Elements of
X-RAY
DIFFRACTION

SECOND EDITION

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Properties of X-rays

1-1 INTRODUCTION

X-rays were discovered in 1895 by the German physicist Roentgen and were so named because their nature was unknown at the time. Unlike ordinary light, these rays were invisible, but they traveled in straight lines and affected photographic film in the same way as light. On the other hand, they were much more penetrating than light and could easily pass through the human body, wood, quite thick pieces of metal, and other "opaque" objects.

It is not always necessary to understand a thing in order to use it, and x-rays were almost immediately put to use by physicians and, somewhat later, by engineers, who wished to study the internal structure of opaque objects. By placing a source of x-rays on one side of the object and photographic film on the other, a shadow picture, or *radiograph*, could be made, the less dense portions of the object allowing a greater proportion of the x-radiation to pass through than the more dense. In this way the point of fracture in a broken bone or the position of a crack in a metal casting could be located.

Radiography was thus initiated without any precise understanding of the radiation used, because it was not until 1912 that the exact nature of x-rays was established. In that year the phenomenon of x-ray *diffraction* by crystals was discovered, and this discovery simultaneously proved the wave nature of x-rays and provided a new method for investigating the fine structure of matter. Although radiography is a very important tool in itself and has a wide field of applicability, it is ordinarily limited in the internal detail it can resolve, or disclose, to sizes of the order of 10^{-1} cm. Diffraction, on the other hand, can indirectly reveal details of internal structure of the order of 10^{-8} cm in size, and it is with this phenomenon, and its applications to metallurgical problems, that this book is concerned. The properties of x-rays and the internal structure of crystals are here described in the first two chapters as necessary preliminaries to the discussion of the diffraction of x-rays by crystals which follows.

1-2 ELECTROMAGNETIC RADIATION

We know today that x-rays are electromagnetic radiation of exactly the same nature as light but of very much shorter wavelength. The unit of measurement in the x-ray region is the angstrom (Å), equal to 10^{-8} cm, and x-rays used in diffraction have wavelengths lying approximately in the range 0.5–2.5 Å, whereas the wavelength of visible light is of the order of 6000 Å. X-rays therefore occupy the region

Frequency,
hertz   Name of
radiation   Photon
energy, eV   Wavelength,
angstroms

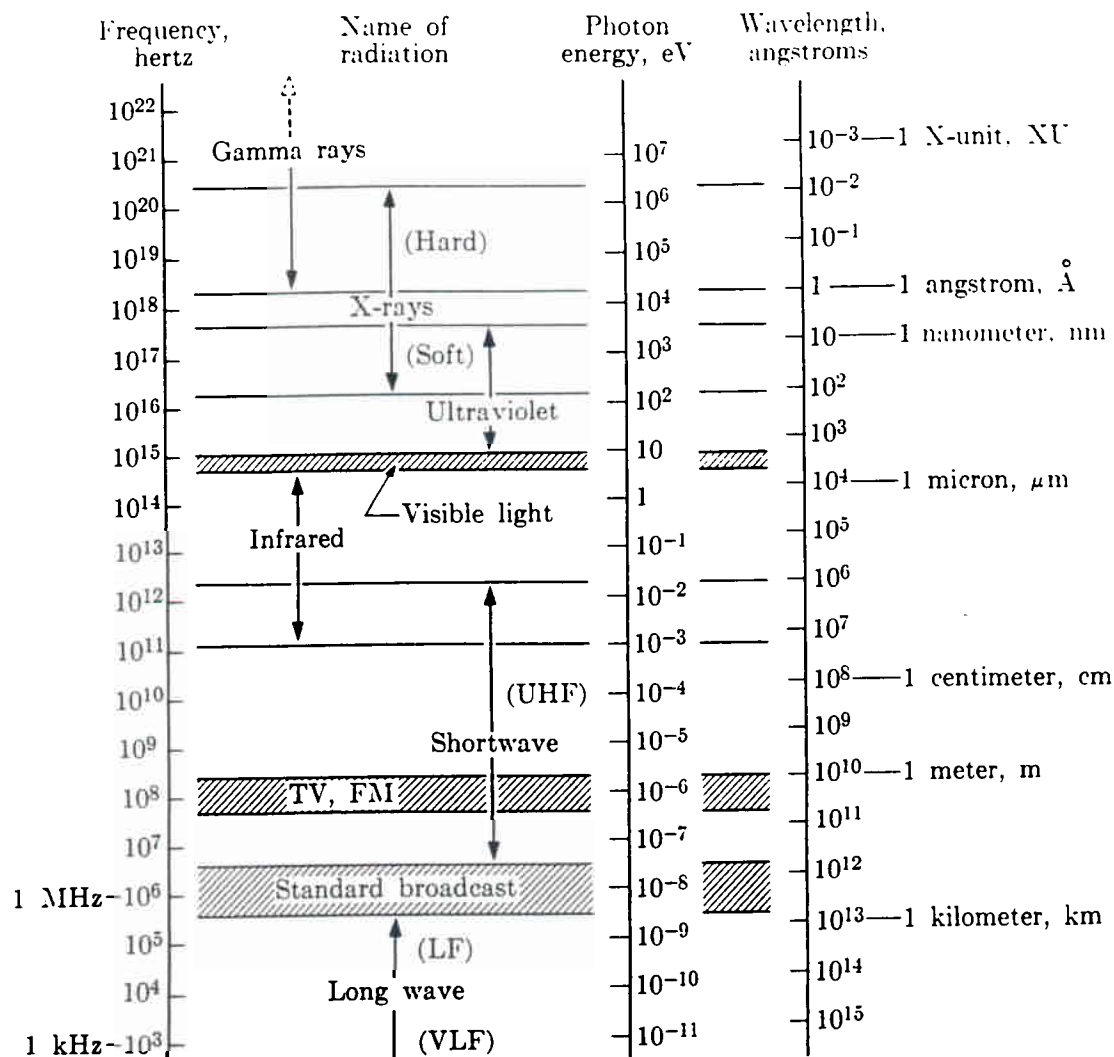| Frequency, hertz	Name of radiation	Photon energy, eV	Wavelength, angstroms
10^{22}	Gamma rays		10^{-3} — 1 X-unit, XU
10^{21}		10^7	
10^{20}		10^6	10^{-2}
10^{19}	(Hard)	10^5	10^{-1}
10^{18}	X-rays	10^4	1 — 1 angstrom, Å
10^{17}	(Soft)	10^3	10 — 1 nanometer, nm
10^{16}	Ultraviolet	10^2	10^2
10^{15}		10	10^3
10^{14}	Visible light	1	10^4 — 1 micron, μm
10^{13}	Infrared	10^{-1}	10^5
10^{12}		10^{-2}	10^6
10^{11}		10^{-3}	10^7
10^{10}	(UHF)	10^{-4}	10^8 — 1 centimeter, cm
10^9	Shortwave	10^{-5}	10^9
10^8	TV, FM	10^{-6}	10^{10} — 1 meter, m
10^7		10^{-7}	10^{11}
1 MHz – 10^6	Standard broadcast	10^{-8}	10^{12}
10^5	(LF)	10^{-9}	10^{13} — 1 kilometer, km
10^4	Long wave	10^{-10}	10^{14}
1 kHz – 10^3	(VLF)	10^{-11}	10^{15}

Fig. 1–1 The electromagnetic spectrum. The boundaries between regions are arbitrary, since no sharp upper or lower limits can be assigned. (H. A. Enge, M. R. Wehr, J. A. Richards, *Introduction to Atomic Physics*, Addison-Wesley Publishing Company, Inc., Reading, Mass., 1972).

between gamma and ultraviolet rays in the complete electromagnetic spectrum (Fig. 1-1). Other units sometimes used to measure x-ray wavelength are the X unit (XU) and the kilo X unit (kX = 1000 XU). The kX unit, whose origin will be described in Sec. 3-4, is only slightly larger than the angstrom. The approved SI unit for wavelengths in the x-ray region is the nanometer:

$$1 \text{ nanometer} = 10^{-9} \text{ m} = 10 \text{ Å}.$$

This unit has not become popular.

