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PART I

CHAPTER ONE

THE GENERAL PROPERTIES OF X-RAYS

A. The nature of X-rays

1. **X-rays** are transverse electromagnetic radiations, like light but of very much shorter wavelengths. It is not possible to fix the limits of their domain with precision. Towards the long wavelengths, X-ray tubes can emit radiations identical with ultra-violet light and, at the other extremity of the spectrum, rays similar to the γ rays emitted by radioactive bodies. But the X-rays used in X-ray crystallography have wavelengths included in the interval 0·5 to 2 A. (One Ångstrom $= 10^{-8}$ cms.) It is, therefore, to this range of wavelengths that our study is limited. We may note that the X-rays used in radiography have, on an average, a much shorter wavelength (from 0·05 to 1 A).

It is known that radiant energy shows itself, according to experiment, in one of its two complementary aspects, as waves or as corpuscles. Sometimes it is better to think of waves, characterized by their wavelengths λ, sometimes it is necessary to picture a beam as a collection of particles moving with the velocity of light c, each "photon" possessing the energy $h\nu = h\frac{c}{\lambda}$. Since the frequency of X-rays is about 1,000 times that of light rays, the X photon possesses an energy much greater than that of the photon of light.

While the optics of X-rays (both geometrical and physical) have just the same theoretical basis as ordinary optics, there are special features which spring from two essential facts . the small value of the wavelength and the large energy of the photon. Thus the interactions of X-rays and of light with matter are profoundly different. Given the constants of the material, a process that is possible in one case is not possible in the other. Thus, the index of refraction of all media for X-rays being very close to 1, the rays cannot be bent to any practical extent ; under normal experimental conditions they are not reflected. Like a beam of light, a beam of X-rays can be partially or completely polarized, but the plane of polarization is not modified by the medium which is traversed, and there is in X-ray technique nothing, therefore, corresponding to polarimetry. The whole interest of the optics of X-rays is concentrated on the phenomena of scattering and diffraction.

2. **Sources of X-rays : their characteristics.** The only source of X-radiation of a sufficient intensity to be of practical use is the impact of

cathode rays, that is to say of high velocity electrons, with matter. An X-ray tube consists, then, of a source of electrons, called the cathode, and a target, the anticathode. Between the two there is set up a big potential difference to give the electrons the desired velocity at the moment of impact with the anticathode.

Unhappily, in the collision the energy which is emitted in the form of X-rays is extremely feeble. The output of an X-ray tube, that is to say, the ratio of the energy contained in the emitted pencil to the energy of the electron beam, is given by the approximate empirical formula: (Compton and Allison, 1935a).

$$\epsilon = 1{\cdot}1 \,.\, 10^{-9} ZV \qquad 1.1$$

Z is the atomic number of the element of the anticathode, and V the tension at the terminals of the tube, in volts. For a tube with a tungsten anticathode working at 100,000 volts $\epsilon = 0{\cdot}8\%$ and for a tube with a copper anticathode working at 30,000 volts $\epsilon = 0{\cdot}2\%$.

In other words, nearly all the energy carried by the electrons per second, let us say iV (where i is the electron current), is transformed into heat. The anticathode would, therefore, heat up and would rapidly melt if this heat were not taken away; but, even if the most powerful means of cooling are employed, a given substance, used as an anticathode, cannot receive more than a certain amount of energy per unit surface without deteriorating. This limiting value is the greater, the better the conductivity and the higher the melting point of the substance; hence the exclusive use of metals as anticathodes, and principally the refractory metals such as tungsten, molybdenum or rhodium, or else very good conductors such as copper and silver. This limitation of the power of X-ray sources is a grave drawback which, up to now, has not been satisfactorily overcome: for in X-ray crystallography one is constantly impeded by a too feeble intensity of the beam, and it is certain that a tube a hundred times more powerful than the present tubes would greatly extend the field of applications of X-rays.

B. Mechanism of the production of X-rays

The X-rays emitted by an anticathode divide themselves into two groups, the continuous spectrum and the rays characteristic of the anticathode.

3. The continuous spectrum. Let us consider a tube with a tungsten anticathode and cause it to operate, at constant current, at tensions progressively increasing from 20 to 50 kV, and let us record, with appropriate apparatus, the intensity of emission as a function of the wavelength. The curves of Fig. 1 are obtained in this way.

The spectrum emitted is a continuous one, in which there are radiations of all wavelengths *starting from a certain lower limit*, the intensity varying in a continuous fashion with the wavelength.

