of the same type, per unit cell located, as noted in Sec. 2.4.1, at 0,0,0; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$. We can therefore insert the atomic coordinates u , v , and w in Eq. (21) and obtain

$$F = f e^{2\pi i(0)} + f e^{2\pi i(\frac{h}{2} + \frac{k}{2})} + f e^{2\pi i(\frac{h}{2} + \frac{l}{2})} + f e^{2\pi i(\frac{k}{2} + \frac{l}{2})} \quad (23)$$

which we can simplify as

$$F = f [1 + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)}] \quad (24)$$

If h , k , and l are all even or all odd (we say they are "unmixed"), then the sums $h+k$, $h+l$, and $k+l$ are even integers, and each term in Eq. (24) has the value 1. Therefore for the fcc structure,

$$F = 4f \quad \text{for unmixed indices}$$

If h , k , and l are mixed (i.e., some are odd and some are even), then the sum of the three exponentials is -1 . Let's suppose that $h = 0$, $k = 1$, and $l = 2$; i.e., the plane has indices (012). Then

$$F = f(1 - 1 + 1 - 1) = 0$$

and there is no reflection. Thus,

$$F = 0 \quad \text{for mixed indices}$$

Hence, for a material with the fcc structure we will see reflections corresponding to planes such as (111), (200), and (220), but we will not see reflections for planes (100), (110), (210), (211), etc.

In our two examples we chose cubic unit cells. *The structure factor is independent of the shape and size of the unit cell.* Any primitive cell will show reflections corresponding to diffraction from all the lattice planes; any face-centered cell will show reflections only when h , k , and l are unmixed. However, not all unmixed reflections may be seen in all face-centered cells; some may be absent depending on the number of atoms present in the unit cell. What we can be certain of is that no reflection will be observed when h , k , and l are mixed.

Now let's consider unit cells containing a basis of two atoms per lattice point. The NaCl structure, illustrated in Fig. 26, is built on the face-centered cubic (cubic F) Bravais lattice with a basis of two atoms, or, to be more accurate, ions (one Na and one Cl), per lattice point. To calculate the structure factor for NaCl, we can use the result for the fcc structure and include the contribution of the basis. The NaCl structure has eight atoms per unit cell, four Na and four Cl. (That we actually have ions instead of atoms makes little difference when determining F since we generally don't take into account the charge of the ion.) The atomic scattering factors for atoms and ions are slightly different at small angles, but at higher angles they are almost identical. In Table 7 we list the values of f as a function of $(\sin \theta)/\lambda$ for Na, Na⁺, Cl, and Cl⁻.

Normally, for NaCl, we take the basis to consist of one Na located at 0,0,0 and one Cl located at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (as we did in Sec. 2.4.3). We could just as well take the basis as the Na ion at 0,0,0 and the Cl ion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Look at Fig. 26 to see why this is so. We can write, using Eq. (21), the structure factor for the NaCl structure as

TABLE 7. Atomic Scattering Factors for Na, Na⁺, Cl, and Cl⁻

$(\sin \theta)/\lambda$ (nm ⁻¹)	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Na ⁺	10	9.546	8.374	6.894	5.471	4.290	3.395	2.753	2.305	1.997	1.785
Na	11	9.760	8.335	6.881	5.471	4.293	3.398	2.754	2.305	1.997	1.784
Cl	17	15.23	11.99	9.576	8.181	7.305	6.595	5.915	5.245	4.607	4.023
Cl ⁻	18	15.69	11.99	9.524	8.162	7.305	6.600	5.920	5.248	4.608	4.024

$$F = \left[f_{\text{Na}} e^{2\pi i(0)} + f_{\text{Cl}} e^{2\pi i(\frac{h}{2} + \frac{k}{2} + \frac{l}{2})} \right] \left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \right] \quad (25)$$

Simplifying gives

$$F = \left[f_{\text{Na}} + f_{\text{Cl}} e^{\pi i(h+k+l)} \right] \left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \right] \quad (26)$$

The first term in Eq. (26) represents the basis of the unit cell, the Na ion at 0,0,0 and the Cl ion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The second term is the same as the term in brackets in Eq. (24); it is the structure factor for the fcc structure. Unlike the calculation of the structure factor for a material with the fcc structure, for NaCl we have to include the atomic scattering factors for the different types of atoms. The selection rules for the NaCl structure are

$$\begin{aligned} F &= 4(f_{\text{Na}} + f_{\text{Cl}}) & \text{if } h, k, l \text{ are even} \\ F &= 4(f_{\text{Na}} - f_{\text{Cl}}) & \text{if } h, k, l \text{ are odd} \\ F &= 0 & \text{if } h, k, l \text{ are mixed} \end{aligned}$$

The third condition is the same for the fcc structure (this shows that NaCl has the face-centered cubic Bravais lattice). The *first two* conditions are new and depend on $f_{\text{Na}} \pm f_{\text{Cl}}$. That the NaCl structure contains more than four atoms per unit cell has not led to elimination of any reflections seen for the fcc structure, but it has led to a change in the intensity of the reflections. For example, the 111 reflection for NaCl will be weaker than the 200 reflection because the former involves the difference, rather than the sum, of the atomic scattering factors of the atoms. (In the next example we will see a case of elimination of reflections.) These intensity calculations help us determine atom positions in a crystal.

You can also arrive at the same set of selection rules for the NaCl structure by doing the determination long-hand. To do this, substitute the atom positions for the eight atoms in the unit cell of the NaCl structure into Eq. (21) and simplify the equation. But whenever a lattice contains a basis, the equation for the structure factor can be written out quickly. The first term is the atom positions in the basis, and the second term is that for the Bravais lattice of the crystal structure.

We will do one more example to illustrate the point we just made; we will determine F for the diamond cubic structure. The diamond cubic structure is based on the face-centered cubic Bravais lattice with a basis of two atoms, giving a total of eight atoms per unit cell. The atoms in the basis are located at 0,0,0 and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. Both atoms are of the same type (in diamond they are all carbon atoms), so

$$F = \left[f_{\text{C}} + f_{\text{C}} e^{2\pi i(\frac{h}{4} + \frac{k}{4} + \frac{l}{4})} \right] \left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \right] \quad (27)$$

The first term represents the basis, and the second term the face-centered cubic Bravais lattice. The selection rules for the diamond cubic structure are a little more complicated:

$$\begin{aligned}
 F &= 0 && \text{if } h, k, l \text{ are mixed (same condition as for the fcc structure)} \\
 F &= 4f_c(1 + e^{i\pi(h+k+l)}) && \text{if } h, k, l \text{ are odd} \\
 F &= 0 && \text{if } h, k, l \text{ are even and } h + k + l = 2N, \text{ where } N \text{ is odd (e.g., the 200 reflection)} \\
 F &= 8f_c && \text{if } h, k, l \text{ are even and } h + k + l = 2N, \text{ where } N \text{ is even (e.g., the 400 reflection)}
 \end{aligned}$$

Once again, $F = 0$ if h, k , and l are mixed. This is the same condition for the fcc structure, but it applies to the diamond cubic structure because it has the same Bravais lattice as the fcc. If all indices are odd, the expression is complex. However, remember that in the diffraction pattern we see the intensities of the reflections (i.e., F^2 not F), so we consider F^2 , which is $32f_c^2$.

The Lorentz-Polarization Factor

The Lorentz-polarization factor is actually a combination of two factors—the Lorentz factor and the polarization factor—that influence the intensity of the diffracted beam. The origin of the polarization factor is that the incident beam from the x-ray source is unpolarized. It may be resolved into two plane-polarized components, and the total scattered intensity is the sum of the intensities of these two components, which depends on the scattering angle (i.e., 2θ).

The Lorentz factor takes into account certain geometrical factors related to the orientation of the reflecting planes in the crystal, which also affect the intensity of the diffracted beam.

$$\text{Lorentz-polarization factor} = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

Values of this factor are given in Appendix 7. The Lorentz-polarization factor varies strongly with Bragg angle, θ , and the overall effect is that the intensity of reflections at intermediate Bragg angles is decreased compared to those at high or low angles. The Lorentz-polarization factor is important in all intensity calculations, and we will use it in Experimental Module 7.

Let's now briefly summarize some of the similarities and differences between the NaCl structure and the diamond cubic structure. Both structures are based on the face-centered cubic Bravais lattice and have eight atoms per unit cell. However, because the atom positions are different in the two structures the x-ray diffraction patterns are different: there are different reflections and different intensities. The absence of some reflections and the differences in intensities (F^2) give us a way to find the atom positions in the lattice. However, in the experimental modules in Part II we do not emphasize this aspect.

As an exercise, what do you think the selection rules would be for the zinc blende structure? The zinc blende structure is similar to the diamond cubic, but the basis consists of two different types of atom, one S at 0,0,0 and one Zn at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. (The answer is given in Table 8.)

Table 8 summarizes the results of structure factor calculations. Note that the intensity of a diffracted beam depends not only on F^2 but on other factors also. The integrated intensity, I , of a diffracted beam is

$$I = F^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M} \quad (28)$$

where p is the multiplicity factor, the term in parentheses is the Lorentz-polarization factor, and e^{-2M} is the temperature factor.

