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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

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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,

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

Although the eV has been superseded by the joule (J)—the SI unit of energy—the eV is a very convenient unit when atomic-level processes are being represented.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 $1 \text{ eV} = 1.602 \times 10^{-19}$ J. Most texts on materials characterization techniques use the electron volt, so you should familiarize yourself with this unit.

The Ångstrom

The ångstrom (Å) is a unit of length equal to 10^{-10} m. The ångstrom 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 Although the ångstrom has been superseded in SI units by the nanometer (1 nm = 10^{-9} m = 10 Å), many crystallographers and microscopists still prefer the older unit.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.

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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

hν [eV]	ν [Hz]	λ [nm]	Radiation
	10^{14}		infrared
1		10^3	visible
	10^{15}		
10		10^2	ultraviolet
	10^{16}		
10^2		10	
	10^{17}		
10^3		1	
	10^{18}		
10^4		10^{-1}	x-rays
	10^{19}		
10^5		10^{-2}	
	10^{20}		
10^6		10^{-3}	
	10^{21}		
10^7		10^{-4}	γ-rays
	10^{22}		
10^8		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:

$$E = h\nu \tag{1}$$

The constant of proportionality is Planck's constant h, which has a value of 4.136×10^{-15} eV·s (or 6.626×10^{-34} J·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

$$\lambda = \frac{hc}{E} \tag{2}$$

where c is 2.998×10^{8} 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-
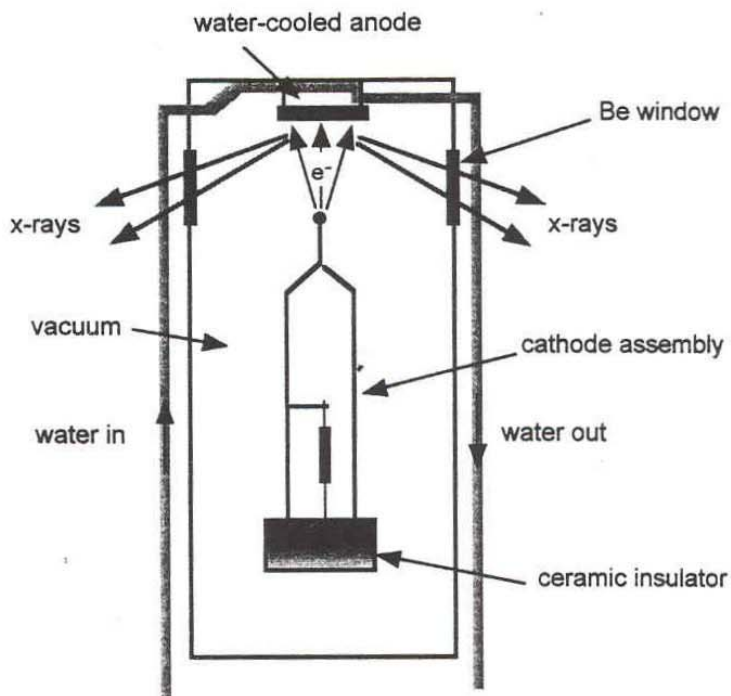
FIG. 2. Schematic showing the essential components of a modern x-ray tube. Beryllium is used for the window because it is highly transparent to x-rays.