The quantum theory accounts in a simple way for this lower limit to the spectrum. The electron of energy eV can, as the result of the collision with matter, give rise to a photon whose energy $h\nu$ is, at most, that of the electron. Hence there is an upper frequency limit to the radiation, given by the relation

$$h\nu_m = \frac{hc}{\lambda_m} = eV \quad . \quad . \quad . \quad 1.2$$

which is, numerically, expressing V in absolute volts and λ in angstroms

$$\lambda_m = \frac{12395}{V} \quad . \quad . \quad . \quad . \quad 1.3$$

If, before the collision which generates the photon, the electron has lost velocity in making its way through the matter, the emitted photon has less energy: hence the appearance of a continuous spectrum extending from the lower limit towards the longer wavelengths. But this quantum explanation does not throw any light on the mechanism of the transference of energy from the electron to the photon. The classical theory relates the emission of a train of waves containing all wavelengths to the sudden retardation of the electron on impact with matter, but it cannot account for the lower limit of the spectrum observed. To sum up, at the present day there is no simple theory which gives a clear picture of the whole of this phenomenon, although it is a fundamental one.

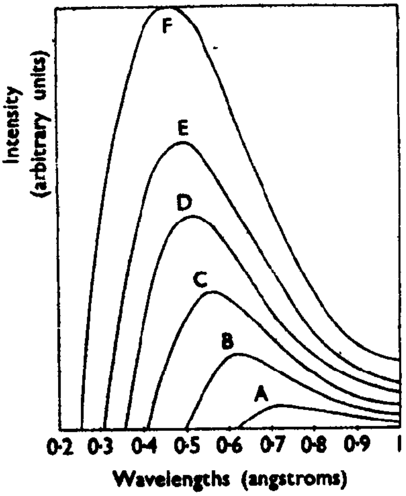

FIG. 1. Intensity of the continuous spectrum as a function of wavelength, for different tube tensions.

A : 20kV B 25kV C : 30kV
D : 35kV E : 40kV F : 50kV

(After Ulrey).

What do we learn from experiment? The intensity of radiation of a given wavelength increases as the tension increases, while the spectrum extends further towards the short wavelengths (Fig. 1). The energy received by the anticathode being proportioned to V and the output, in radiated energy (formula 1.1), to ZV, the total energy of the spectrum (represented by the area under one curve of figure 1) is proportional to ZV^2. For given conditions of operation of a tube (iV), the intensity of the continuous spectrum is proportional to the atomic number of the anticathode element: it is, therefore, advantageous to *use heavy elements*.

It should be noted from figure 1 that the continuous spectrum begins in a very abrupt way at the threshold, that is to say, it contains a notable proportion of radiations whose wavelengths are very close to the lower limit.

To sum up, when one needs " white " radiation, *i.e.* radiation in which all wavelengths are present, a tube with *an anticathode of a heavy metal* *must be used* (tungsten is two and a half times more efficient than copper) *under high tension.* The increase of tension extends the spectrum towards the short wavelengths (formula 1.3) and improves the output of the tube for the whole spectrum. Moreover, it must be kept in mind, for the interpretation of diagrams in polychromatic radiation (Laue), that the intensities of emission of radiations of two different wavelengths are not equal and that it is impossible to predict in a simple way the ratio of these intensities.

4. Characteristic spectrum. On the continuous spectrum there may be superimposed a line spectrum of which the wavelengths, which are independent of the conditions of operation of the tube, depend only on the *nature* of the anticathode. These are the lines characteristic of the atoms of the anticathode.

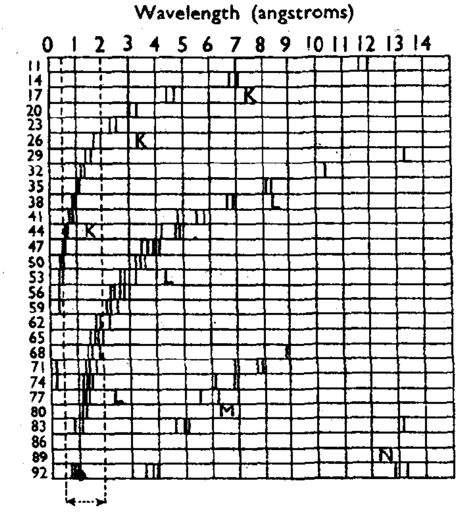

FIG. 2. Spectra of different elements. (After Siegbahn " Röntgenstrahlen Spectroscopie ").

Figure 2 gives a chart of the wavelengths of the principal lines of a series of elements of regularly increasing atomic number. Two essential facts emerge clearly: the spectra, which are very simple, only contain a small number of lines; and the spectra of all the elements are analogous; they consist of groups of lines known as the K, L, M, etc., series. Each series contains a set of lines which follow, in similar fashion, in the spectra of all the elements. The frequency of a line in a particular position varies with the atomic number, according to the simple law discovered by Moseley:

$$\sqrt{\nu}=C(Z-\sigma)$$

Z being the atomic number (C and σ being constants, $\sigma \simeq 1$).