TABLE 8. Examples of Selection Rules for Different Crystal Structures

Crystal Type	Bravais Lattice	Reflections Present for	Reflections Absent for
Simple	Primitive	Any h, k, l	None
Body-centered	Body-centered	$h + k + l$ even	$h + k + l$ odd
Face-centered	Face-centered	h, k , and l unmixed	h, k , and l mixed
NaCl	Face-centered cubic	h, k , and l unmixed	h, k , and l mixed
Zinc blende	Face-centered cubic	h, k , and l unmixed	h, k , and l mixed
Diamond cubic	Face-centered cubic	As fcc, but if all even and $h + k + l \neq 4N$; then absent	h, k , and l mixed and if all even and $h + k + l \neq 4N$
Base-centered	Base-centered	h and k both even or both odd ^a	h and k mixed ^a
Hexagonal close-packed	Hexagonal	$h + 2k = 3N$ with l even $h + 2k = 3N \pm 1$ with l odd $h + 2k = 3N \pm 1$ with l even	$h + 2k = 3N$ with l odd $h + 2k = 3N \pm 1$ with l odd $h + 2k = 3N \pm 1$ with l even

^aThese relations apply to a cell centered on the C face. If reflections are present only when h and k are unmixed, or when k and l are unmixed, then the cell is centered on the B or A face, respectively.

The Temperature Factor

The temperature factor takes into consideration the effect of temperature on the intensity of the reflections in the x-ray diffraction pattern. At all temperatures, even at the absolute zero of temperature, the atoms in a crystal are undergoing thermal vibration about their mean positions. One of the effects of this vibration is that the intensities of the reflections decrease as the temperature increases. It is easy to see why. We normally view each lattice plane as consisting of atoms in very well defined positions and the planes themselves are perfectly flat and of uniform thickness. Thermal vibration of the atoms causes the spacing of the planes to become rather ill defined. Diffraction by sets of parallel planes at the Bragg angle is no longer perfect, as it would be if the atoms were not moving.

If the average displacement of an atom from its mean position is u , the intensity of the reflections decreases as u increases (i.e., as the temperature increases). The value of u depends on the elastic constants of the crystal—the stiffer the crystal the lower the value of u .

At a fixed temperature (say room temperature) the intensity decreases as θ increases because at large Bragg angles planes with low values of d are diffracting. Hence, high-angle reflections are decreased in intensity relative to low-angle reflections. This effect is taken into account by the temperature factor e^{-2M} , where M is a function of several variables, including u and the diffraction angle 2θ .

Calculation of the temperature factor is quite complicated, and the data required to do this calculation are not readily available for nonmetallic materials and alloys. For this reason we will not use the temperature factor in our calculation of intensities in Experimental Module 7.

2.9. DIFFRACTION FROM AMORPHOUS MATERIALS

X-ray diffraction can also be used to provide information about the structure of amorphous or noncrystalline materials such as glass. In fact, it was early x-ray diffraction work by Warren and his colleagues that led to some of the early theories of glass structure. X-ray diffraction patterns from amorphous SiO_2 (silica glass) and a crystalline form of SiO_2 (cristobalite) are shown in Fig. 39. The crystalline material shows a series of sharp peaks, or reflections, due to diffracted beams arising from different lattice planes. The glass shows one broad peak centered in the range in which the strong peak was seen in the diffraction pattern of the crystalline material of the same composition. This observation led to the conclusion that in an amorphous material there is no long-range order as there is in a crystal. The amorphous material only exhibits short-range order. You

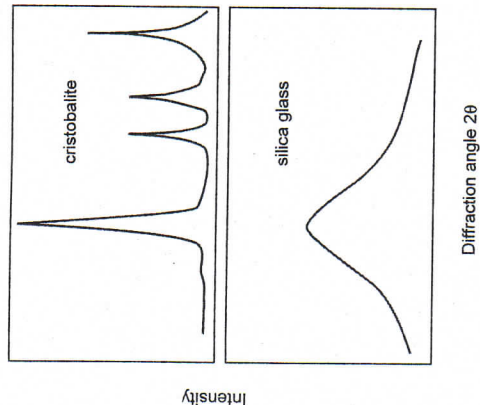


FIG. 39. X-ray diffraction patterns from (a) crystalline cristobalite and (b) silica glass.

will find out in Experimental Module 6 that broadening of the x-ray peaks occurs when the crystallite or grain size of the material is very small ($<0.1 \mu\text{m}$). Peak broadening increases with decreasing crystallite size. Figure 40 illustrates the difference between (a) an ordered crystalline form and (b) a possible structure of a glassy form of the same composition.

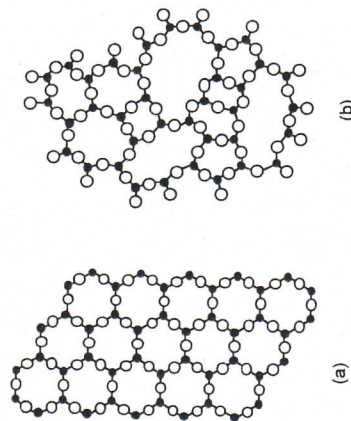


FIG. 40. Schematic representation of (a) a crystalline form and (b) an amorphous form of the same composition.

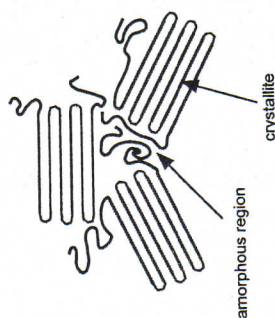


FIG. 41. Crystallites in a polymer.

Polymers are composed of long molecular chains normally arranged in a random way. In some polymers, particularly those with simple linear conformations, the chains can become organized into ordered regions as shown in Fig. 41. These ordered regions are called crystallites. Many polymers are partly crystalline; they have crystallites dispersed in an otherwise amorphous matrix. For example, polyethylene (PE) consists of molecular chains of composition $-(CH_2-CH_2)_n-$ and polytetrafluoroethylene (PTFE) has molecular chains of composition $-(CF_2-CF_2)_n-$ and both show high volume fractions of crystallites. The size of the crystallites in a partly crystalline polymer can be determined by x-ray diffraction by measuring the broadening of the diffraction peaks.

Practical Aspects of X-Ray Diffraction

3.1. GEOMETRY OF AN X-RAY DIFFRACTOMETER

In this and the following sections we provide some general experimental background to the x-ray diffraction technique. Each manufacturer's instrument has its unique features, and for specific details you should refer to the instrument operating manual that came with your diffractometer. The experimental geometry used in the powder diffraction method is illustrated in Fig. 42. The three basic components of an x-ray diffractometer are the

- X ray source
- Specimen
- X ray detector

and they all lie on the circumference of a circle, which is known as the *focusing circle*. The angle between the plane of the specimen and the x-ray source is θ , the Bragg angle. The angle between the projection of the x-ray source and the detector is 2θ . For this reason the x-ray diffraction patterns produced with this geometry are often known as θ - 2θ (theta-two theta) scans. In the θ - 2θ geometry the x-ray source is fixed, and the detector moves through a range of angles. The radius of the focusing circle is not constant but increases as the angle 2θ decreases, as you can see from Fig. 42. The 2θ measurement range is typically from 0° to about 170° . In an experiment you need not necessarily scan the whole range of detector angles. A 2θ range from 30° to 140° is an example of a typical scan. The choice of range depends on the crystal structure of the material

of the diffractometer circle is fixed. The diffractometer circle is also referred to as the *goniometer circle*. The goniometer is the central component of an x-ray diffractometer and contains the specimen holder. It has arms to which the x-ray source and the detector are mounted. In most powder diffractometers the goniometer is vertically mounted, but in other diffractometers, for example those used to study thin films, the goniometer may be horizontally mounted.

3.2. COMPONENTS OF AN X-RAY DIFFRACTOMETER

3.2.1. The X-Ray Source

X-rays are generated, as described in Sec. 1.2, by directing an electron beam of high voltage at a metal target anode inside an evacuated x-ray tube. The voltage and current are both variables, and you should check the operating manual or with the instrument operator or technician to see what values you should use. For all of the experimental modules in Part II use whatever values of voltage and current are recommended for your instrument. Suitable operating voltages depend on the target metal (remember that they should be above the critical excitation potential for knocking out K electrons), e.g., molybdenum 50 to 55 kV, copper 25 to 40 kV, iron 25 to 30 kV, and chromium 25 kV. Copper is the most frequently used target, and typical operating conditions are 40 kV and 30 mA.

The choice of radiation depends on several factors, including how penetrating it is (we do not want the x-rays absorbed by the specimen). Recall from Sec. 1.2 that when an incident electron has sufficient energy it can knock out an electron from the K shell of an atom. When the atom returns to the ground state, an x-ray is emitted (a characteristic x-ray). In a similar way, an incident x-ray, with enough energy, can also knock out an electron from the K shell of the atom. The atom is now in an excited state, and an electron in a higher energy level then fills the hole in the K shell, to return the atom to its ground state, with the emission of an x-ray. The emitted radiation in this case is known as *fluorescent radiation*. It radiates in all directions and has exactly the same wavelength as the characteristic radiation.