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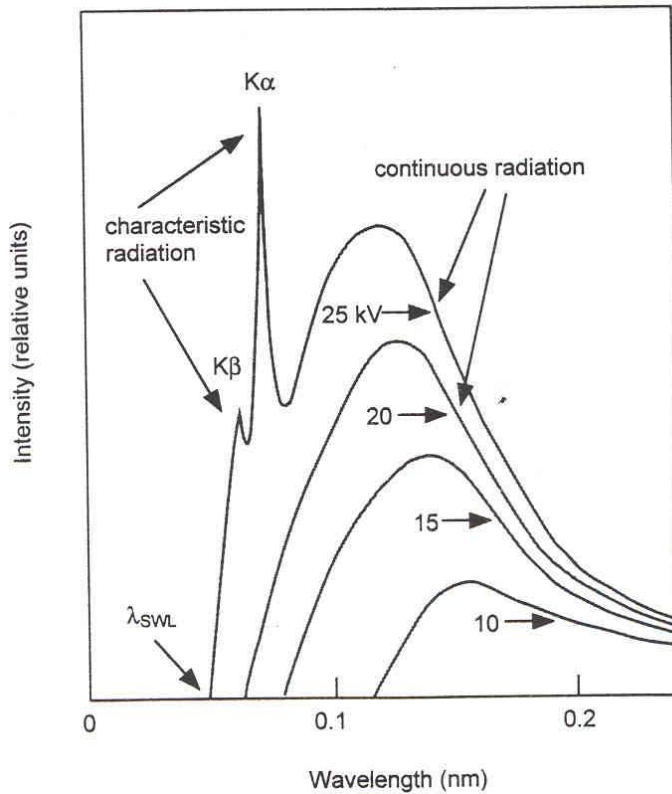
FIG. 3. X-ray spectrum of molybdenum at different potentials. The potentials refer to those applied between the anode and cathode. (The linewidths of the characteristic radiation are not to scale.)
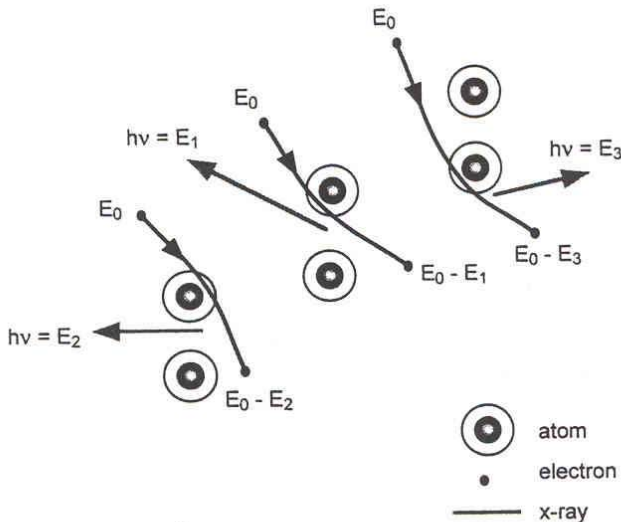

FIG. 4. Illustration of the origin of continuous radiation in the x-ray spectrum. Each electron, with initial energy E_0, loses some, or all, of its energy through collisions with atoms in the target. The energy of the emitted photon is equal to the energy lost in the collision.
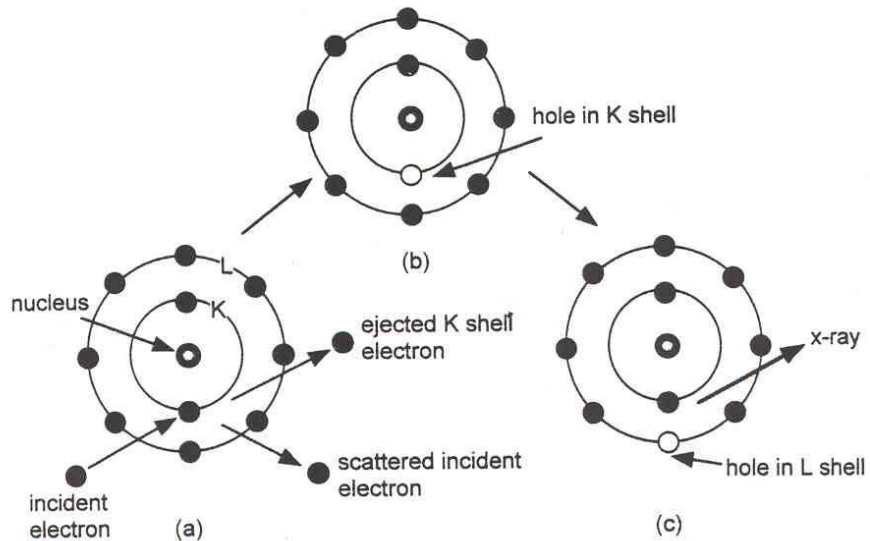
FIG. 5. Illustration of the process of inner-shell ionization and the subsequent emission of a characteristic x-ray: (a) an incident electron ejects a K shell electron from an atom, (b) leaving a hole in the K shell; (c) electron rearrangement occurs, resulting in the emission of an x-ray photon.