The characteristic radiations that occur in the range of wavelengths used in X-ray crystallography are marked in Figure 2. The L series is complex, whereas the K series consists of only three lines of notable intensity, a very close doublet K_{α_2} and K_{α_1} (of separation 0·004 A) and a single line K_β, the intensities of these lines being as the numbers 50; 100; 22. In practice the doublet often cannot be resolved; there are then only two lines, K_α and K_β, the second having an intensity seven times weaker than the first. When a radiation of a single known wavelength is required *the* K_α *line is always used.* The table below gives the wavelengths of the K lines of the elements which, owing to their physical properties, make good anticathodes, and whose line is in a suitable region.

The theory of the production of characteristic lines is as follows. As a result of the impact of the electrons of the cathode stream, certain atoms of the anticathode are ionized, that is to say, an electron is expelled from one of the deep layers of the atom. The place which is thus freed is then occupied by an electron from an orbit farther from the nucleus: this jump is accompanied by the emission of a photon in which there reappears the energy that the electron has lost in approaching the nucleus. If W_i and W_f are the initial and final energies of the electron the emitted line has a frequency such that $h\nu = W_i - W_f$. As, in the atom, the electrons are all at well-defined energy levels, it follows that the energy of the photon, that is to say its frequency, is fixed: hence the emission of a certain number of characteristic radiations. For example, the K_α line is emitted on the transition of an electron from an L level to a K level, whence

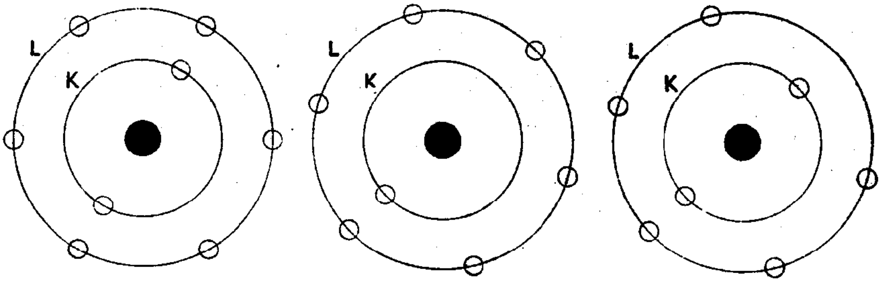

FIG. 2A. Production of characteristic lines.

$$h\nu_{K_\alpha} = W_K - W_L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 1.4$$

TABLE I

Anticathodes		Wavelengths		Threshold of Excitation of the K_α line V_K volts
Substance	Atomic Number	$K_{\alpha_2} - K_{\alpha_1}$ (Angstroms)	K_β (Angstroms)	
Chromium	24	2·294 – 2·290	2·085	5,950
Iron	26	1·940 – 1·936	1·757	7,100
Cobalt	27	1·793 – 1·789	1·621	7,700
Nickel	28	1·662 – 1·658	1·500	8,300
Copper	29	1·544 – 1·540	1·392	9,000
Molybdenum	42	0·7135 – 0·7093	0·6323	20,000
Rhodium	45	0·6176 – 0·6132	0·5456	23,400
Palladium	46	0·5898 – 0·5854	0·5205	24,500
Silver	47	0·5638 – 0·5594	0·4970	25,600
Tungsten*	74	0·2138 – 0·2090	0·1844	69,500

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* In practice the tube with a tungsten anticathode is not used as a source of monochromatic radiation.

The electronic layers which take part in the emission of X-rays are the deep layers of the atom : the energy levels which the electrons can occupy are few ; they depend, to a first approximation, solely on the charge of the central nucleus and are independent of the outer electrons which determine the chemical properties of the atoms and their optical spectra. From these facts result the simplicity of X-ray spectra, their regularity as a function of the atomic number, and the fact that the lines are characteristic of the atom whatever the chemical or physical states of the body in which it occurs.

In order that a line of the K series, for instance, shall be emitted the K layer must be ionized : the electron of the cathode stream must, therefore, possess an energy at least equal to the energy of binding of a K electron to the atom, W_K. The X-ray tube will, then, only emit a K line if it functions at a potential greater than a minimum potential V_K given by the relation :

$$eV_K = W_K \quad \dots\dots\dots\dots \quad 1.5$$

Note : For the characteristic lines, the minimum excitation potential is not, therefore, given by the relation $V = \frac{12395}{\lambda}$ which holds for the continuous spectrum : the necessary potential is higher since the energy of the photon is less than that of the electron which gives rise to it. In Table I will be found the values of the excitation potential V_K corresponding to the K_α lines of the usual anticathodes.