It is worth while to review briefly some properties of electromagnetic waves. Suppose a monochromatic beam of x-rays, i.e., x-rays of a single wavelength, is traveling in the x direction (Fig. 1-2). Then it has associated with it an electric field E in, say, the y direction and, at right angles to this, a magnetic field H in the z direction. If the electric field is confined to the xy-plane as the wave travels along, the wave is said to be plane-polarized. (In a completely unpolarized wave, the
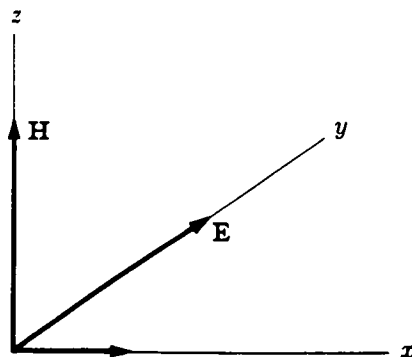
Fig. 1–2 Electric and magnetic fields associated with a wave moving in the x-direction.

electric field vector **E** and hence the magnetic field vector **H** can assume all directions in the yz-plane.) The magnetic field is of no concern to us here and we need not consider it further.

In the plane-polarized wave considered, **E** is not constant with time but varies from a maximum in the $+y$ direction through zero to a maximum in the $-y$ direction and back again, at any particular point in space, say $x = 0$. At any instant of time, say $t = 0$, **E** varies in the same fashion with distance along the x-axis. If both variations are assumed to be sinusoidal, they may be expressed in the one equation

$$E = A \sin 2\pi \left(\frac{x}{\lambda} - vt \right), \tag{1-1}$$

where A = amplitude of the wave, λ = wavelength, and v = frequency. The variation of **E** is not necessarily sinusoidal, but the exact form of the wave matters little; the important feature is its periodicity. Figure 1–3 shows the variation of **E** graphically. The wavelength and frequency are connected by the relation

$$\lambda = \frac{c}{v}, \tag{1-2}$$

where c = velocity of light = 3.00×10^8 m/sec.

Electromagnetic radiation, such as a beam of x-rays, carries energy, and the rate of flow of this energy through unit area perpendicular to the direction of motion of the wave is called the *intensity I*. The average value of the intensity is proportional to the square of the amplitude of the wave, i.e., proportional to A^2. In absolute units, intensity is measured in joules/m²/sec, but this measurement is a difficult one and is seldom carried out; most x-ray intensity measurements are made on a relative basis in arbitrary units, such as the degree of blackening of a photographic film exposed to the x-ray beam.

An accelerated electric charge radiates energy. The acceleration may, of course, be either positive or negative, and thus a charge continuously oscillating about some mean position acts as an excellent source of electromagnetic radiation. Radio waves, for example, are produced by the oscillation of charge back and forth in the broadcasting antenna, and visible light by oscillating electrons in the atoms
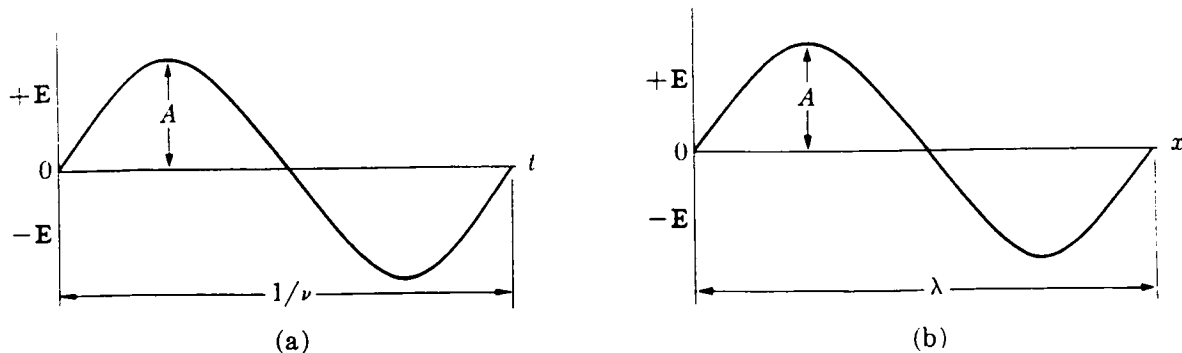
Fig. 1-3 The variation of E, (a) with t at a fixed value of x and (b) with x at a fixed value of t.

of the substance emitting the light. In each case, the frequency of the radiation is the same as the frequency of the oscillator which produces it.

Up to now we have been considering electromagnetic radiation as *wave* motion in accordance with classical theory. According to the quantum theory, however, electromagnetic radiation can also be considered as a stream of *particles* called quanta or photons. Each photon has associated with it an amount of energy $h\nu$, where h is Planck's constant (6.63×10^{-34} joule·sec). A link is thus provided between the two viewpoints, because we can use the frequency of the wave motion to calculate the energy of the photon. Radiation thus has a dual wave-particle character, and we will use sometimes one concept, sometimes the other, to explain various phenomena, giving preference in general to the classical wave theory whenever it is applicable.

1-3 THE CONTINUOUS SPECTRUM

X-rays are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. Electrons are usually used for this purpose, the radiation being produced in an *x-ray tube* which contains a source of electrons and two metal electrodes. The high voltage maintained across these electrodes, some tens of thousands of volts, rapidly draws the electrons to the anode, or *target*, which they strike with very high velocity. X-rays are produced at the point of impact and radiate in all directions. If e is the charge on the electron (1.60×10^{-19} coulomb) and V the voltage across the electrodes, then the kinetic energy (in joules) of the electrons on impact is given by the equation

$$\text{KE} = eV = \tfrac{1}{2}mv^2, \tag{1-3}$$

where m is the mass of the electron (9.11×10^{-31} kg) and v its velocity in m/sec just before impact. At a tube voltage of 30,000 volts, this velocity is about one-third that of light. Most of the kinetic energy of the electrons striking the target is converted into heat, less than 1 percent being transformed into x-rays.

When the rays coming from the target are analyzed, they are found to consist
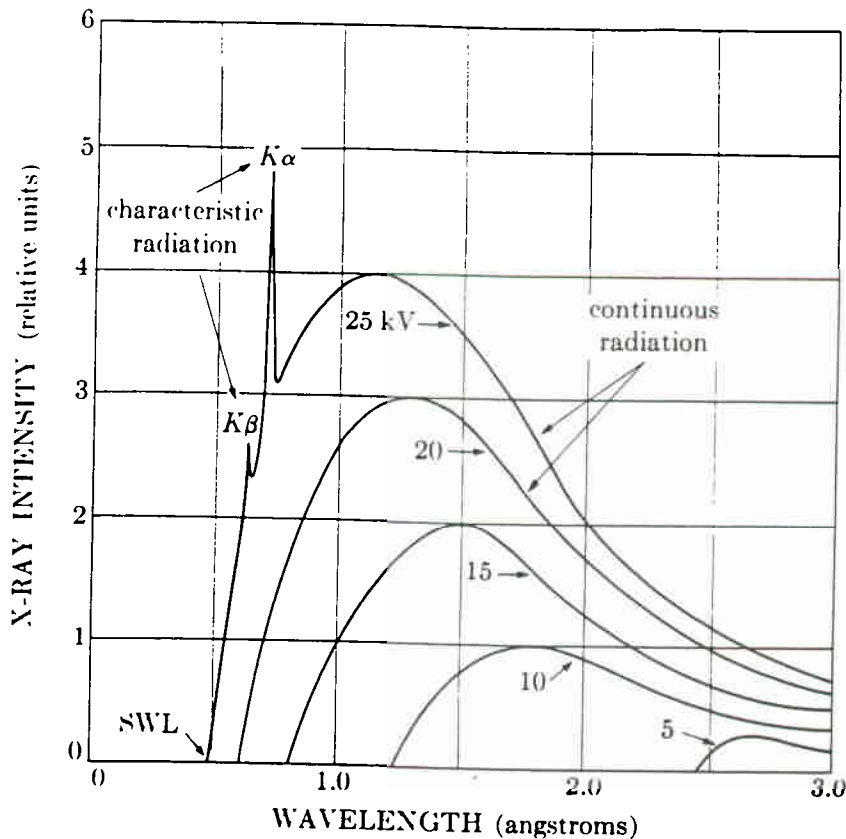
Fig. 1–4 X-ray spectrum of molybdenum as a function of applied voltage (schematic). Line widths not to scale.

of a mixture of different wavelengths, and the variation of intensity with wavelength is found to depend on the tube voltage. Figure 1–4 shows the kind of curves obtained. The intensity is zero up to a certain wavelength, called the *short-wavelength limit* (λ_{SWL}), increases rapidly to a maximum and then decreases, with no sharp limit on the long wavelength side. When the tube voltage is raised, the intensity of all wavelengths increases, and both the short-wavelength limit and the position of the maximum shift to shorter wavelengths. We are concerned now with the smooth curves in Fig. 1–4, those corresponding to applied voltages of 20 kV or less in the case of a molybdenum target. The radiation represented by such curves is called *heterochromatic, continuous,* or *white* radiation, since it is made up, like white light, of rays of many wavelengths. White radiation is also called *bremsstrahlung*, German for "braking radiation," because it is caused by electron deceleration.