If an element in the specimen has an atomic number slightly below that of the target metal, the x-rays will be strongly absorbed. This results in a decrease in the intensity of the diffracted beam and a large amount of fluorescent radiation, which increases the background signal. For example, if we are using Cu K α x-rays, which have an energy of 8.04 keV,

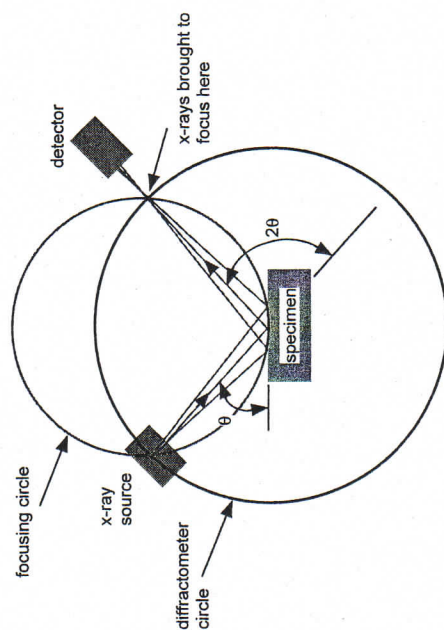


FIG. 42. Geometry of an x-ray diffractometer.

(if known) and the time you want to spend obtaining the diffraction pattern. For an unknown specimen a large range of angles is often used because the positions of the reflections are not known, at least not yet!

The θ - 2θ geometry is the most common, but you may come across other geometries. In the θ - θ (theta-theta) geometry both the x-ray source and the detector move in the vertical plane in opposite directions above and below the specimen. In some forms of x-ray diffraction analysis the sample is tilted about an axis ψ (psi). This scan, often known as an ω (omega) scan, provides a measure of the strain (change in length divided by original length, $\Delta l/l$) in the specimen, from which it is then possible to determine the stress (force per unit area, F/A). The specimen can be rotated about the ψ axis and about an orthogonal axis called the ϕ (phi) axis. This type of scan, sometimes called a ϕ scan, is particularly useful for characterizing oriented polycrystalline thin films where the rotation axis of the grain boundaries is often predominantly aligned perpendicular to the surface of the film. The ω scan and ϕ scan are very specialized techniques, yet, although very useful, are not widely used. In the remainder of this chapter we consider only the θ - 2θ geometry.

The *diffractometer circle* in Fig. 42 is different from the focusing circle. The diffractometer circle is centered at the specimen, and both the x-ray source and the detector lie on the circumference of the circle. The radius

Absorption

Radiation incident upon a material is absorbed when electrons in the atoms that make up the material are excited from a lower energy state (usually the ground state) to a higher energy state. In a solid, consisting of many atoms, the energy levels are in the form of bands. When we are talking about electronic applications, we refer to the outer two bands as the valence band and the conduction band. But when we are talking about optical properties of materials it is common to refer to the two bands as the valence band and the absorption band, respectively. The selective absorption of radiation gives rise to color in many materials.

to examine a specimen containing iron (atomic number 26), the x-rays have enough energy to eject a K shell electron from iron (the critical ionization energy for a K shell electron in iron is about 7 keV). The result is the emission of fluorescent radiation. To avoid fluorescence from specimens containing iron and other transition elements, Cr K α radiation, which has an energy of 5.41 keV (lower than the critical ionization energy for a K shell electron in iron), may be used.

As noted in Sec. 1.2, the intensity of the characteristic lines in the x-ray spectrum increases with an increase in the applied voltage. But the values of current and voltage will not affect the positions (2 θ values) of the reflections in the diffraction pattern. The load (product of voltage and current) is usually kept just under the maximum rating (typically around 2 kW) for the x-ray tube in order to make it last longer.

In most diffractometers a fixed value of the x-ray wavelength λ , is used. For example, in the experiments described in the experimental modules we have assumed that Cu K α radiation will be used, which has a weighted average wavelength $\lambda = 0.154184$ nm. Some of the commonly used K wavelengths were listed in Table 2, but Cu K α is generally the most useful because of its high intensity.

3.2.2. The Specimen

In a typical x-ray diffraction experiment, a thin layer of crystalline powder is spread onto a planar substrate, which is often a nondiffracting material such as a glass microscope slide, and exposed to the x-ray beam. You will use this procedure to complete the experimental modules in Part II. The quantity of powder used for each experiment is quite small, usually a few milligrams (1 mg = 10^{-3} g).

Ideally, the specimen should contain numerous small, equiaxed randomly oriented grains. The grain size of the powders should be ≤ 50 μm ; i.e., the powder can pass through a U.S. standard 325 mesh sieve. For materials with high symmetry, such as cubic or hexagonal, the grain size of the powder can be up to about 70 μm , because of the multiplicity factor. If you refer to Sec. 2.6 you will see why the multiplicity factor becomes important for crystals with high symmetry. In such crystals several planes can contribute to each reflection; e.g., diffraction from the (100), (010), (001), ($\bar{1}00$), ($0\bar{1}0$), and ($00\bar{1}$) planes in a cubic crystal all contribute to the same reflection (the 100 reflection).

When the grains are very small, <1 μm , broadening of the peaks in the diffraction pattern occurs, as illustrated in Experimental Module 6. If the grains in the specimen are too large, then effects associated with preferred orientation may become significant. Later in this section we describe what these effects are.

It is important that the specimen you choose for analysis be representative of the entire sample. For example, if you are going to characterize a mixture of two powders (as in Experimental Module 7) or if a standard has been added (as in Experimental Modules 6 and 7), be sure that the two powders are thoroughly mixed, otherwise the small amount you take for x-ray diffraction analysis may not contain the two powders in the same proportion as in the global mixture. In addition to using powders, the specimen may also be a sheet or film of a polycrystalline material, for example a sheet of aluminum or a polycrystalline film on a substrate (e.g., a TiN film on steel).

As noted, in a θ - 2θ scan the position of the incident x-ray beam with respect to the specimen is fixed. In a powder or a polycrystalline material in general, the grains are often randomly oriented, and some grains will always be oriented in a favorable direction with respect to the x-ray beam, to allow diffraction to occur from a specific set of lattice planes. Each set of lattice planes in the crystal having spacings $d_1, d_2, d_3, \dots$, will diffract at different angles $\theta_1, \theta_2, \theta_3, \dots$, where θ increases as d decreases in such a way as to satisfy Bragg's law. The intensity of the diffracted beam at each of these different angles is detected, and this is what forms the x-ray diffraction pattern.

If the specimen is textured (i.e., there is a preferred grain orientation) then some of the reflections in the x-ray diffraction pattern may be anomalously intense or some may be absent. In other words, there may be a change in the relative intensities of the reflections compared to those obtained with a randomly oriented powder specimen. By comparing the relative intensities of the reflections from the textured specimen with the

random powder pattern, we can determine the degree of preferred orientation. Texturing is common in materials that have a layered structure with easy cleavage between the layers (e.g., mica), thin films, and heavily cold-worked metals. The reflections missing in a diffraction pattern obtained from a textured material are missing not because they are forbidden by the structure factor but because the grains are not oriented in the correct way to allow diffraction to occur from these planes. For example, in a cubic material in which the [100] direction of all the grains is oriented perpendicular to the surface of the specimen, diffraction occurs from the (100) planes but not from the (001) or the (010) planes. Therefore, we would expect the relative intensity of the 100 reflection to be weaker in the textured specimen than in the randomly oriented specimen.

Most specimens are flat, and as you can see in Fig. 42 the face of a flat specimen forms a tangent to the focusing circle. However, for perfect focusing the specimen should be curved to fit the circumference of the focusing circle. For most specimens it is not possible to meet this requirement. The flat specimen causes some broadening of the diffracted beam and can result in a small shift in peak position toward smaller angles, particularly at 2θ angles less than about 60° . These effects can be reduced by decreasing the horizontal divergence (the spread or width) of the incident beam, but this, in turn, leads to a decrease in intensity.

3.2.3. The Optics

On the x-ray source side, a line source of x-rays passes through a series of slits called Soller slits. These slits consist of a series of closely spaced parallel metal plates that define and collimate (i.e., make it parallel) the incident beam. Soller slits are typically about 30 mm long and 0.05 mm thick, and the distance between the plates is about 0.5 mm. The slits are usually made of a metal with a high atomic number, such as molybdenum or tantalum (because of their high absorption capacity). The arrangement of slits in an x-ray diffractometer is illustrated in Fig. 43. The divergence slit on the incident beam side defines the divergence (or width) of the incident beam.