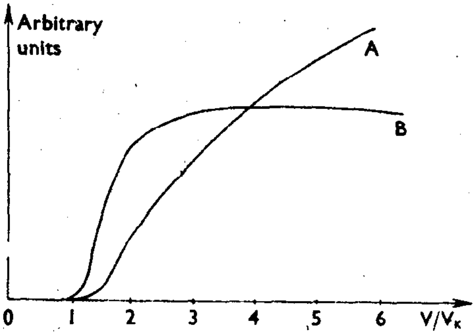

FIG. 3. Curve A : Maximum intensity of emission of a charaeteristic line K_α.
Curve B : Ratio of the intensities of a line K_α and of the continuous spectrum.

The intensity emitted by a given tube for a characteristic line is a function of the current i consumed by the tube and of the potential, V. The experimental results are represented by the following law :

$$I = Ci(V - V_K)^n \quad n \text{ being about } 1{\cdot}5 \quad \dots\dots \quad 1.6$$

Let W be the maximum power the anticathode can take : the current i will, at the most, be equal to $\frac{W}{V}$ and the maximum intensity of the line will be

$$I = CW\frac{(V - V_K)^{1{\cdot}5}}{V} = CWV_K^{0{\cdot}5} \cdot \frac{\left(\frac{V}{V_K} - 1\right)^{1{\cdot}5}}{\frac{V}{V_K}} \quad \dots\dots \quad 1.7$$

This function $\frac{V}{V_K}$ is represented in Figure 3 (Curve A): the intensity of the line is greater the higher the tension, but its increase becomes less and less rapid.

5. Comparison between the continuous spectrum and the line spectrum. The existence of characteristic lines and, in particular, of the very intense and well-isolated K_α line, is fundamental in X-ray crystallography. *An X-ray tube can function as a source of nearly monochromatic radiation.* Let us define the value of that approximation and indicate the best working conditions for its realization.

In the first place, besides the K_α line, there is the K_β line, though this is more feeble. This introduces no difficulty for we shall see later on an excellent means of eliminating it (§ 6). That leaves us with the continuous spectrum: how do the respective energies of the K_α line and of the continuous spectrum depend on the conditions of operation of the tube? In practice the question presents itself in two different ways. Let us imagine that the spectrum of the radiations emitted by the tube has been recorded on a photographic plate. The K_α line stands out from the continuous background. What is the contrast? Without giving the exact figure, for which it would be necessary to define the experimental conditions, it can be said that it is very large, if the potential across the tube is distinctly greater than the minimum excitation potential of the line (for example $V > 2V_K$) and if the element of the anticathode has a small atomic weight (copper). To obtain, in the continuous spectrum adjoining the line, a blackening comparable with that of the line the exposure time would have to be multiplied by a factor of the order of 100, but the continuous spectrum is of greater relative importance with anticathodes made of heavy metals (Mo, Ag) for its intensity increases with the atomic number (formula 1.1).

On the other hand, for certain problems, it is necessary to compare the energy of the K_α line with the energy of the whole continuous spectrum or, at least, of a wide band. There again a precise answer is impossible unless the conditions are specified, but one can predict how the ratio of the intensities of the line and of the continuous spectrum will vary with the potential across the tube.

The line intensity is given by the formula 1.7. The total intensity of the continuous spectrum is, according to 1.1, proportional to W.Z.V. The required ratio is, therefore, proportional to:

$$\frac{1}{Z \cdot V_K^{0\cdot 5}} \cdot \frac{\left(\frac{V}{V_K} - 1\right)^{1\cdot 5}}{\left(\frac{V}{V_K}\right)^2}.$$

Curve B, figure 3, gives the variation of this ratio for a given anticathode, as a function of $\frac{V}{V_K}$. It increases up to $\frac{V}{V_K} = 3$, remains stationary over a long range and then decreases very slowly. For any given value of $\frac{V}{V_K}$ the continuous spectrum is the more important, the higher the atomic weight of the anticathode, since Z and V_K both increase together.

Thus we arrive at the following conclusions.

1. In practice, one can make use of a tube as a source of homogeneous radiation, by using the K_α emission line of the anticathode. The optimum tube potential is about three times the excitation potential of the line under consideration. When this tension is exceeded the relative importance of the continuous spectrum increases, though fairly slowly. The energy of the K_α line, compared with that contained in a band of the same width from the continuous spectrum, is very large for anticathodes of low atomic weight. On the other hand, when a wide band of continuous spectrum takes part in a phenomenon, it must be remembered that its action can be important compared with that of the K_α line alone.