The continuous spectrum is due to the rapid deceleration of the electrons hitting the target since, as mentioned above, any decelerated charge emits energy. Not every electron is decelerated in the same way, however; some are stopped in one impact and give up all their energy at once, while others are deviated this way and that by the atoms of the target, successively losing fractions of their total kinetic energy until it is all spent. Those electrons which are stopped in one impact will give rise to photons of maximum energy, i.e., to x-rays of minimum wave-

length. Such electrons transfer all their energy eV into photon energy and we may write

$$eV = h\nu_{max},$$

$$\lambda_{SWL} = \lambda_{min} = \frac{c}{\nu_{max}} = \frac{hc}{eV},$$

$$\lambda_{SWL} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^8)}{(1.602 \times 10^{-19})\,V} \text{ meter,}$$

$$\boxed{\lambda_{SWL} = \frac{12.40 \times 10^3}{V}}. \tag{1-4}$$

This equation gives the short-wavelength limit (in angstroms) as a function of the applied voltage V. If an electron is not completely stopped in one encounter but undergoes a glancing impact which only partially decreases its velocity, then only a fraction of its energy eV is emitted as radiation and the photon produced has energy less than $h\nu_{max}$. In terms of wave motion, the corresponding x-ray has a frequency lower than ν_{max} and a wavelength longer than λ_{SWL}. The totality of these wavelengths, ranging upward from λ_{SWL}, constitutes the continuous spectrum.

We now see why the curves of Fig. 1-4 become higher and shift to the left as the applied voltage is increased, since the number of photons produced per second and the average energy per photon are both increasing. The total x-ray energy emitted per second, which is proportional to the area under one of the curves of Fig. 1-4, also depends on the atomic number Z of the target and on the tube current i, the latter being a measure of the number of electrons per second striking the target. This total x-ray intensity is given by

$$I_{cont.\ spectrum} = AiZV^m, \tag{1-5}$$

where A is a proportionality constant and m is a constant with a value of about 2. Where large amounts of white radiation are desired, it is therefore necessary to use a heavy metal like tungsten ($Z = 74$) as a target and as high a voltage as possible. Note that the material of the target affects the intensity but not the wavelength distribution of the continuous spectrum.

1-4 THE CHARACTERISTIC SPECTRUM

When the voltage on an x-ray tube is raised above a certain critical value, characteristic of the target metal, sharp intensity maxima appear at certain wavelengths, superimposed on the continuous spectrum. Since they are so narrow and since their wavelengths are characteristic of the target metal used, they are called *characteristic lines*. These lines fall into several sets, referred to as K, L, M, etc., in the order of increasing wavelength, all the lines together forming the *characteristic spectrum* of the metal used as the target. For a molybdenum target the K lines have wavelengths of about 0.7 Å, the L lines about 5 Å, and the M lines still longer wavelengths. Ordinarily only the K lines are useful in x-ray diffraction,

the longer-wavelength lines being too easily absorbed. There are several lines in the K set, but only the three strongest are observed in normal diffraction work. These are the $K\alpha_1$, $K\alpha_2$, and $K\beta_1$, and for molybdenum their wavelengths are approximately:

$$K\alpha_1: \quad 0.709 \text{ Å,}$$
$$K\alpha_2: \quad 0.714,$$
$$K\beta_1: \quad 0.632.$$

The α_1 and α_2 components have wavelengths so close together that they are not always resolved as separate lines; if resolved, they are called the $K\alpha$ *doublet* and, if not resolved, simply the $K\alpha$ *line*.* Similarly, $K\beta_1$ is usually referred to as the $K\beta$ *line*, with the subscript dropped. $K\alpha_1$ is always about twice as strong as $K\alpha_2$, while the intensity ratio of $K\alpha_1$ to $K\beta_1$ depends on atomic number but averages about 5/1.

These characteristic lines may be seen in the uppermost curve of Fig. 1-4. Since the critical K *excitation voltage*, i.e., the voltage necessary to excite K characteristic radiation, is 20.01 kV for molybdenum, the K lines do not appear in the lower curves of Fig. 1-4. An increase in voltage above the critical voltage increases the intensities of the characteristic lines relative to the continuous spectrum but *does not change their wavelengths*. Figure 1-5 shows the spectrum of molybdenum at 35 kV on a compressed vertical scale relative to that of Fig. 1-4; the increased voltage has shifted the continuous spectrum to still shorter wavelengths and increased the intensities of the K lines relative to the continuous spectrum but has not changed their wavelengths.

The intensity of any characteristic line, measured above the continuous spectrum, depends both on the tube current i and the amount by which the applied voltage V exceeds the critical excitation voltage for that line. For a K line, the intensity is given approximately by

$$I_{K\text{ line}} = Bi(V - V_K)^n, \tag{1-6}$$

where B is a proportionality constant, V_K the K excitation voltage, and n a constant with a value of about 1.5. (Actually, n is not a true constant but depends on V and varies from 1 to 2.) The intensity of a characteristic line can be quite large: for example, in the radiation from a copper target operated at 30 kV, the $K\alpha$ line has an intensity about 90 times that of the wavelengths immediately adjacent to it in the continuous spectrum. Besides being very intense, characteristic lines are also very narrow, most of them less than 0.001 Å wide measured at half their maximum intensity, as indicated in Fig. 1-5. The existence of this strong sharp $K\alpha$ line is what makes a great deal of x-ray diffraction possible, because many diffraction

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* The wavelength of an unresolved $K\alpha$ doublet is usually taken as the weighted average of the wavelengths of its components, $K\alpha_1$ being given twice the weight of $K\alpha_2$, since it is twice as strong. Thus the wavelength of the unresolved Mo $K\alpha$ line is