After the beam has been diffracted by the specimen, it passes through another set of slits, as shown in Fig. 43. The antiscatter slit reduces the background radiation, improving the peak-to-background ratio, by making sure that the detector can receive x-rays only from the specimen area. The beam converges on passing the receiving slit, which defines the width of the beam admitted to the detector. An increase in slit width increases the maximum intensity of the reflections in the diffraction pattern but

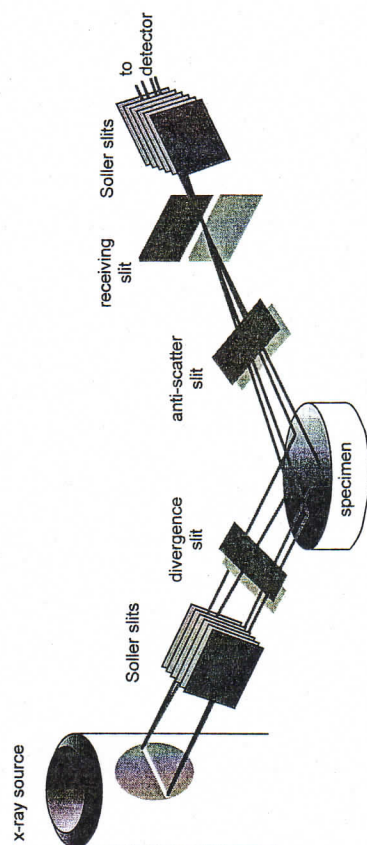


FIG. 43. Arrangement of slits in a diffractometer.

generally results in some loss of resolution. However, the integrated intensity, I , of a reflection is independent of slit width. The integrated intensity is the peak area as shown in Fig. 44. A change in slit width does not change the ratio of integrated intensities of two peaks, I_1/I_2 , but it most

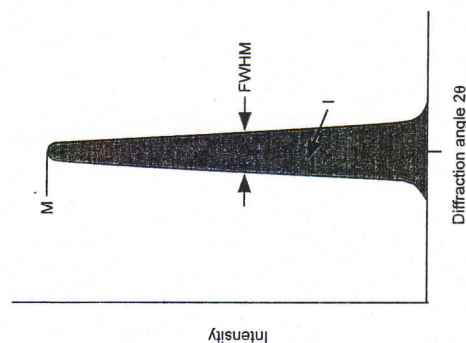


FIG. 44. Typical peak in an x-ray diffraction pattern.

likely will change the ratio of the maximum intensities M_1/M_2 . That is why we always use the integrated intensity. Furthermore, because it is difficult to measure absolute intensities, we always take the relative integrated intensities of the reflections. This is what we use in all the experimental modules in Part II.

Another set of Soller slits is placed after the receiving slit on the diffracted beam side, before the monochromator. We now describe the function of the monochromator.

To achieve monochromatic radiation, we must remove unwanted radiation, say the $K\beta$ radiation. In early x-ray diffractometers this was achieved with a filter that strongly absorbed the $K\beta$ radiation. In most modern diffractometers a monochromating graphite crystal is used. The graphite monochromator is usually placed in the diffracted beam, i.e., after the specimen (Fig. 45) because it suppresses the background radiation (such as fluorescent radiation) originating from the specimen. The monochromator is oriented in such a way that it diffracts *only* the $K\alpha$ radiation. The beam still consists of the wavelengths $K\alpha_1$ and $K\alpha_2$. Although it is possible to further isolate the $K\alpha_1$ component from the $K\alpha_2$ component by using a high-quality monochromator placed in the path of the incident beam (i.e., before the specimen), in most cases this is not done because there may be a loss in beam intensity. Further, it is often very useful to have both components in the x-ray diffraction pattern, as you will see in Experimental Module 3 when we demonstrate how to obtain precise measurements of the lattice parameter. If a monochromator

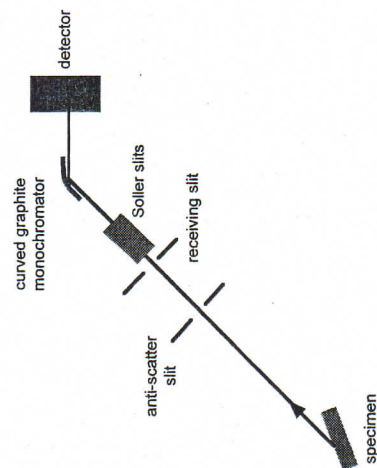


FIG. 45. Schematic of a diffractometer with a monochromating crystal in the diffracted beam.

is used, the set of Soller slits on the diffracted beam side, situated just before the monochromator, is not essential because the monochromating crystal reduces the divergence of the beam.

There has been, and continues to be, considerable research and development activities in x-ray optics. These activities are directed primarily toward collimating or focusing x-rays. For x-ray diffraction we require a well-collimated beam of x-rays. The approach discussed so far to achieve this uses a slit to eliminate x-rays not traveling in the preferred direction. The limitation of this approach is that it rejects most of the output from the x-ray source and results in a relatively low flux of x-rays delivered to the specimen. One method, first proposed in 1986, to capture a large amount of x-rays from the source and deliver a significant proportion of them to the specimen is the use of a special type of optical fiber called a polycapillary optical fiber. Each optical fiber consists of hundreds or even thousands of tiny hollow glass capillaries. The outer diameter of the fibers varies from 300 to 600 μm , and each capillary has an inner diameter between 3 and 50 μm . The hollow glass capillaries act as waveguides, and the x-rays undergo total reflection at the capillary surface, as shown in Fig. 46. In a capillary of length 100 mm, the photon may undergo as many as 100 reflections. After several years of research and development, these polycapillary optical fibers are now commercially available.

Another method developed for collimating and focusing x-rays uses a mirror consisting of a series of layers (called a multilayer) (Fig. 47). Typically the mirror has 50 layers each of tungsten and silicon. For

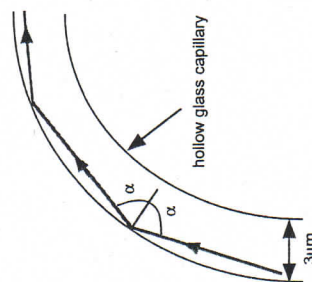


FIG. 46. X-ray beam undergoing multiple total reflections in a hollow glass capillary.

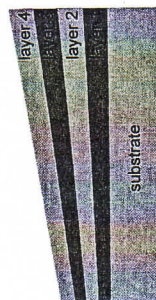


FIG. 47. Schematic of multilayer mirror.

collimating x-rays the mirror is parabolic, and for focusing x-rays the mirror is elliptical. The thickness of the layers is not uniform across the substrate, and this is the key to why these mirrors work. The incident angle of a divergent beam of x-rays onto a parabolic or elliptical surface changes from point to point along the length of the mirror. If the multilayer coating was uniform across the substrate surface, it would not reflect the same wavelength of radiation across its surface. Careful grading of the spacing of the layers makes it possible to collect a large solid angle from an x-ray source. A further advantage of these multilayer mirrors is that they render the beam monochromatic. Parallel beam x-ray diffraction using a parabolic mirror on the incident beam side has particular application in the analysis of irregularly shaped specimens, transparent materials, and high-resolution x-ray diffraction.

3.2.4. The Detector

Three main types of x-ray detector are used on x-ray diffractometers:

1. Proportional
2. Scintillation
3. Solid-state

To determine which type of detector is used on your apparatus, consult the equipment manual or ask the technician. In many new instruments, particularly those dedicated to powder work, a proportional detector is probably used. Scintillation detectors, although common on early instruments and still available, are not widely installed on new diffractometers. The solid-state detector offers many advantages, as we will see, but its high cost is often a factor against its use. Although you don't need to know how the detector works in order to use it, a basic understanding will help you realize why certain experimental procedures are adopted.

Proportional Detector

The gas proportional detector (Fig. 48) is the most commonly used. It consists of a tube filled with a noble gas (e.g., xenon) and has a thin positively charged tungsten wire running down the center. When an x-ray photon enters the tube through a thin window, it is absorbed by an atom of the gas and causes a photoelectron to be ejected. A photoelectron is simply an electron produced by ionization of an atom by a photon. The ionization energy of the noble gases is about 30 eV; one copper x-ray photon (8.04 keV) gives rise to about 270 electron-ion pairs. The photoelectron loses its energy by ionizing other gas atoms. The released electrons are attracted to the positively charged tungsten wire, giving rise to a charge pulse. For each x-ray photon entering the detector a few hundred electrons are created. This produces only a small amount of charge, which needs further amplification. However, if the positive potential on the tungsten wire is large enough (about 1 kV), then the electrons produced as a result of the initial x-ray photon are accelerated. When they collide with other gas atoms, they produce further ionization (known as secondary ionization or "avalanche" production), which results in a large increase in the number of electrons and, hence, an increase in the charge by several orders of magnitude. The collected charge (the size of the pulse) is proportional to the energy of the incident photon, and hence the term "proportional detector." The proportionality is important because it allows us to distinguish between x-ray photons with different energies (wavelengths).

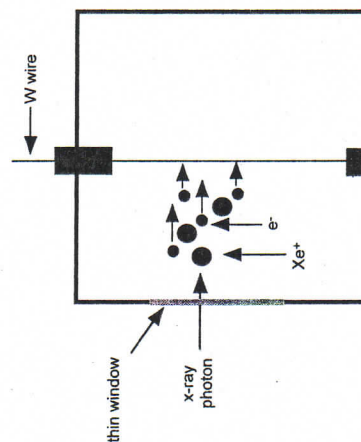


FIG. 48. Gas proportional detector.