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:

$$E = \frac{hc}{\lambda} = eV \tag{3}$$

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

$$\lambda = \frac{hc}{eV} \tag{4}$$

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

$$\lambda \text{ [nm]} = \frac{1.243}{V} \tag{5}$$

when the potential V is expressed in kV. This wavelength corresponds to λ_{SWL}; the characteristic lines will have wavelengths longer than λ_{SWL}. 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_{SWL} 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

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

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 Kα x-ray, but if we fill the hole with an electron from the M shell, we get a Kβ x-ray. If the hole is in the L shell and we fill it with an electron from the M shell we get an Lα 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 Kα 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
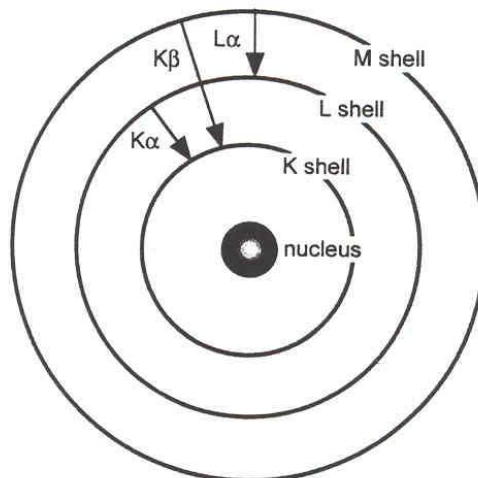

FIG. 6. Electron transitions in an atom, which produce the Kα, Kβ, and Lα characteristic x-rays.

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_{II}, 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_{II}, and L_{III} Levels of Molybdenum

Level	Energy (keV)
K	−20.00
L_{II}	−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_{II} 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

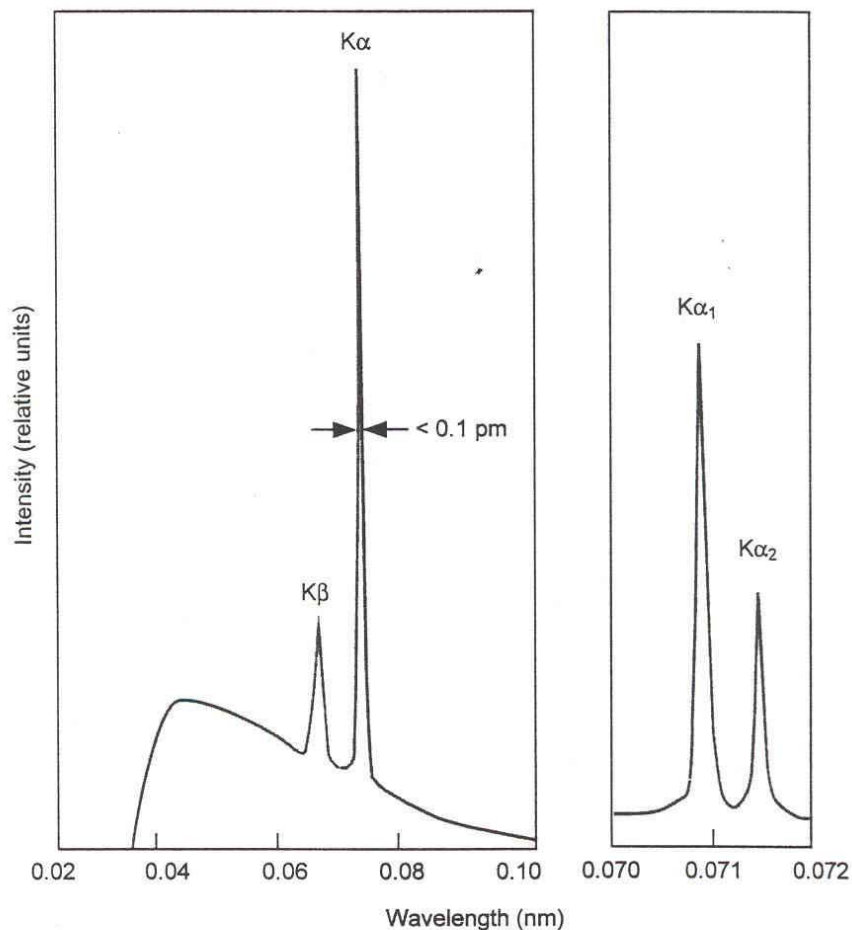$$\frac{1}{3}(2 \times 0.0709 + 0.0714) = 0.0711 \text{ nm}$$