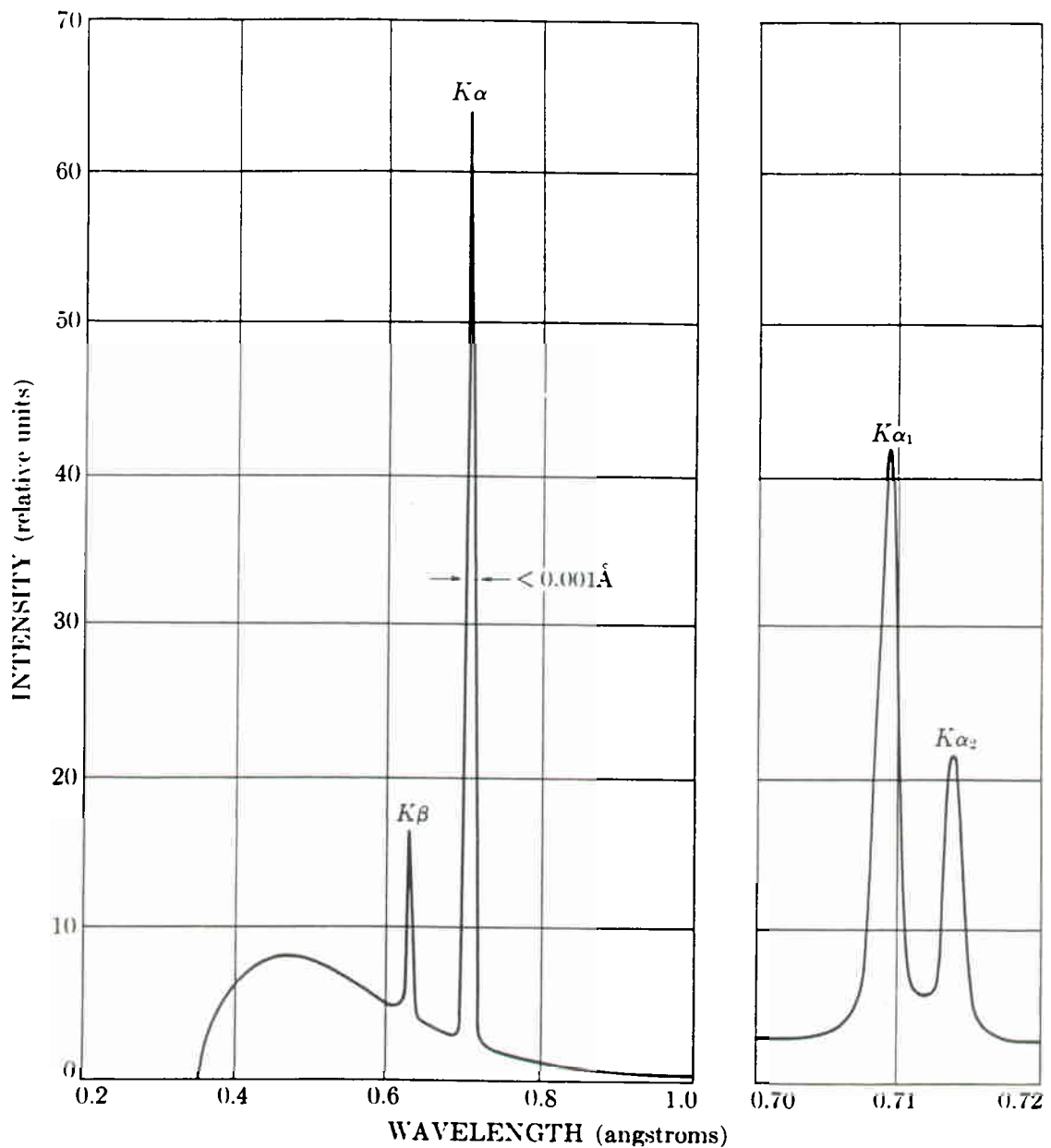$$\tfrac{1}{3}(2 \times 0.709 + 0.714) = 0.711 \text{ Å.}$$

Fig. 1–5 Spectrum of Mo at 35 kV (schematic). Line widths not to scale. Resolved $K\alpha$ doublet is shown on an expanded wavelength scale at right.

experiments require the use of monochromatic or approximately monochromatic radiation.

The characteristic x-ray lines were discovered by W. H. Bragg and systematized by H. G. Moseley. The latter found that the wavelength of any particular line decreased as the atomic number of the emitter increased. In particular, he found a linear relation (Moseley's law) between the square root of the line frequency ν and the atomic number Z:

$$\sqrt{\nu} = C(Z - \sigma), \tag{1-7}$$

where C and σ are constants. This relation is plotted in Fig. 1–6 for the $K\alpha_1$ and $L\alpha_1$ lines, the latter being the strongest line in the L series. These curves show,
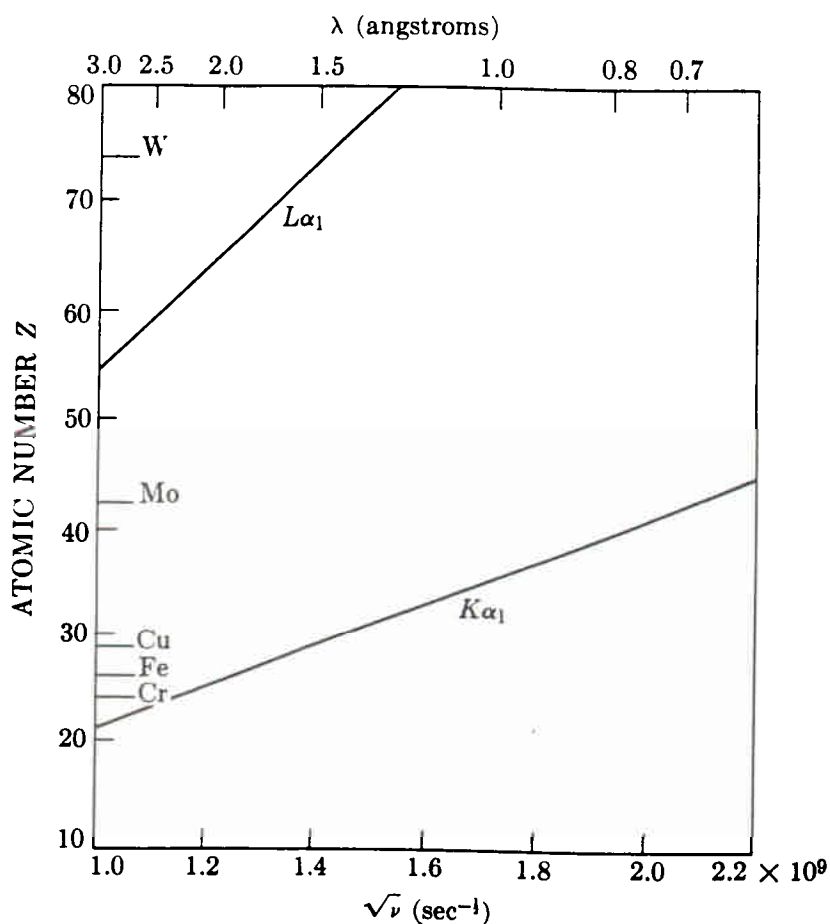
Fig. 1–6 Moseley's relation between $\sqrt{v}$ and Z for two characteristic lines.

incidentally, that L lines are not always of long wavelength: the $L\alpha_1$ line of a heavy metal like tungsten, for example, has about the same wavelength as the $K\alpha_1$ line of copper, namely about 1.5 Å. The wavelengths of the characteristic x-ray lines of almost all the known elements have been precisely measured, mainly by M. Siegbahn and his associates, and a tabulation of these wavelengths for the strongest lines of the K and L series will be found in Appendix 7. Data on weaker lines can be found in Vol. 4 of the *International Tables for X-Ray Crystallography* [G.11].*

While the continuous spectrum is caused by the rapid deceleration of electrons by the target, the origin of the characteristic spectrum lies in the atoms of the target material itself. To understand this phenomenon, it is enough to consider an atom as consisting of a central nucleus surrounded by electrons lying in various shells (Fig. 1–7), where the designation $K, L, M, \ldots$ corresponds to the principal quantum number $n = 1, 2, 3, \ldots$. If one of the electrons bombarding the target has sufficient kinetic energy, it can knock an electron out of the K shell, leaving the atom in an excited, high-energy state. One of the outer electrons immediately falls into the vacancy in the K shell, emitting energy in the process, and the atom is

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* Numbers in square brackets relate to the references at the end of the book. "G" num-
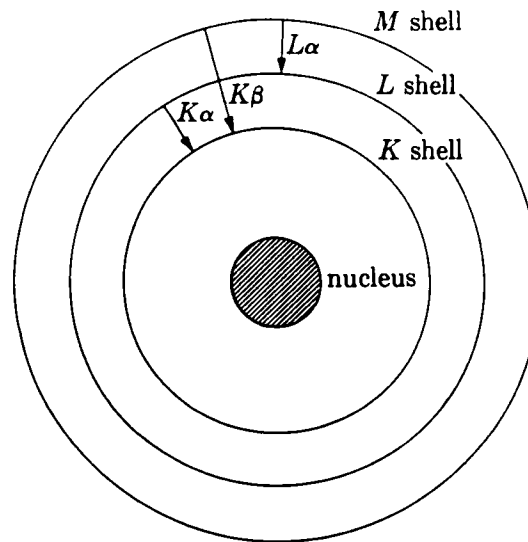bers are keyed to the General References.

Fig. 1–7 Electronic transitions in an atom (schematic). Emission processes indicated by arrows.

once again in its normal energy state. The energy emitted is in the form of radiation of a definite wavelength and is, in fact, characteristic *K* radiation.