Fluorescence

Fluorescence is the emission of electromagnetic radiation, normally visible light, from a material when it goes from an excited state, in which it has absorbed energy, to a lower energy state. In fluorescence, this transition occurs very rapidly (within 10 ns). Figure 50 shows an energy-band diagram for a material with a band gap (an energy gap E_g) between the valence and conduction bands. Absorption of a photon with energy equal to the energy gap causes an electron in the valence band to be excited into the conduction band. When the electron falls back into the valence band, a photon with energy E_g is emitted. If E_g is in the visible part of the electromagnetic spectrum, visible light is emitted. In the NaI:Tl⁺ crystal described in this section, the x-rays excite some of the electrons from the valence band to the conduction band in NaI. The alkali halides have large band gaps and so do not produce fluorescence; however, these excited electrons transfer some of their energy to the electrons in the Tl⁺ ion. When the Tl⁺ ion returns to its ground state, light is emitted. The difference between the energy levels in the Tl⁺ ion corresponds to light in the visible part of the electromagnetic spectrum.

In a position-sensitive proportional detector, the tungsten wire is long, and the time required for the pulse to travel from the point of impact of the electrons with the wire to the end of the wire is used to determine the position of the x-ray.

Scintillation Detector

In a scintillation detector (Fig. 49) the incident x-rays cause a crystal (for example, sodium iodide doped with 1% thallium) to fluoresce. For an NaI crystal doped with Tl⁺ the fluorescence is in the violet part ($\lambda \approx 420$ nm) of the electromagnetic spectrum. A flash of light (a scintillation) is produced in the crystal for every x-ray photon absorbed. The amount of light emitted is proportional to the x-ray intensity and can be measured by a photomultiplier. The size of the pulses is proportional to the energy of the x-ray photon absorbed.

Although, the scintillation detector is very efficient over a range of x-ray wavelengths, its energy resolution is not as good as the proportional or solid-state detectors (Fig. 51). The energy resolution is determined by the peak widths: the narrower the peaks the better the energy resolution. As a result, it is more difficult to discriminate, using a scintillation detector, between x-ray photons of different wavelengths (energies) on the basis

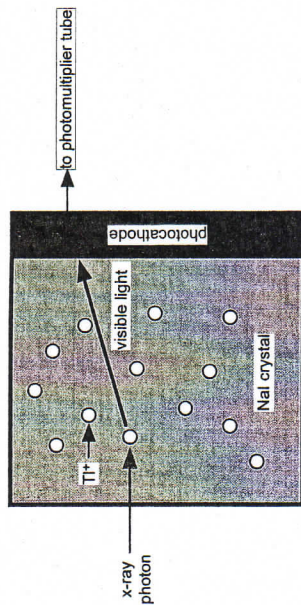


FIG. 49. Scintillation detector.

of pulse size. Scintillation detectors are rare on modern x-ray diffractometers.

Solid-State Detector

Figure 52 is a schematic of a solid-state detector. The detector is a single crystal consisting of a sandwich of intrinsic (pure) silicon between a *p*-type layer (where holes are the majority charge carriers) and an *n*-type layer (where electrons are the majority charge carriers), forming a *p-i-n* (*p*-type-intrinsic-*n*-type) diode. Intrinsic silicon is essential for the detec-

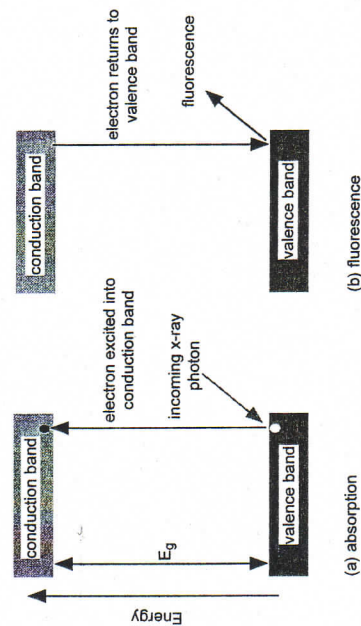
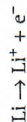


FIG. 50. Illustration of fluorescence.

Intrinsic silicon is very difficult to make commercially and usually contains impurities (mostly boron) that make it act as a *p*-type semiconductor (i.e., there are excess holes). To compensate for these unintentionally present impurities, we add lithium (we say that the Li is "drifted" in) either by thermal diffusion under an applied potential or by ion implantation. On one side of the silicon crystal the lithium concentration is high, and on the other side it is low. The lithium exists in the crystal as Li^+ , so, as indicated by the following reaction, free electrons are produced:



One side of the crystal (where the concentration of Li^+ is high) becomes *n*-type (because there are now excess free electrons). In the middle there is a region where the crystal is intrinsic because the free electrons produced by the reaction have recombined with the excess holes that were already there. The other side of the crystal is *p*-type because of the impurities present in the original crystal. The crystal is called a lithium-drifted silicon crystal and denoted $\text{Si}(\text{Li})$. Very thin films of gold are deposited onto the front and back faces of the crystal for the electrical contacts.

When x-rays interact with the silicon crystal they excite electrons from the valence band into the conduction band, creating an electron-hole pair (the band gap in silicon is 1.1 eV). When a reverse-bias potential is applied to the crystal (i.e., a negative charge is applied to the *p*-type region and a positive charge to the *n*-type region), the electrons and holes are separated and a charge pulse of electrons can be measured. The number of electrons or holes created is directly proportional to the energy of the incoming x-ray. Creation of an electron-hole pair in silicon at 77 K, the operating temperature of the detector, requires an average energy of 3.8 eV. It is important to realize that this energy is not the energy of the band gap. Silicon has an indirect band gap (a topic beyond the scope of this book), and transitions from the valence band to the conduction band involve the participation of a phonon (a quantum unit of lattice vibrational energy). Direct transitions (without the help of a phonon) are not permissible below about 3.4 eV.

The number of electron-hole pairs (n) created by absorption of one photon is

$$n = \frac{\text{energy of the photon}}{\text{energy required to create one electron-hole pair}} \quad (29)$$

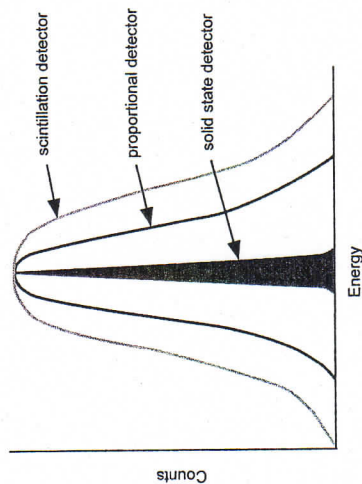


FIG. 51. Pulse-height distribution curves for three kinds of detector. (Peak widths exaggerated.)

tor because it has a high electrical resistivity, particularly at low temperatures, since very few electrons have enough energy to cross the energy band gap. This characteristic is important because the only electrons we want to cross the energy band gap are those excited by an x-ray photon. As we discuss in more detail later, thermally excited electrons just produce noise in the diffraction pattern.

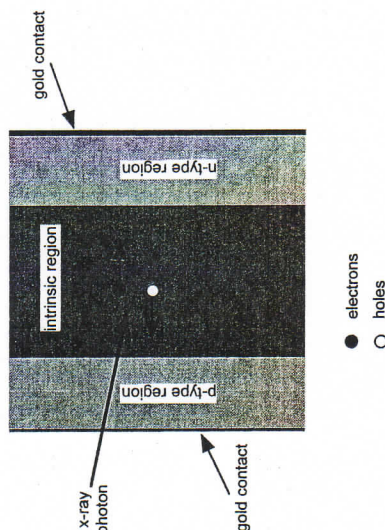


FIG. 52. Solid-state detector.

The absorption of a Cu K α photon, with energy 8.04 keV, should therefore create $8040/3.8 = 2116$ pairs. However, successive photons create slightly different numbers of electron-hole pairs. For example, the first photon may produce 2110 electron-hole pairs, the second 2121 pairs, the third 2126 pairs, and so on. This difference leads to a variation in the size of the output pulse and is the reason for the peak width in Fig. 51. Even so, solid-state detectors produce much narrower peaks (have better energy resolution) than either proportional detectors or scintillation detectors (Fig. 51).

The Si(Li) solid-state detector must be kept at liquid nitrogen temperature (77 K or -196°C) at all times (even when not in use). We have to cool the detector for two reasons: (1) minimize thermal excitation of electrons; at room temperature, thermal energy is sufficient to produce numerous electron-hole pairs, giving a noise level that would swamp the x-ray signals we want to detect; (2) minimize thermal diffusion of lithium, which would upset the distribution obtained during detector fabrication.

Many solid-state detectors are cooled with a Dewar filled with liquid nitrogen connected to the Si(Li) detector via a cold finger. In newer solid-state detectors, however, cooling is achieved by Peltier thermoelectric cooling. Such detectors are small and lightweight, and there is no need for the bulky liquid nitrogen Dewar.

The solid-state detector is extremely efficient, almost 100% over a large range of energies, where efficiency is defined as the ratio of the number of pulses produced to the number of photons striking the detector.

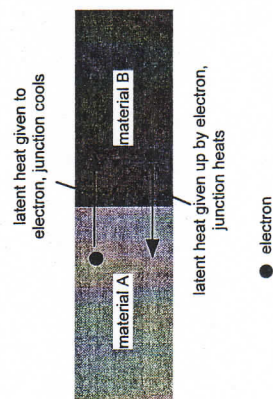


FIG. 53. Peltier effect.