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_I 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_I to K transition is not allowed.
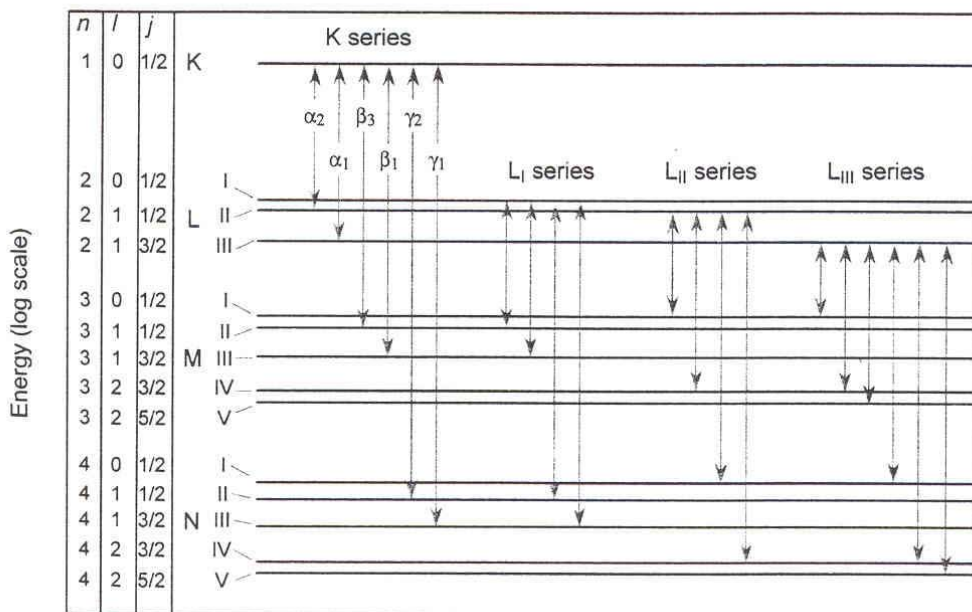

FIG. 8. Energy-level diagram showing all the allowed electron transitions in a molybdenum atom.

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

Element	Kα (weighted average)	Kα$_2$ (strong)	Kα$_1$ (very strong)	Kβ (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 Kβ radiation, and zirconium will remove Mo Kβ 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 Kα radiation, and not the Kβ radiation. The beam is still made up of the Kα$_1$ and Kα$_2$ wavelengths.

For x-ray diffraction studies there is a wide choice of characteristic Kα lines obtained by using different target metals, as shown in Table 2, but, Cu Kα is the most common radiation used. The Kα lines are used because they are more energetic than Lα 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.
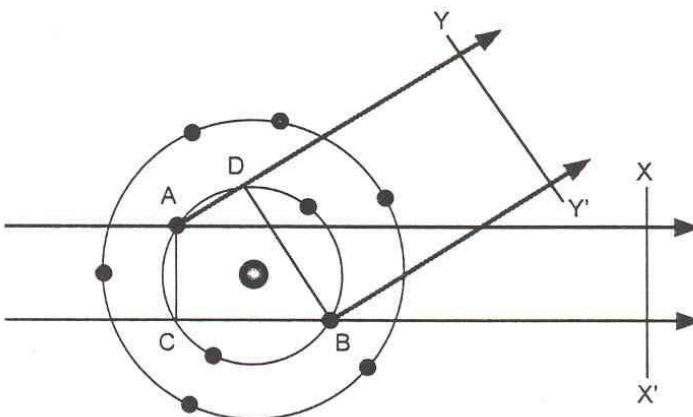

FIG. 9. Scattering of x-rays by an atom.