The *K*-shell vacancy may be filled by an electron from any one of the outer shells, thus giving rise to a series of *K* lines; *Kα* and *Kβ* lines, for example, result from the filling of a *K*-shell vacancy by an electron from the *L* or *M* shells, respectively. It is *possible* to fill a *K*-shell vacancy from either the *L* or *M* shell, so that one atom of the target may be emitting *Kα* radiation while its neighbor is emitting *Kβ*; however, it is more *probable* that a *K*-shell vacancy will be filled by an *L* electron than by an *M* electron, and the result is that the *Kα* line is stronger than the *Kβ* line. It also follows that it is impossible to excite one *K* line without exciting all the others. *L* characteristic lines originate in a similar way: an electron is knocked out of the *L* shell and the vacancy is filled by an electron from some outer shell.

We now see why there should be a critical excitation voltage for characteristic radiation. *K* radiation, for example, cannot be excited unless the tube voltage is such that the bombarding electrons have enough energy to knock an electron out of the *K* shell of a target atom. If W_K is the work required to remove a *K* electron, then the necessary kinetic energy of the electrons is given by

$$\tfrac{1}{2}mv^2 = W_K. \qquad (1\text{-}8)$$

It requires less energy to remove an *L* electron than a *K* electron, since the former is farther from the nucleus; it therefore follows that the *L* excitation voltage is less than the *K* and that *K* characteristic radiation cannot be produced without *L*, *M*, etc., radiation accompanying it.

1-5 ABSORPTION

Further understanding of the electronic transitions which can occur in atoms can be gained by considering not only the interaction of electrons and atoms, but also the interaction of x-rays and atoms. When x-rays encounter any form of matter, they are partly transmitted and partly absorbed. Experiment shows that the fractional decrease in the intensity I of an x-ray beam as it passes through any homogeneous substance is proportional to the distance traversed x. In differential form,

$$-\frac{dI}{I} = \mu \, dx, \tag{1-9}$$

where the proportionality constant μ is called the *linear absorption coefficient* and is dependent on the substance considered, its density, and the wavelength of the x-rays. Integration of Eq. (1-9) gives

$$I_x = I_0 e^{-\mu x}, \tag{1-10}$$

where I_0 = intensity of incident x-ray beam and I_x = intensity of transmitted beam after passing through a thickness x.

The linear absorption coefficient μ is proportional to the density ρ, which means that the quantity μ/ρ is a constant of the material and independent of its physical state (solid, liquid, or gas). This latter quantity, called the *mass absorption coefficient*, is the one usually tabulated. Equation (1-10) may then be rewritten in a more usable form:

$$\boxed{I_x = I_0 e^{-(\mu/\rho)\rho x}}. \tag{1-11}$$

Values of the mass absorption coefficient μ/ρ are given in Appendix 8 for various characteristic wavelengths used in diffraction.

It is occasionally necessary to know the mass absorption coefficient of a substance containing more than one element. Whether the substance is a mechanical mixture, a solution, or a chemical compound, and whether it is in the solid, liquid, or gaseous state, its mass absorption coefficient is simply the weighted average of the mass absorption coefficients of its constituent elements. If w_1, w_2, etc., are the weight fractions of elements 1, 2, etc., in the substance and $(\mu/\rho)_1$, $(\mu/\rho)_2$, etc., their mass absorption coefficients, then the mass absorption coefficient of the substance is given by

$$\frac{\mu}{\rho} = w_1 \left(\frac{\mu}{\rho}\right)_1 + w_2 \left(\frac{\mu}{\rho}\right)_2 + \cdots. \tag{1-12}$$

The way in which the absorption coefficient varies with wavelength gives the clue to the interaction of x-rays and atoms. The lower curve of Fig. 1-8 shows this variation for a nickel absorber; it is typical of all materials. The curve consists of two similar branches separated by a sharp discontinuity called an *absorption edge*.
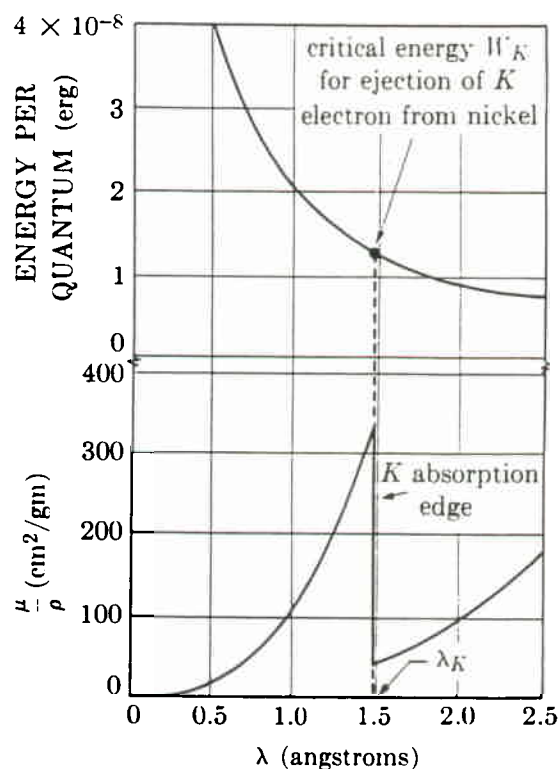
Fig. 1–8 Variation with wavelength of the energy per x-ray quantum and of the mass absorption coefficient of nickel.

Along each branch the absorption coefficient varies with wavelength approximately according to a relation of the form

$$\frac{\mu}{\rho} = k\lambda^3 Z^3, \tag{1-13}$$

where k = a constant, with a different value for each branch of the curve, and Z = atomic number of absorber. Short-wavelength x-rays are therefore highly penetrating and are termed *hard*, while long-wavelength x-rays are easily absorbed and are said to be *soft*.

Matter absorbs x-rays in two distinct ways, by scattering and by true absorption, and these two processes together make up the total absorption measured by the quantity μ/ρ. The *scattering* of x-rays by atoms is similar in many ways to the scattering of visible light by dust particles in the air. It takes place in all directions, and since the energy in the scattered beams does not appear in the transmitted beam, it is, so far as the transmitted beam is concerned, said to be absorbed (Fig. 1-9). The phenomenon of scattering will be discussed in greater detail in Chap. 4; it is enough to note here that, except for the very light elements, it is responsible for only a small fraction of the total absorption. *True absorption* is caused by electronic transitions within the atom and is best considered from the viewpoint of the quantum theory of radiation. Just as an electron of sufficient energy can knock a K electron, for example, out of an atom and thus cause the emission of K characteristic radiation, so also can an incident quantum of x-rays,
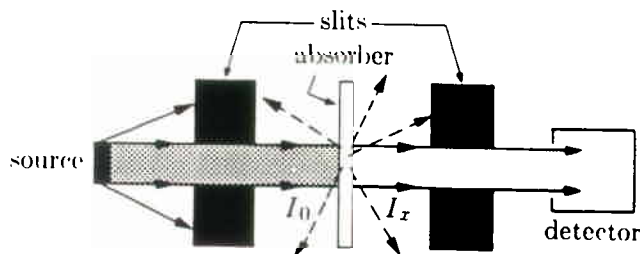
Fig. 1–9 Experimental arrangement for measuring absorption. Narrow slits or pinholes define the beam. The detector measures the intensity I_0 of the incident beam when the absorber is removed and the intensity I_x of the transmitted beam when the absorber is in place. Although the scattered radiation (dashed lines) does not represent energy absorbed *in* the specimen, it does constitute energy removed from the beam and accordingly forms part of the total absorption represented by the coefficient μ/ρ.

provided it has the same minimum amount of energy W_K. In the latter case, the ejected electron is called a *photoelectron* and the emitted characteristic radiation is called *fluorescent radiation*. It radiates in all directions and has exactly the same wavelength as the characteristic radiation caused by electron bombardment of a metal target. (In effect, an atom emits the same K radiation no matter how the K-shell vacancy was originally created.) This phenomenon is the x-ray counterpart of the photoelectric effect in the ultraviolet region of the spectrum; there, photoelectrons can be ejected from the outer shells of a metal atom by the action of ultraviolet radiation, provided the latter has a wavelength less than a certain critical value.