Peltier Effect

When a current flows through a junction of dissimilar conductors, heat can be absorbed or liberated, depending on the current polarity. This phenomenon is known as the *Peltier effect*. Semiconductors are particularly suitable for making devices that utilize the Peltier effect because of their high efficiencies. For semiconductor devices the junction can be a p - n junction (i.e., a junction formed between a p -type semiconductor and an n -type semiconductor) or a metal-semiconductor junction. If electron transfer across the junction results in the electron's absorbing energy, then a cooling effect is observed (Fig. 53). This effect is required for refrigeration applications.

Silicon is not the only semiconductor used for a solid-state x-ray detector. Germanium single-crystal detectors are widely used for γ -rays and high-energy (>20 keV) x-rays because Ge is heavier than Si and therefore is a better absorber of the more energetic radiation. It is easier to produce high-purity single crystals of Ge than it is silicon, so Li drifting is not required. Another advantage of Ge detectors is that they have better energy resolution and a higher signal-to-noise ratio than Si detectors, because the energy to create an electron-hole pair is only about 2.9 eV compared with about 3.8 eV in silicon. The resolution R is inversely proportional to $\sqrt{n}$:

$$R \propto \frac{1}{\sqrt{n}} \quad (30)$$

where n is the number of electron-hole pairs. Using Eq. (29), we obtain for the absorption of a Cu K α photon by a Ge crystal $8040/2.9 = 2772$ electron-hole pairs (remember for Si we were getting about 2116 electron-hole pairs per incoming x-ray photon). Typical best values of resolution for a solid-state detector are 145 eV for a high-purity Ge detector and 165 eV for a Si(Li) detector. Since the resolution is the *smallest* measurable difference in a quantity, in this case energy (the resolution, or resolving power, of an electron microscope is much smaller than that of a visible light microscope—one reason why electron microscopes are essential in the study of materials), the smaller the resolution the better the detector.

Of course, there are some disadvantages with using Ge detectors. Silicon solid-state detectors are slightly more efficient than Ge detectors from 1 to 20 keV. The useful x-ray energies for x-ray diffraction studies

Escape Peaks

Not all the x-ray energy incident upon the detector is transformed to electron-hole pairs. Some of the energy may produce fluorescent radiation that escapes from the intrinsic region of the detector, carrying with it energy that would normally be absorbed. An escape peak is then formed. More escape peaks occur in Ge because we can produce both the $\text{Ge K}\alpha$ (9.89 keV) and La (1.19 keV) characteristic x-rays in the detector. X-ray photons having an energy a little higher than the critical ionization energy of the detector material are the most efficient at producing fluorescence. For example, the most efficient x-ray to fluoresce Si $\text{K}\alpha$ x-rays is the P $\text{K}\alpha$. When the x-ray energy is much larger than the critical ionization energy, x-rays are not absorbed by the detector.

fall within this energy range (for example, Cu $\text{K}\alpha$ x-rays have an energy of 8.04 keV). Si(Li) solid-state detectors are easier to manufacture and are more reliable than Ge detectors. Also, there are more interferences from escape peaks. Germanium solid-state detectors are not used on conventional x-ray diffractometers.

The next generation of solid-state detectors may well use $p-i-n$ diodes based on compound semiconductors (a semiconductor consisting of two or more elements). These devices can be made very thin, and it is possible to control the energy of the band gap. If the semiconductor has a large band gap (i.e., the top of the valence band and the bottom of the conduction band are separated by a large amount of energy), then thermal excitation of electrons becomes less probable and only an incident x-ray has enough energy to produce a significant number of electron-hole pairs. Use of these so-called wide-band-gap semiconductors makes it possible to eliminate cooling the detector. The best energy resolution for a detector using a wide-band-gap semiconductor is approaching that of the elemental solid-state detectors.

3.3. EXAMINATION OF A STANDARD X-RAY DIFFRACTION PATTERN

An example of a typical x-ray diffraction pattern is shown in Fig. 54a. The pattern is actually from aluminum, but the general features of the pattern are independent of the specimen. The pattern consists of a series of peaks. The peak intensity is plotted on the ordinate (y axis) and the measured diffraction angle, 2θ , along the abscissa (x axis). As in Sec. 2.7,

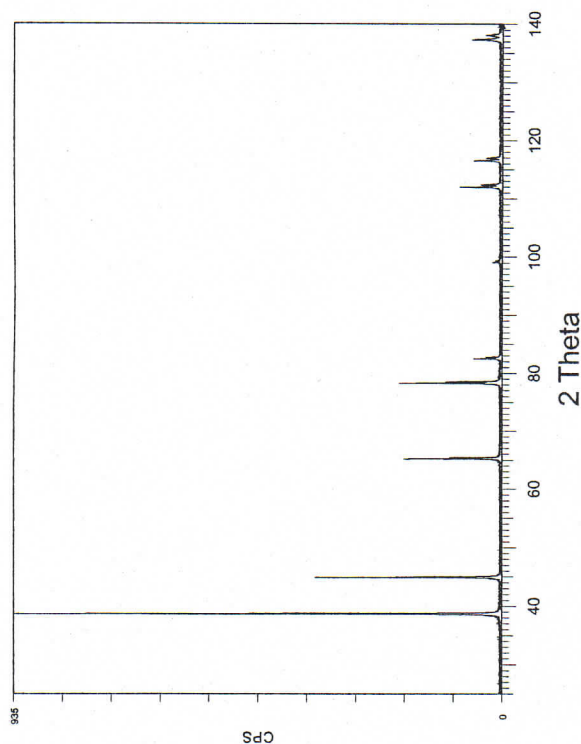


FIG. 54. (a) X-ray diffraction pattern of aluminum.

the peaks are also called reflections. (When recorded in a camera, they were always called lines.) Each peak, or reflection, in the diffraction pattern corresponds to x-rays diffracted from a specific set of planes in the specimen, and these peaks are of different heights (intensities). The intensity is proportional to the number of x-ray photons of a particular energy that have been counted by the detector for each angle 2θ . The intensity is usually expressed in arbitrary units because it is difficult to measure the absolute intensity. Fortunately, we are generally not interested in the absolute intensity of the peak but rather the relative intensities of the peaks and the relative differences in their integrated intensity (the area under the peak). The intensities of the reflections depend on several factors, including structure factor (Sec. 2.8), incident intensity, slit width, and values of current and voltage used in the x-ray source.

The as-recorded x-ray diffraction patterns generally have a background. The background is usually subtracted and the peaks smoothed. We have done this in Fig. 54a. Further, since the most intense peak may have a much higher intensity than the other peaks in the diffraction

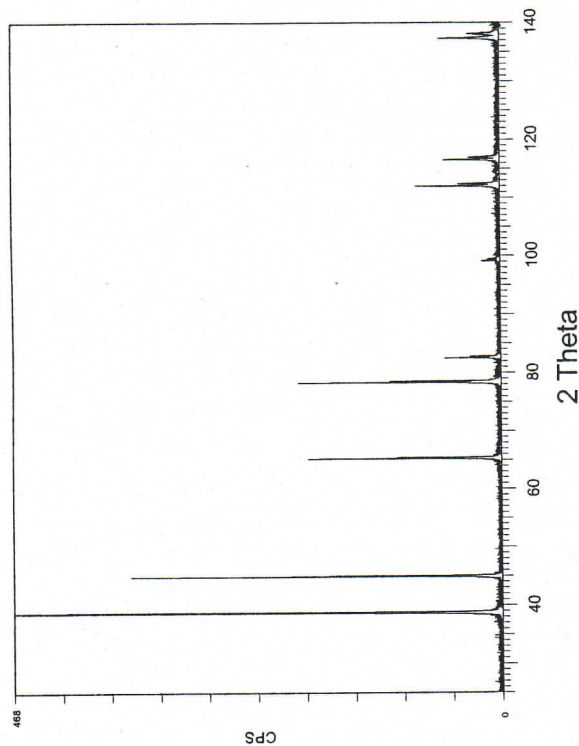


FIG. 54. (b) X-ray diffraction pattern of aluminum where the relative peak intensities have been increased by cutting off the peak height of the most intense peak.

pattern, the intensity scale is often adjusted so as to have a reasonable intensity for all peaks. We have done this in Fig. 54b. The 111 reflection (the first one) is off-scale but the other reflections are now more clearly visible. Hence, you should use these patterns not to evaluate the intensities but to locate peak positions. However, if the intensities of the reflections are required, as in Experimental Modules 7 and 8, the x-ray diffraction patterns are presented without changing the intensity scale. The background is, however, subtracted.

The positions of the peaks in an x-ray diffraction pattern depend on the crystal structure (more specifically, the shape and size of the unit cell) of the material (we are ignoring the effects of texture and assuming that we have an ideal polycrystalline specimen consisting of randomly oriented equiaxed grains), and this is what enables us to determine the structure and lattice parameter of the material. (The positions of the peaks also depend on the wavelength of the x-rays used. In Exercise 2 at the

end of Experimental Module 1 we ask you to show how λ affects the positions of the peaks in the x-ray diffraction pattern of copper.)