2. If "white" radiation is required, a tube with a tungsten anticathode run at 60–80 kV is the most suitable. Upon the continuous spectrum are superposed the weak L lines of tungsten ; the K lines only appear at a tension above 69 kV (Table I) but their intensity remains relatively weak since $\frac{V}{V_K}$ is only a little greater than unity (Figure 3).

C. Interaction of X-rays and matter

A beam of X-rays is weakened by passage through matter. The interaction of radiation with matter is rather complex. The photons which do not reappear in the emergent beam may have suffered various transformations.

(*a*) They may remain photons but have been deviated from their path, either without loss of energy, *which corresponds to radiation scattered without change of wavelengths*, or with a slight loss of energy, which is scattering with a change of wavelength, the *Compton effect.*

(*b*) The photons may have been absorbed by the atoms. This is the photoelectric effect. The excited atom re-emits two kinds of secondary radiation, electrons, and fluorescent X-rays whose wavelength has no relationship to the primary wavelength but is characteristic of the excited atom.

We shall first study the effect of all these phenomena together without analysing them in detail, that is to say we shall study the absorption of X-rays by matter.

6. Absorption of X-rays and photoelectric effect

(*a*) **Coefficient of absorption.** A very thin layer of any given substance, containing the mass dp per unit area (gm./cm.^{2}), absorbs a fraction dI/I of the incident intensity proportional to dp ; thence we can write

$$\frac{dI}{I} = \mu \, dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 18$$

For a layer of finite thickness, of mass per unit surface p, the ratio of transmitted intensity I to the incident intensity I_0 is given by the following formula deduced from 1.8 by integration

$$I/I_0 = e^{-\mu p}\,* \qquad 1.8a$$

that is:

$$I/I_0 = e^{-\mu\rho x}$$

where x is the thickness in centimetres and ρ the specific mass (gm./cm.^{3}) of the absorbing material.

An absorbing medium whose mass per unit surface is $1/\mu$ reduces the intensity of the beam in the ratio $\frac{1}{e} = 0{\cdot}35$. That which absorbs one half of the energy of the beam has a mass per unit surface of $\frac{0{\cdot}69}{\mu}$ and a thickness of $\frac{0{\cdot}69}{\mu\rho}$.

The coefficient μ thus defined is the *mass coefficient* of the substance. Other coefficients of absorption are often introduced (linear, atomic etc.). We shall make exclusive use of the mass coefficient as it has the advantage of being independent of the physical state of the substance †. Appendix V gives a list of mass absorption coefficients of elements for various wavelengths. It permits the calculation of the absorption of any substance whose elementary analysis is known. X-ray absorption is, actually, an atomic phenomenon and is independent of the state of the component elements, whose action is simply additive.

To calculate the absorption of a compound the following formulae are used:

(1) Suppose the percentage composition, by weight, of the substance is known. If it contains x_1% of the element of coefficient μ_1, x_2% of that of coefficient μ_2, etc., the mass coefficient of the compound will be

$$\mu = \frac{x_1\mu_1 + x_2\mu_2 + \ldots}{100} \qquad 1.9$$

(2) Suppose the chemical formula of the compound is known, as $A^1_{y_1}\,A^2_{y_2}\ldots$. The formula to be used is then the following.

$$\mu = \frac{y_1a_1\mu_1 + y_2a_2\mu_2 + \ldots}{y_1a_1 + y_2a_2 + \ldots} \qquad 1.10$$

$a_1 . a_2 \ldots$ being the atomic weights of $A^1A^2, \ldots$.

(*b*) **Laws of absorption.** The absorption coefficient of an element is a function of the wavelength and of the atomic number of the element.

(1) *Variation with wavelength.* In general, the absorption of a substance increases with increase of wavelength. The rays of short wavelengths are

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* e base of Naperian logarithms = 2·71828.

† The linear coefficient of absorption is $\mu\rho$: in many books it is this coefficient which is designated by the letter μ.

called *hard* or penetrating while those of long wavelengths are called *soft*. But, as is shown in fig. 4, the coefficient of absorption of a given element does not increase smoothly with λ, in a continuous way. It is essential to realise the existence of *discontinuities*. The coefficient falls abruptly when the wavelength exceeds certain critical values, known as the absorption limits λ_K, λ_{L_I}, $\lambda_{L_{II}}$ ... etc.,

It should be noted that we are considering the total absorption due, simultaneously, to the photoelectric effect and to scattering, but the effect of the latter is almost negligible in the range of wavelengths we are considering, for the majority of bodies ; it only acquires some importance for rays of very short wavelengths or for very light elements. The absorption discontinuities must, therefore, be attributed to the photoelectric effect.