To say that the energy of the incoming quanta must exceed a certain value W_K is equivalent to saying that the wavelength must be less than a certain value λ_K, since the energy per quantum is $h\nu$ and wavelength is inversely proportional to frequency. These relations may be written

$$W_K = h\nu_K = \frac{hc}{\lambda_K}, \tag{1-14}$$

where ν_K and λ_K are the frequency and wavelength, respectively, of the K absorption edge. Now consider the absorption curve of Fig. 1–8 in light of the above. Suppose that x-rays of wavelength 2.5 Å are incident on a sheet of nickel and that this wavelength is continuously decreased. At first the absorption coefficient is about 180 cm^2/gm, but, as the wavelength decreases, the frequency increases and so does the energy per quantum, as shown by the upper curve, thus causing the absorption coefficient to decrease, since the greater the energy of a quantum the more easily it passes through an absorber. When the wavelength is reduced just below the critical value λ_K, which is 1.488 Å for nickel, the absorption coefficient suddenly increases about eightfold in value. True K absorption is now occurring and a large fraction of the incident quanta simply disappear, their energy being converted into K fluorescent radiation and the kinetic energy of ejected photoelectrons. Since energy must be conserved in the process, it follows that the energy per quantum of the fluorescent radiation must be less than that of the incident radiation. or that the wavelength λ_K of the K absorption edge must be shorter than that

of any K characteristic line. (The eight-fold increase in μ/ρ mentioned above means a tremendous decrease in transmitted intensity, because of the exponential nature of Eq. (1–11). If the transmission factor I_x/I_0 of a particular nickel sheet is 0.1 for a wavelength just longer than λ_K, then it is only 10^{-8} for a wavelength just shorter.)

As the wavelength of the incident beam is decreased below λ_K, the absorption coefficient begins to decrease again, even though the production of K fluorescent radiation and photoelectrons is still occurring. At a wavelength of 1.0 Å, for example, the incident quanta have more than enough energy to remove an electron from the K shell of nickel. But the more energetic the quanta become, the greater is their probability of passing right through the absorber, with the result that less and less of them take part in the ejection of photoelectrons.

If the absorption curve of nickel is plotted for longer wavelengths than 2.5 Å, i.e., beyond the limit of Fig. 1–8, other sharp discontinuities will be found. These are the L, M, N, etc., absorption edges; in fact, there are three closely spaced L edges (L_I, L_{II}, and L_{III}), five M edges, etc. (Fig. 1–10). Each of these discontinuities marks the wavelength of the incident beam whose quanta have just sufficient energy to eject an L, M, N, etc., electron from the atom. The right-hand branch of the curve of Fig. 1–8, for example, lies between the K and L absorption edges; in this wavelength region incident x-rays have enough energy to remove L, M, etc., electrons from nickel but not enough to remove K electrons. Absorption-edge wavelengths vary with the atomic number of the absorber in the same way, but not quite as exactly, as characteristic emission wavelengths, that is, according to Moseley's law. Values of the K and L absorption-edge wavelengths are given in Appendix 7.
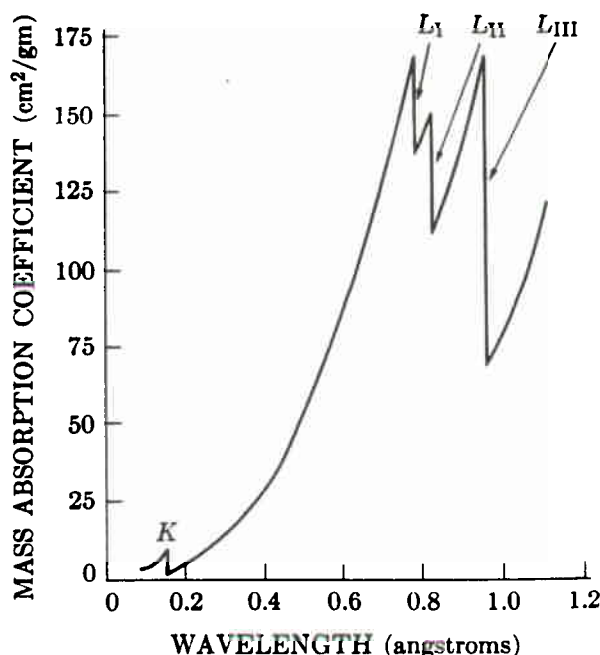

Fig. 1–10   Absorption coefficients of lead, showing K and L absorption edges [1.6].

The measured values of the absorption edges can be used to construct an energy-level diagram for the atom, which in turn can be used in the calculation of characteristic-line wavelengths. For example, if we take the energy of the neutral atom as zero, then the energy of an ionized atom (an atom in an excited state) will be some positive quantity, since work must be done to pull an electron away from the positively charged nucleus. If a K electron is removed, work equal to W_K must be done and the atom is said to be in the K energy state. The energy W_K may be calculated from the wavelength of the K absorption edge by the use of Eq. (1-14). Similarly, the energies of the L, M, etc., states can be calculated from the wavelengths of the L, M, etc., absorption edges and the results plotted in the form of an energy-level diagram for the atom (Fig. 1-11).

Although this diagram is simplified, in that the substructure of all the levels is not shown, it illustrates the main principles. The arrows show the transitions of the *atom*, and their directions are therefore just the opposite of the arrows in Fig. 1-7,
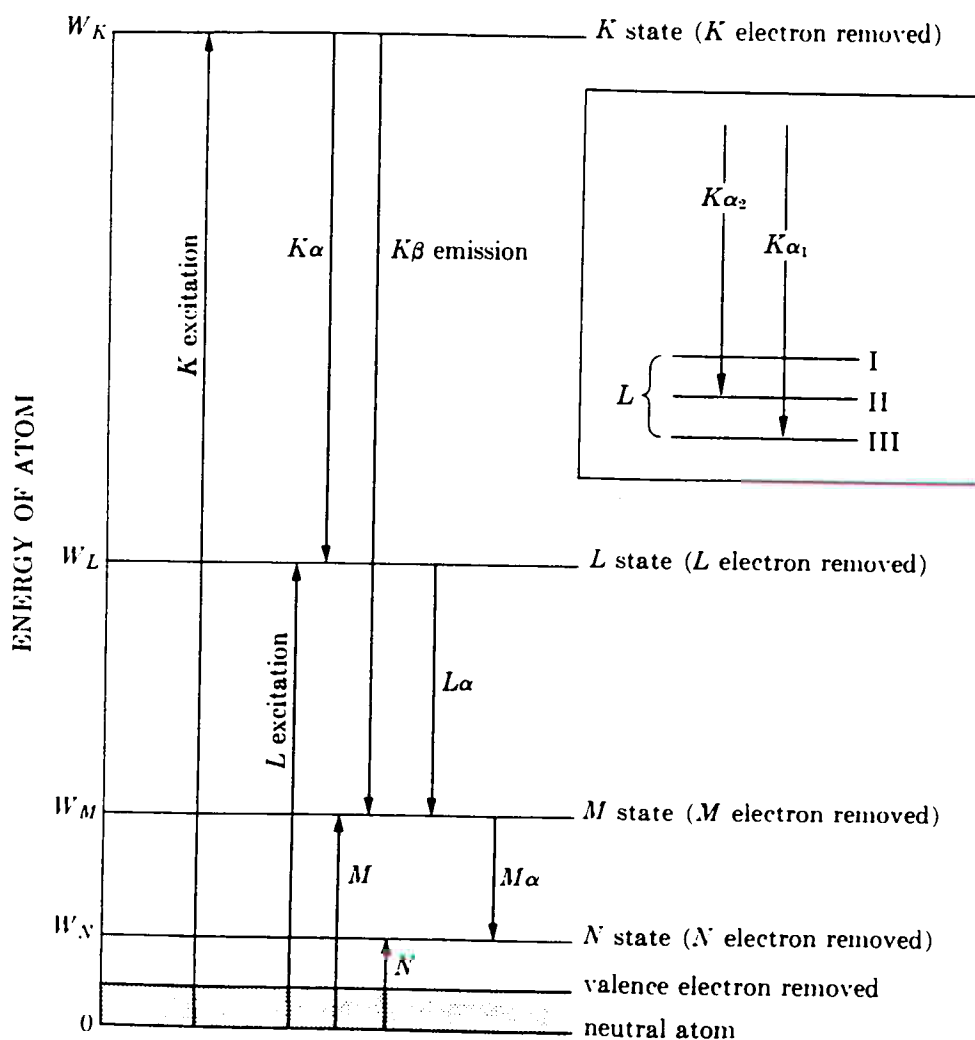

Fig. 1-11 Atomic energy levels (schematic). Excitation and emission processes indicated by arrows. The insert at top right shows the fine structure of the L state. After Barrett [1.7].

which shows the transitions of the *electron*. Thus, if a K electron is removed fro[m] an atom (whether by an incident electron or x-ray), the atom is raised to the K stat[e]. If an electron then moves from the L to the K level to fill the vacancy, the ato[m] undergoes a transition from the K to the L state. This transition is accompanie[d] by the emission of $K\alpha$ characteristic radiation and the arrow indicating $K\alpha$ emissio[n] is accordingly drawn *from* the K state *to* the L state.