As the symmetry of the crystal structure *decreases*, there is an *increase* in the number of peaks. For example, diffraction patterns from materials with cubic structures have few peaks. On the other hand, materials with hexagonal (and other less symmetric) structures show many more peaks in their diffraction patterns. (Compare your results from Experimental Modules 1 and 2 to confirm this observation.)

Diffraction patterns from cubic materials can usually be distinguished at a glance from those of noncubic (less symmetric) materials. Figure 55 shows the calculated diffraction patterns (for $a = 0.4$ nm and $\text{Cu K}\alpha_1$ radiation) of the four cubic crystal structures (simple cubic, bcc, fcc, and diamond cubic). You can see from Fig. 55 that in simple cubic and bcc structures, the peaks are approximately equally spaced. In the diffraction pattern from the fcc structure, the peaks appear alternatively as a pair and a single peak. In the diamond cubic structure, the peaks are alternatively more widely and less widely spaced. The reason for these differences in the diffraction patterns is a result of reflections forbidden by the structure factor (see Sec. 2.8). In Experimental Module 1 you will use the structure factor to index x-ray diffraction patterns from a variety of materials with cubic crystal structures. You also need to be aware of which reflections

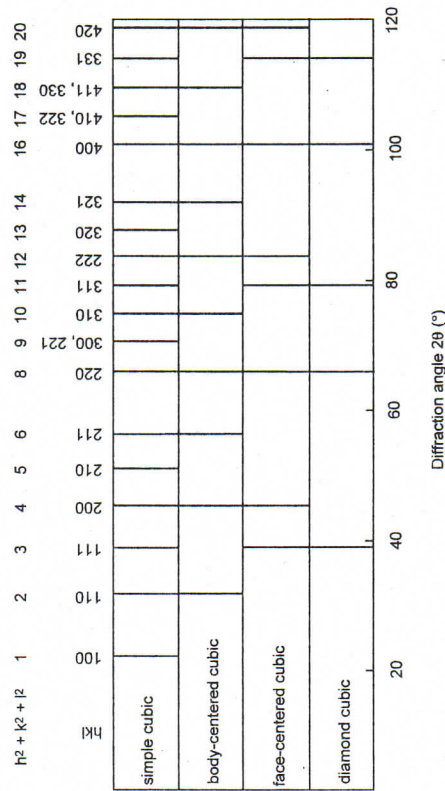


FIG. 55. Comparison of x-ray diffraction patterns from materials with different cubic crystal structures.

are allowed and which are forbidden when you work through some of the other experimental modules.

The intensities of the reflections in a single-phase material provide us with information about the atom positions in the crystal. If you refer to Sec. 2.8 you will see why. In this book we do not go into the exact determination of atom positions from peak intensities. It is beyond what would normally be covered in an undergraduate materials science course, but you will use the relative intensities of the peaks to determine the extent of ordering in the Cu_3Au alloy in Experimental Module 4 or to estimate the relative proportion of phases in Experimental Module 7.

The width of an individual peak, often defined as the full width at half the maximum height (see Fig. 44 for the definition of FWHM), can be used to determine crystallite size and the presence of lattice distortions (strain) in the crystal. You will use peak broadening in Experimental Module 6. (This is somewhat similar to the fine structure in the electron diffraction patterns obtained in a transmission electron microscope.)

For low values of 2θ each reflection appears as a single sharp peak. For larger values of 2θ (above 80° for the aluminum patterns in Fig. 54) each reflection consists of a pair of peaks, which correspond to diffraction of the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ wavelengths. Recall from Bragg's law ($\lambda = 2d \sin \theta$) that a peak is produced at a Bragg angle θ and for a specific value of d . Even if d is the same, we have one θ value for $\text{K}\alpha_1$ and another for $\text{K}\alpha_2$. Also note that the separation between the α_1 and α_2 components at any angle is larger when we expand the 2θ scale and, therefore, we may see α_1 and α_2 separated even at lower values (2θ less than 80°). It is useful to remember that a peak *always* contains the α_1 and α_2 components. Whether we see it resolved or not depends on the 2θ values, the scale on the x axis, and the resolution of the diffractometer. At low values of 2θ the separation of the peaks is quite small, but increases at larger 2θ values. The separation of the $\text{Cu K}\alpha_1$ and $\text{K}\alpha_2$ peaks increases from 0.05° at 20° (2θ) to 1.08° at 150° (2θ). As you will see in Experimental Module 3, the additional peaks (due to α_1 and α_2 resolution) in the x-ray diffraction pattern can be extremely useful.

One parameter that you may very well wish to vary is the length of time it takes to obtain the diffraction pattern. It depends on two factors:

1. The range of 2θ values you want to incorporate into the pattern
2. The length of time you want to spend collecting data at each 2θ value

In most of the experimental modules we give you the suitable range of 2θ values, but for an unknown specimen you may need to cover the full

range of angles in order to avoid missing any of the important reflections. The longer you spend collecting data at each angle the better your counting statistics will be—you will have a higher signal-to-noise ratio and better resolution. On the other hand, the amount of time (and money) you have available will provide a practical limit to the length of each scan. The time to record each x-ray diffraction pattern in Part II was between 15 and 60 min.

On modern instruments peak searches are performed on a computer. The computer computes the 2θ angles, the FWHM, and integrated intensities for each peak. In addition, the peak shape can be defined, and overlapping peaks deconvoluted. Most commercial software allows the user to compare standard patterns (from the JCPDS-ICDD data base; see Sec. 3.4) with experimentally observed patterns, allowing rapid matching of patterns and material identification. Certain software packages also allow you to

- Determine lattice strain
- Calculate crystallite size
- Refine calculation of lattice parameter(s) (Rietveld method)
- Calculate diffraction patterns, and other operations

There are continuous advances in the software accompanying x-ray diffractometers, and all these advances help to make life easier.

It is essential that the diffractometer be aligned and calibrated properly. Failure to do so degrades instrument performance, leading to a loss of intensity and resolution, increased background, incorrect profile shapes, and various errors that cannot be readily diagnosed. Procedures and devices for this purpose are often provided by the manufacturer. As a new user of an x-ray diffractometer it is unlikely that you will be required to perform any of the alignment and calibration procedures, but it is important that someone has already done so.

3.4. SOURCES OF INFORMATION

One of the most useful sources of information for crystal structure data is the Powder Diffraction File (PDF). The PDF is a collection of single-phase x-ray powder diffraction patterns in the form of tables of interplanar spacings (d) and corresponding relative intensities. The files also contain other information, such as some physical and crystallographic properties of the material. The origin of the PDF goes back to 1936 when Hanawalt and others started collecting about 1000 standard x-ray diffraction patterns as a repository. Since the number of standard patterns started

growing, this effort was taken over in 1941 by several societies, including the American Society for Testing and Materials (ASTM). In 1969 the organization was constituted as a Pennsylvania nonprofit corporation under the title of The Joint Committee on Powder Diffraction Standards (JCPDS). In 1978, the organization was renamed the International Centre for Diffraction Data (ICDD). The acronym JCPDS is still widely used to refer to both the organization and the patterns. In 1976 the PDF comprised about 26,000 diffraction patterns; there are now about 80,000 patterns. The data base is continually growing as new materials are synthesized and their crystal structures determined. The substances included in the PDF are elements, alloys, inorganic compounds, minerals, organic compounds, and organometallic compounds. The PDF is also continually updated, and incorrect patterns are deleted and replaced.

In the early days the full details of each pattern [d spacings, relative intensities, Miller indices of planes, optical information, density, number of atoms (molecules) in the unit cell, etc.] were printed in the form of 3" x 5" file cards. Later, these cards were printed (three per page) in books (the PDF now consists of 47 sets of cards), and now all the data are available on CD-ROM. In either form these tabulations are invaluable to anyone doing materials characterization using x-ray diffraction (and, by the way, when you do electron diffraction in the transmission electron microscope). Most modern x-ray diffractometers have these files on computer, so they can be easily accessed and printed. People still use the term "cards" to indicate the standard x-ray diffraction pattern, so we use this term in the experimental modules.

The contact information for the International Centre for Diffraction Data is

International Centre for Diffraction Data
Newtown Square Corporate Campus
12 Campus Boulevard
Newtown Square, Pennsylvania 19073-3273
Phone 610-325-9810; Fax 610-325-9823,
Internet INFORMATION@ICDD.COM

Figure 56 shows a typical data "card" obtained from a computer version of the PDF. Most of the information for these cards was generated with a powder camera and Cu K α radiation in earlier years, but a diffractometer is now used. However, with modern computer facilities you can convert or transform the data to other radiations quite easily. In Table 9 we explain the features of the card (refer to the Fig. 57 for the meanings of the numbers in column 1).