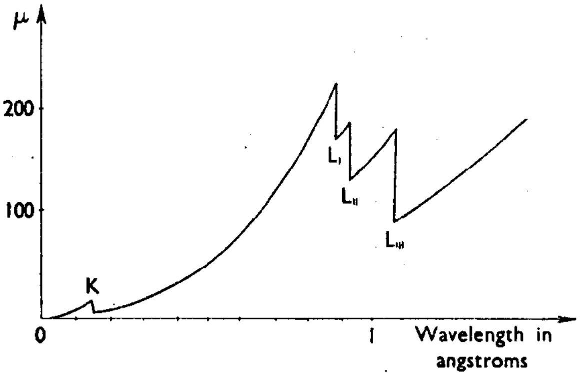

FIG. 4. Variations of the mass absorption coefficient of platinum with wavelength.

The collision of the photon and the atom is closely comparable to the collision of the electron and the atom which we have described in the study of the emission of characteristic rays. The atom, having absorbed the photon, is ionized, that is to say, an electron is expelled from it. In order that a certain electron shell can be ionized the energy of the photon, $h\nu$, must be greater than the combining energy of the electron. A given shell, K, for example, will only be ionized by radiations of frequency ν greater than ν_K such that

$$h\nu_K = W_K = hc/\lambda_K,$$

the wavelength λ must, then, be less than

$$\lambda_K = \frac{hc}{W_K}.$$

To each electron layer K, L_1, ... there corresponds a limiting wavelength λ_K, λ_{L_1} as there corresponds to it a limiting excitation potential of V_K, V_{L_1} ... (expression 1.5) ; these two values are connected by the relation

$$\lambda_K(\text{A}) = \frac{hc}{W_K} = \frac{hc}{eV_K} = \frac{12395}{V_K(\text{volts})}.$$

There is a difference between the ionizing action of the photon and of the electron. When the energy of the electron exceeds the minimum energy, the number of atoms ionized (and consequently the intensity of the emitted rays) begins at zero and increases with $V - V_K$ (formula 1.6), on the other hand the absorption of the photons has its maximum value just as the limiting wavelength is passed; hence these discontinuities in the absorption curve. The action of the electron layers is the more important the deeper they are. Thus, the coefficient of absorption at the K limit is multiplied by a factor of the order of 8; at the L_{III} limit this factor is about 3.

Within a certain region of wavelengths (above λ_L, between λ_K and λ_L etc.), the coefficient varies approximately as λ^3.

(2) *Variation with the element.* In general, for a given monochromatic radiation the absorption increases with the number of the absorbing element The light elements (organic bodies, aluminium) absorb only a little, while the heavy elements, like lead, absorb much more strongly; a property which is profited by in the construction of screens. But the increase of absorption with the atomic number is not continuous, it suffers from discontinuities owing to the existence of the absorption limits pointed out above. Let us consider the wavelength

$$\lambda = 1{\cdot}542\text{A} \quad (\text{CuK}_\alpha).$$

For elements of atomic number less than 27 (cobalt), λ is below the critical wavelength λ_K, while λ is above the discontinuity λ_K of the elements which follow cobalt (nickel, copper). There is, between cobalt and nickel, a very sudden drop in the coefficient of absorption. Another fall occurs between the elements 66 and 67 where λ passes the value of the λ_L discontinuity.

While the wavelength remains in a single region (below λ_K, between λ_K and λ_L, etc....). the coefficient of absorption is approximately proportional to Z^3, the cube of the atomic number, but this law is less rigorous than that which relates μ and λ.

These empirical laws, relating the coefficient of absorption to λ and Z, are mainly useful because they allow us to calculate by interpolation from the table of Appendix V (page 299) the values of coefficients which are not given there.

(*c*) **Fluorescent radiation.** When the atom has been ionized by a photon it drops back to the normal state by the same process as if the ionisation had been produced by an electron: it therefore emits its characteristic rays, with exactly the same wavelengths and the same relative intensities as if it had been excited by cathode rays. These secondary X-radiations, known as "fluorescent radiations", play an important part in X-ray crystallography because they are a nuisance. They are superimposed on the diffracted radiations which we are trying to record, the intensity of which may be feeble in contrast with this parasitic radiation. In order to avoid them we adopt one or other of the following methods. Either a primary radiation is chosen which does not excite the K series of any element in the specimen ; in these circumstances the L lines are emitted, but, except for the heavy elements, they interfere very little owing to their long wavelengths. Or else, if the K lines are emitted, their wavelengths must be sufficiently far from those of the primary radiations for an absorbing medium to be able to transmit a very small proportion of the parasitic lines and not to weaken the principal lines. The fluorescent radiation can thus be eliminated from the diagram. Details of the application of these methods that are very useful to know will be found in Chapter VII.