Figure 1–11 shows clearly how the wavelengths of characteristic emission line[s] can be calculated, since the difference in energy between two states will equal $h[\nu]$ where ν is the frequency of the radiation emitted when the atom goes from one sta[te] to the other. Consider the $K\alpha_1$ characteristic line, for example. The "L level" [of] an atom is actually a group of three closely spaced levels (L_I, L_{II}, and L_{III}), and th[e] emission of the $K\alpha_1$ line is due to a $K \to L_{III}$ transition. The frequency $\nu_{K\alpha_1}$ of th[e] line is therefore given by the equations

$$h\nu_{K\alpha_1} = W_K - W_{L_{III}},$$
$$h\nu_{K\alpha_1} = h\nu_K - h\nu_{L_{III}},$$
$$\frac{1}{\lambda_{K\alpha_1}} = \frac{1}{\lambda_K} - \frac{1}{\lambda_{L_{III}}}, \qquad (1\text{-}1[5])$$

where the subscripts K and L_{III} refer to absorption edges and the subscript $K\alpha[_1]$ to the emission line.

Excitation voltages can be calculated by a relation similar to Eq. (1–4). T[o] excite K radiation, for example, in the target of an x-ray tube, the bombardin[g] electrons must have energy equal to W_K. Therefore

$$eV_K = W_K = h\nu_K = \frac{hc}{\lambda_K},$$
$$V_K = \frac{hc}{e\lambda_K},$$
$$V_K = \frac{12.40 \times 10^3}{\lambda_K}, \qquad (1\text{-}16[)]$$

where V_K is the K excitation voltage and λ_K is the K absorption edge wavelengt[h] (in angstroms).

Figure 1–12 summarizes some of the relations developed above. This curv[e] gives the short-wavelength limit of the continuous spectrum as a function o[f] applied voltage. Because of the similarity between Eqs. (1–4) and (1–16), the sam[e] curve also enables us to determine the critical excitation voltage from th[e] wavelength of an absorption edge.

Auger effect [1.1, 1.2]. It might be inferred, from the last two sections, that ever[y] atom that has a vacancy in, for example, the K shell will always emit K radiation. Tha[t] is not so. An atom with a K-shell vacancy is in an ionized, high-energy state. It can los[e] this excess energy and return to its normal state in two ways: (1) by emitting K radiatio[n] ("normal" production of characteristic radiation), or (2) by emitting an electron (*Auge[r] effect*). In the Auger process a K-shell vacancy is filled from, say, the L_{II} level; th[e]
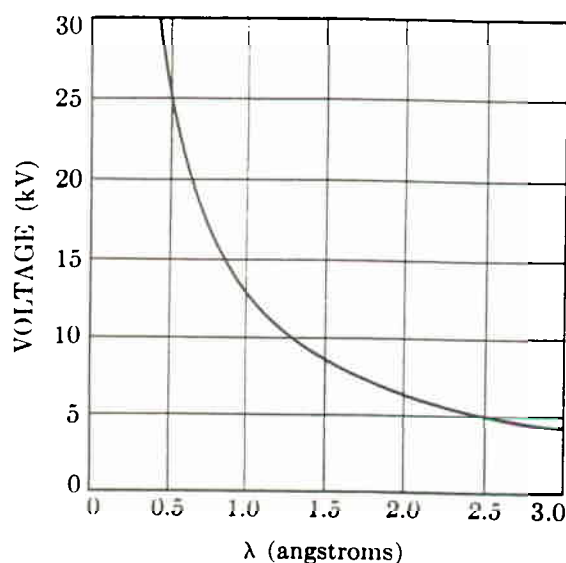
Fig. 1–12 Relation between the voltage applied to an x-ray tube and the short-wavelength limit of the continuous spectrum, and between the critical excitation voltage of any metal and the wavelength of its absorption edge.

resulting K radiation does not escape from the atom but ejects an electron from, say, the L_{III} level. The ejected electron, called an *Auger electron*, has a kinetic energy related to the energy difference between the K and L_{II} states.

The Auger effect is by no means a minor one. In fact, atoms with an atomic number Z less than 31 (gallium) are more likely to eject Auger electrons than to emit x-rays. The likelihood of the Auger process can be found from the fluorescence yield ω, which is defined, for the K shell, by

$$\omega_K = \frac{\text{number of atoms that emit } K \text{ radiation}}{\text{number of atoms with a } K\text{-shell vacancy}}. \qquad (1\text{–}17)$$

(This quantity is called the *fluorescence* yield, whether the vacancy is caused by incident x-rays or by electrons.) Some values of ω_K are 0.03 for Mg ($Z = 12$), 0.41 for Cu ($Z = 29$), and 0.77 for Mo ($Z = 42$) [G.31, p. 131]. The probability of the Auger process occurring is $(1 - \omega_K)$, which amounts to some 97 percent for Mg and 23 percent for Mo.

Electrons of moderate energy like Auger electrons cannot travel very far in a solid, and an Auger electron emitted by one atom in a solid specimen cannot escape from the specimen unless the atom is situated within about 10 Å of the surface. The electrons that do escape have kinetic energies related to the differences between energy levels of the parent atom, i.e., their energies are characteristic of that atom. Means are available for measuring these energies, and we therefore have a method for chemical analysis of very thin surface layers, called *Auger electron spectroscopy*, used in studies of catalysts, corrosion, impurity segregation at surfaces, etc.

1–6 FILTERS

Many x-ray diffraction experiments require radiation which is as closely monochromatic as possible. However, the beam from an x-ray tube operated at a voltage above V_K contains not only the strong $K\alpha$ line but also the weaker $K\beta$ line and the

continuous spectrum. The intensity of these undesirable components can be decreased relative to the intensity of the $K\alpha$ line by passing the beam through a *filter* made of a material whose K absorption edge lies between the $K\alpha$ and $K\beta$ wavelengths of the target metal. Such a material will have an atomic number one less than that of the target metal, for metals with Z near 30.

A filter so chosen will absorb the $K\beta$ component much more strongly than the $K\alpha$ component, because of the abrupt change in its absorption coefficient between these two wavelengths. The effect of filtration is shown in Fig. 1-13, in which the partial spectra of the unfiltered and filtered beams from a copper target ($Z = 29$) are shown superimposed on a plot of the mass absorption coefficient of the nickel filter ($Z = 28$).