TABLE 9. Details of the Data Available on the JCPDS-ICDD Files

Number	Feature
1	File number. Each card in the PDF has its own unique number. The first number refers to the series. The last four digits (after the dash) represent the actual card number.
2	The wavelength of the radiation used to obtain the diffraction pattern.
3	The quality of the data. In the computer-generated files the quality is given as high, indexed, not indexed, and questionable. In the cards the following symbols are used: * (high quality), i (peaks indexed, intensities fairly reliable), c (calculated pattern), and o (low reliability).
4	The name of the material and its chemical formula. "Syn." means the material was not obtained from a natural source but was synthesized.
5	The diffraction pattern information. The data given are the interplanar spacing, d (in Å) (the computer can readily convert the d values to the diffraction angle 2θ), $1/d$, or $1/l$, the relative intensity of the reflections expressed as percentages of the strongest peak in the pattern, and hkl are their Miller indices.
6	The lattice and space group (S.G.) of the material.
7	Lattice parameters (a , b , c). Note that the lattice parameters are given in Å ($1 \text{ Å} = 0.1 \text{ nm} = 10^{-10} \text{ m}$).
8	Lattice parameters (α , β , γ) and number of molecules (atoms in the case of pure metals) per unit cell.
9	Molecular weight, volume, and experimental (D_x) and measured (D_m) density in g/cm ³ . I/I_{ref} is the ratio of the peak height of the strongest reflection of the specimen to the strongest reflection of corundum (α -Al ₂ O ₃).
10	How the sample was prepared/obtained. Optical and other properties of the material are also included here, although this information may not be complete for each material in the PDF.
11	The reference to the original source of the diffraction pattern information. CAS is the Chemical Abstract Series number.
12	The type of radiation used and its wavelength. The SS/FOM number is the Smith Schneider figure of merit. It gives the total number of reflections in the pattern and provides a measure of data reliability.
13	Other experimental information, including the type of instrument used.

These cards can be retrieved with the help of a computer when you know the card number or the name of the material or the chemical constituents. In the experimental modules you can use the PDF in two ways. First, you can use it to check your indexing. If the diffraction pattern you obtained is from a known material (e.g., silicon), then, after you have indexed the reflections and calculated the lattice parameter, you can check your results against the relevant card number (e.g., for silicon the card number is 27-1402). The card numbers for the materials referred to in the experimental modules are listed in Appendix 9.

In Experimental Module 8 we show you how to use the PDF to identify an unknown material. This method is known as the Hanawalt method and uses the PDF Search Manual (another invaluable resource from ICDD). In the Search Manual the positions of eight peaks (in terms of

Si Silicon, syn [NR] / Silicon		Lattice : Cubic S.G. : Fd3m (227)		a = 5.43088 b = 5.43088 c = 5.43088 a/b = 1.00000 c/b = 1.00000	Alpha = 90.00 Beta = 90.00 Gamma = 90.00 Z = 8 I/cor = 4.70	TEMP. OF DATA COLLECTION : Pattern at 25(1) °C SAMPLE SOURCE OR LOCALITY : This sample is NBS Standard Reference Material No. 640. GENERAL COMMENTS : Reflections calculated from precision measurement of a0. ADDITIONAL PATTERN : To replace 5-565 and 26-1481. COLOR : Gray	d (Å) 3.1355 100 55 22 11 1 1 30 1.6375 1.3577 1.2459 1.1086 1.0452 0.9600 0.9180 0.8587 0.8282	h k l 1 1 2 0 1 1 3 4 0 0 1 2 2 4 1 5 3 6 5 8 3	Radiation = 1.540560 Quality : High
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FIG. 56. JCPDS-ICDD card for silicon.

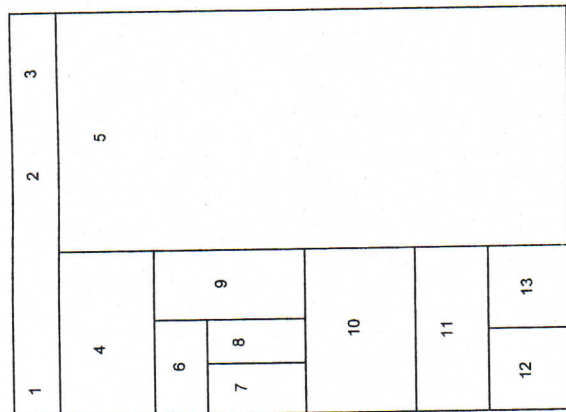


FIG. 57. Schematic of a JCPDS-ICDD card.

their d values) from the diffraction pattern are listed in order of decreasing intensity. The subscript under each d spacing represents the intensity of the peak rounded off to the nearest 10. For example, 5 represents 50% and 3 represents 30%. The highest intensity, namely 100%, should be represented by 10 but in the listing it is represented by x . The d value of the strongest peak determines the group (there are 40 groups) into which the material is placed; the d value of the next strongest peak specifies the subgroup, i.e., the location of the material within the group. The next strongest six peak positions can be used to confirm the identification. The groups are divided into ranges of d (in Å), as shown in Table 10.

To identify an unknown specimen, start by matching the strongest peak, then the next strongest, and so on. If you can match the eight peak positions and intensities in the PDF with the eight strongest peaks and intensities in your experimentally determined diffraction pattern, that is usually more than sufficient to identify the unknown specimen. The details of how to do this are presented in Experimental Module 8. The International Centre for Diffraction Data also publishes an Alphabetical

TABLE 10. Groups of d Spacings (in Å) in the PDF Search Manual (Hanawalt Method)

999-99-8.00 (-0.20)	3.31-3.25 (±0.02)	2.64-2.58 (±0.01)
7.99-7.00 (±0.10)	3.24-3.20 (±0.01)	2.57-2.51 (±0.01)
6.99-6.00 (±0.10)	3.19-3.15 (±0.01)	2.50-2.44 (±0.01)
5.99-5.50 (±0.05)	3.14-3.10 (±0.01)	2.43-2.37 (±0.01)
5.49-5.00 (±0.05)	3.09-3.05 (±0.01)	2.36-2.30 (±0.01)
4.99-4.60 (±0.04)	3.04-3.00 (±0.01)	2.29-2.23 (±0.01)
4.59-4.30 (±0.03)	2.99-2.95 (±0.01)	2.22-2.16 (±0.01)
4.29-4.10 (±0.03)	2.94-2.90 (±0.01)	2.15-2.09 (±0.01)
4.09-3.90 (±0.02)	2.89-2.85 (±0.01)	2.08-2.02 (±0.01)
3.89-3.75 (±0.02)	2.84-2.80 (±0.01)	2.01-1.86 (±0.01)
3.74-3.60 (±0.02)	2.79-2.75 (±0.01)	1.85-1.68 (±0.01)
3.59-3.50 (±0.02)	2.74-2.70 (±0.01)	1.67-1.38 (±0.01)
3.49-3.40 (±0.02)	2.69-2.65 (±0.01)	1.37-1.00 (±0.01)
3.39-3.32 (±0.02)		

Index that lists all the compounds in alphabetical order. The index can be used when you know what the material is but do not know the positions of the major reflections.

Other useful sources of information about crystal structure data are

1. P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (in four volumes), ASM International, Materials Park, OH (1991); includes information on pure metals, semiconductors, and ceramic compounds, in addition to intermetallic phases.
2. W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1 (1958) and Vol. 2 (1967), Pergamon Press, Oxford, UK; lists lattice spacings of alloys and compounds as a function of solute content.

3.5. X-RAY SAFETY

It is important to be aware of the potential hazards associated with the use of x-ray diffraction apparatus. With modern x-ray equipment these hazards have been reduced to a minimum, and with responsible use of the equipment you should not be in any danger. However, x-rays are extremely dangerous and must be treated with caution and respect.

X-rays are damaging because they penetrate the human body and break up molecules of DNA in our cells. Sometimes the DNA molecules repair themselves and there is no lasting effect of the radiation. Sometimes

the molecules are not repaired and the cells die. If this process occurs on the surface of the skin, then the skin will be sloughed, much like a bad case of sunburn. However, if after the DNA molecules have been broken they rejoin in the wrong way, then a mutant cell is produced and this can lead to cancer.

Most students who use x-ray diffraction and other x-ray instruments experience no significantly greater exposure to radiation than a normal member of the public. In the United States the average exposure to radiation is about 360 mrem/year. The largest contribution to this dose is indoor radon inhalation, which averages about 200 mrem/year in the United States. Although we cannot avoid exposure to radiation, we want to keep our exposure *as low as reasonably achievable (alara)*.

How can you keep your exposure *alara*? Three factors limit your total exposure:

1. Distance
2. Time
3. Shielding

The further you are from the source of radiation, the less time you spend in the vicinity of a radiation source, and the greater the amount of shielding between you and the x-ray source the less your exposure will be. Because x-rays are so energetic, they are very penetrating; hence, the most effective shielding material has a high mass absorption coefficient, i.e., a large atomic number (Z). The most common shielding material is lead ($Z = 82$). However, although the intensity of radiation can be reduced ("attenuated" is the term used by x-ray safety people) by shielding, it cannot be completely eliminated.

Most x-ray diffractometers have a safety screen (or door) that encloses the instrument. The screen is opened before loading your specimen. While the screen is open, the x-ray source cannot be operated. Never tamper with this safety mechanism. After your specimen is loaded into the diffractometer, the screen is closed and the x-ray source can be energized. When you want to change specimens, turn off the x-ray source and lift

Units of Radiation Dose

The rem is a unit of radiation dose, known as the biological equivalent dose, and is the amount of energy absorbed by the body multiplied by a factor related to how effectively the radiation is absorbed by the body. The rem has been superseded by the SI unit the sievert (Sv): $1 \text{ Sv} = 100 \text{ rem}$.