(*d*) **Applications.** The phenomenon of absorption is very important in X-ray crystallographic experiments. The positions of the absorption limits of the elements in a specimen with reference to the primary radiation tell us what fluorescent radiations will be emitted. The coefficient of absorption of the specimen is indispensable for determining the shape which it must be given and the method to be used for its examination.

We give, in Table II, some values of the relative amounts of intensity transmitted by some substances which are often used in X-ray equipment.

TABLE II

Absorbing Material	Thickness	Transmission Factor		
		Mo K_α $\lambda = 0{\cdot}711$A	Cu K_α $\lambda = 1{\cdot}542$A	Cr K_α $\lambda = 2{\cdot}291$A
Air (normal conditions)	10 cm.	0·99	0·89	0.68
Argon (normal conditions)	10 cm.	0·79	0·13	$1{\cdot}4 \times 10^{-3}$
Aluminium	1/100 mm.	0·99	0·88	0·68
	1/10 mm.	0·87	0·27	0·018
	1 mm.	0·24	$1{\cdot}9 \times 10^{-6}$	$0{\cdot}3 \times 10^{-17}$
Beryllium	2/10 mm.	0·99	0·94	0·96
	5/10 mm.	0·91	0·86	0·79
Black paper	1/10 mm.	0·99	0·93	0·80
Copper	1/10 mm.	0·016	0·018	$1{\cdot}12 \times 10^{-6}$
Pyrex glass	1 mm.	0·4	10^{-4}	10^{-10}
	1/10 mm.	0·93	0·5	0·1
Lindemann glass	1 mm.	0·85	0·23	0·01
	5/10 mm.	0·92	0·48	0·09
	1/10 mm.	0·99	0·86	0·62

Absorbing filters are used to modify the spectral distribution of the radiation and, thanks to the discontinuities in the absorption, there is a considerable number of different possibilities available. A filter of a light element (aluminium), of which the λ_K limit is much higher than the usual wavelengths, has an absorption which increases regularly with the wavelength, it is made use of to eliminate the long wavelengths and thus to confine the radiation to a band in the continuous spectrum.

A filter whose discontinuity λ_K is situated in the usual range of wavelengths, strongly absorbs the radiations of wavelengths shorter than λ_K. We shall mention two applications of this property.

(1) *The elimination of the* K_β *line* We have seen that the lines of the K series emitted by an anticathode may be divided into two sets, K_α and K_β, and that the subsidiary, K_β, has an intensity comparable with that of the principal line K_α; the diffraction phenomena due to K_β superpose themselves on those due to K_α and can give rise to ambiguities in the diagrams. Now, since the line K_β has a shorter wavelength than that of the K_α line, a filter can be found which absorbs K_β strongly and K_α only a little It is necessary to choose an element whose absorption discontinuity λ_K falls between the two lines Table III shows the characteristics of the filters appropriate to different common anticathodes chosen so as to reduce the ratio of the intensities of the K_β and K_α lines to 1/600 (Edwards and Lipson, 1941) If possible these filters are made of thin foil of the pure element, or else of a layer of powder attached to paper. The powder used can be that of a compound where, apart from the required element, there is only a light element present (oxygen for instance).

(2) *Isolation of a narrow spectral band* or " differential filtration " (Ross 1928 : Kirkpatrick 1939). Let us take two filters composed of neighbouring elements in the periodic table, for example, cobalt and nickel. It is known (Appendix V and Fig 4A) that the coefficients of absorption of these two elements are almost in the same ratio for all wavelengths except when