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.
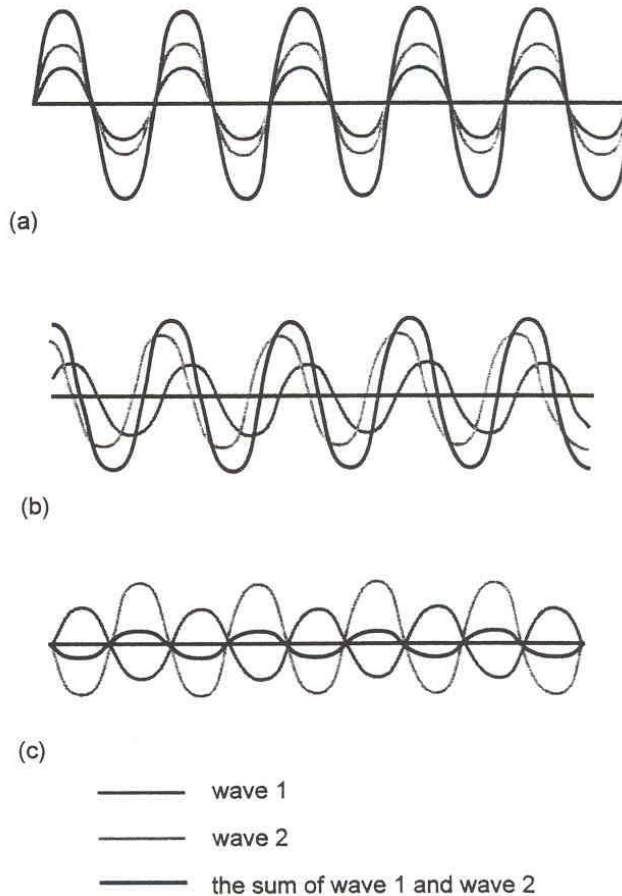
(a)

(b)

(c)

———— wave 1

———— wave 2

———— the sum of wave 1 and wave 2

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:

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

When scattering is in the forward direction (i.e., the scattering angle, θ = 0°) $f = Z$ (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
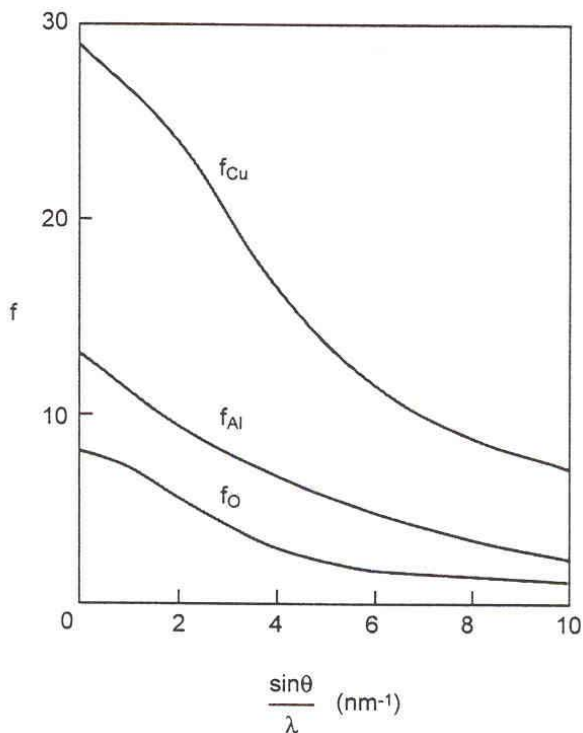

FIG. 11. Variation of the atomic scattering factor of copper, aluminum, and oxygen with $(\sin\theta)/\lambda$.

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 $\theta \approx 0°$.

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
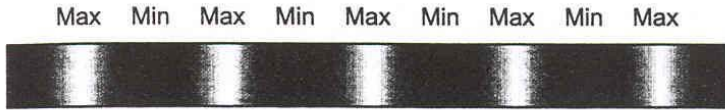
Max   Min   Max   Min   Max   Min   Max   Min   Max

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.