The thicker the filter the lower the ratio of intensity of $K\beta$ to $K\alpha$ in the transmitted beam. But filtration is never perfect, of course, no matter how thick the filter, and one must compromise between reasonable suppression of the $K\beta$ component and the inevitable weakening of the $K\alpha$ component which accompanies it. In practice it is found that a reduction in the intensity of the $K\alpha$ line to about half its original value will decrease the ratio of intensity of $K\beta$ to $K\alpha$ from about $\frac{1}{9}$ in the incident beam to about $\frac{1}{500}$ in the transmitted beam; this level is sufficiently low for most purposes. Table 1-1 shows the filters used in conjunction with the common target metals, the thicknesses required, and the transmission factors for the $K\alpha$ line. Filter materials are usually used in the form of thin foils. If it is not
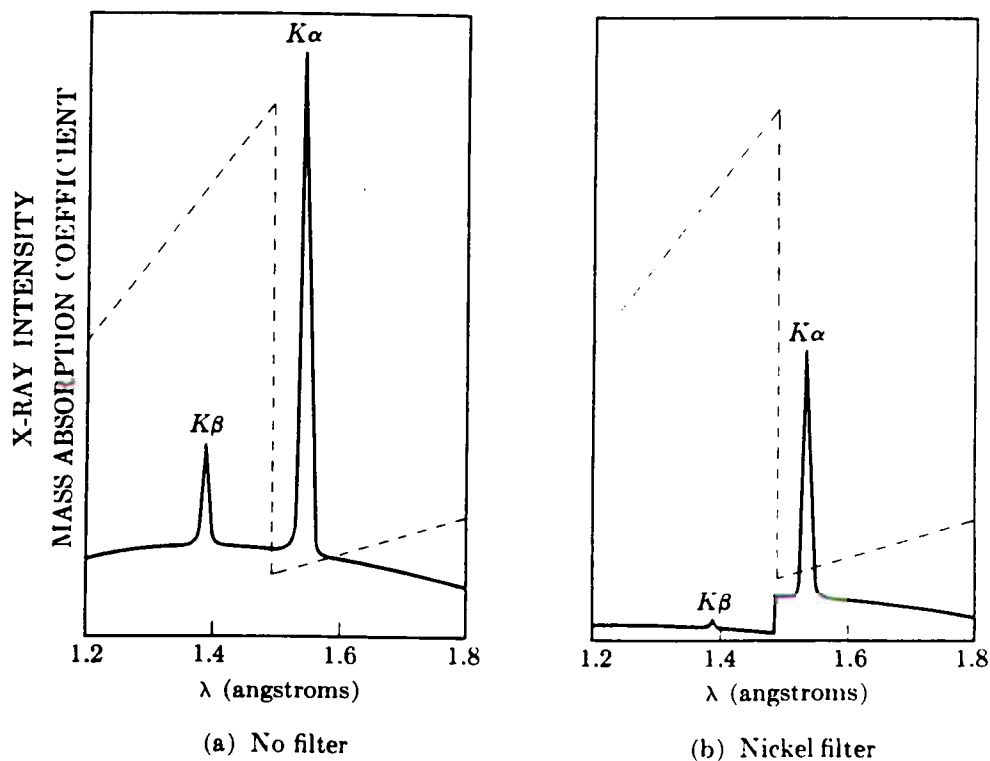

(a) No filter   (b) Nickel filter

Fig. 1-13 Comparison of the spectra of copper radiation (a) before and (b) after passage through a nickel filter (schematic). The dashed line is the mass absorption coefficient of nickel.

<div align="center">

Table 1-1

Filters for Suppression of $K\beta$ Radiation

</div>

Target	Filter	Incident beam* $\dfrac{I(K\alpha)}{I(K\beta)}$	Filter thickness for $\dfrac{I(K\alpha)}{I(K\beta)} = \dfrac{500}{1}$ in trans. beam		$\dfrac{I(K\alpha) \text{ trans.}}{I(K\alpha) \text{ incident}}$
			mg/cm²	in.	
Mo	Zr	5.4	77	0.0046	0.29
Cu	Ni	7.5	18	0.0008	0.42
Co	Fe	9.4	14	0.0007	0.46
Fe	Mn	9.0	12	0.0007	0.48
Cr	V	8.5	10	0.0006	0.49

* This is the intensity ratio *at the target* [G.11, Vol. 3, p. 71]. This ratio outside the x-ray tube will be changed somewhat by the differential absorption of $K\alpha$ and $K\beta$ by the tube window, typically beryllium, 0.01 inch (0.25 mm) thick.

possible to obtain a given metal in the form of a stable foil, the oxide of the metal may be used. The powdered oxide is mixed with a suitable binder and spread on a paper backing, the required mass of metal per unit area being given in Table 1-1.

1-7 PRODUCTION OF X-RAYS

We have seen that x-rays are produced whenever high-speed electrons collide with a metal target. Any x-ray tube must therefore contain (*a*) a source of electrons, (*b*) a high accelerating voltage, and (*c*) a metal target. Furthermore, since most of the kinetic energy of the electrons is converted into heat in the target, the latter is almost always water-cooled to prevent its melting.

All x-ray tubes contain two electrodes, an anode (the metal target) maintained, with few exceptions, at ground potential, and a cathode, maintained at a high negative potential, normally of the order of 30,000 to 50,000 volts for diffraction work. X-ray tubes may be divided into two basic types, according to the way in which electrons are provided: gas tubes, in which electrons are produced by the ionization of a small quantity of gas (residual air in a partly evacuated tube), and filament tubes, in which the source of electrons is a hot filament.

Gas Tubes

These resemble the original x-ray tube used by Roentgen. They are now obsolete.

Filament Tubes

These were invented by Coolidge in 1913. They consist of an evacuated glass envelope which insulates the anode at one end from the cathode at the other, the cathode being a tungsten filament and the anode a water-cooled block of copper containing the desired target metal as a small insert at one end. Figure 1-14 is a photograph of such a tube, and Fig. 1-15 shows its internal construction. One lead of the high-voltage transformer is connected to the filament and the other to
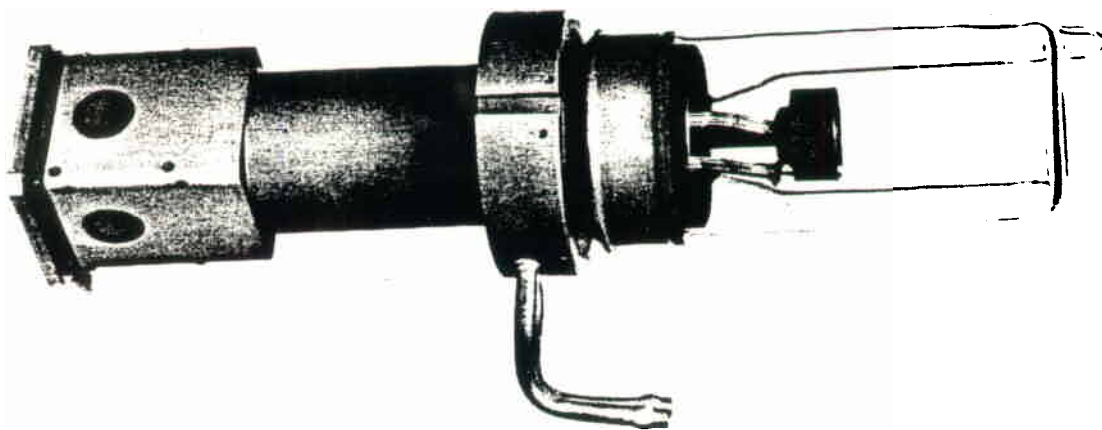
Fig. 1–14 Sealed-off filament x-ray tube. Cooling-water tubes at center connect with internal ducts leading to anode at left end. Three windows: two for projecting square focal spots and one for projecting a line focal spot. Focal spots of three sizes are available with this tube (Type A-5): 1.2 × 12.5 mm, 0.75 × 12.5 mm, and 0.45 × 12.5 mm. (Courtesy of Machlett Laboratories, Inc.)

ground, the target being grounded by its own cooling-water connection. The filament is heated by a *filament current* of about 3 amp and emits electrons which are rapidly drawn to the target by the high voltage across the tube. Surrounding the filament is a small metal cup maintained at the same high (negative) voltage as the filament: it therefore repels the electrons and tends to focus them into a narrow region of the target, called the *focal spot*. X-rays are emitted from the focal spot in all directions and escape from the tube through two or more windows in the tube housing. Since these windows must be vacuum tight and yet highly transparent to x-rays, they are usually made of beryllium.

Although one might think that an x-ray tube would operate only from a dc source, since the electron flow must occur only in one direction, it is actually possible to operate a tube from an ac source such as a transformer because of the rectifying properties of the tube itself. Current exists during the half-cycle in which the filament is negative with respect to the target; during the reverse half-cycle the filament is positive, but no electrons can flow since only the filament is hot enough to emit electrons. Thus a simple circuit such as shown in Fig. 1–16 suffices for many installations, although more elaborate circuits, containing rectifying tubes, smoothing capacitors, and voltage stabilizers, are often used, particularly when the x-ray intensity must be kept constant within narrow limits. In Fig. 1–16, the voltage applied to the tube is controlled by the autotransformer which controls the voltage applied to the primary of the high-voltage transformer. The voltmeter shown measures the input voltage but may be calibrated, if desired, to read the output voltage applied to the tube. The milliammeter measures the *tube current*, i.e., the flow of electrons from filament to target. This current is normally of the order of 10 to 25 mA and is controlled by the filament rheostat. The rheostat controls