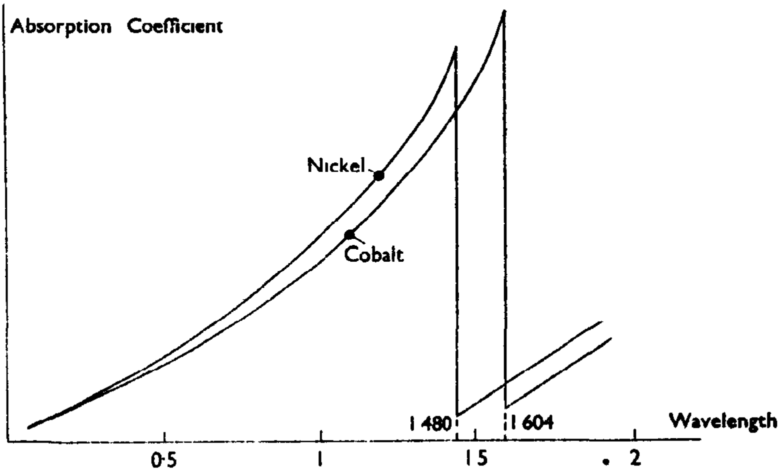

Fig 4A. Absorption of Nickel and Cobalt

these fall between the two absorption discontinuities. It follows that, if the mass per unit area of the cobalt filter is 1 $\frac{\text{gm.}}{\text{cm.}^2}$, that of the nickel 0·9 $\frac{\text{gm.}}{\text{cm.}^2}$, the absorption of the two filters will be very approximately equal, except between 1·487 and 1·607A. Let us suppose that first one filter and then the other is successively interposed in front of the source of X-rays; the difference in intensity recorded will represent the effect of the wavelengths of the band 1·487–1·607, since for the other radiations the two filters are equivalent to one another. If the tube has a copper anticathode, the CuK_α line (1·542) which it emits is exactly within the isolated band and it is very intense relative to the narrow band of the continuous spectrum which surrounds it. The use of this double filter method is, therefore equivalent to working with almost monochromatic radiation.

TABLE III

Anticathode	Wavelengths in Angstroms		Filters $\left(\text{for } \frac{IK_\beta}{IK_\alpha} = \frac{1}{600}\right)$			Transmission factor for the K_α line
	K_{α_2} K_{α_1}	K_β	Material	Thickness		
				gm./cm.²	mm.	
Silver	0·564 0·559	0·497	Rhodium ($\lambda_K = 0{\cdot}534$)	0·096	0·079	0·29
Molybdenum	0·714 0·709	0·632	Zirconium ($\lambda_K = 0{\cdot}688$)	0·069	0·108	0·31
Copper	1·544 1·540	1·392	Nickel ($\lambda_K = 1{\cdot}487$)	0·019	0·021	0·40
Cobalt	1·793 1·789	1·621	Iron ($\lambda_K = 1{\cdot}743$)	0·014	0·018	0·44
Iron	1·940 1·936	1·757	Manganese ($\lambda_K = 1{\cdot}895$)	0·012	0·016	0·46
Chromium	2·294 2·290	2·085	Vanadium ($\lambda_K = 2{\cdot}268$)	0·009	0·016	0·50

7. **" Coherent " or " classical " scattering.** When a photon is simply deviated without loss of energy, it gives rise to scattered radiation of the same wavelength as the primary radiation: it is then more advantageous no longer to consider its corpuscular aspect but to concentrate on its wave aspect. The elementary theory of the phenomenon is as follows: when an electron is hit by an electromagnetic wave, it begins to vibrate and becomes the source of a wave whose phase is determined by that of the incident wave. All the electrons of the material that the wave meets then

form a group of coherent sources whose radiations can *interfere*. Now it happens that the distances between atoms in condensed systems are of the same order of size as the wavelengths of X-rays. Thanks to these favourable conditions, interesting interference phenomena can be observed. Instead of a very feeble energy being distributed throughout space, it is concentrated in certain particular directions, thus, diffraction patterns are obtained from which it is possible to deduce facts about the respective positions of the atoms. *This is the foundation of X-ray crystallography.*

This phenomenon of coherent (or classic) scattering plays the principal part in the whole of this work. We shall only give here the expressions for the intensities scattered by an electron and an atom. In later chapters the effects of interference between waves scattered by the various atoms of a body will be studied in detail.

Let us consider a free electron in an unpolarized beam of X-rays; that is to say, such a beam as is emitted by ordinary sources. We will call the intensity of the beam per unit area I_0, the energy transferred per second across an area 1 cm.^{2} normal to the beam. The energy scattered per second by the electron in a solid angle $d\omega$ in the mean direction which makes the angle 2θ with the direction of the incident rays is:

$$I_e = I_0 \frac{e^4}{m^2c^4}\left(\frac{1+\cos^2 2\theta}{2}\right) d\omega$$

where e and m are the charge and mass of the electron (electrostatic C.G.S. units) and c the velocity of light (cms./sec.).

The energy received by unit area at a distance r (cms.) from the specimen is therefore

$$I_e = \frac{I_0}{r^2}\frac{e^4}{m^2c^4}\left(\frac{1+\cos^2 2\theta}{2}\right) = 7{\cdot}94 \times 10^{-26}\frac{I_0}{r^2}\left(\frac{1+\cos^2 2\theta}{2}\right) \quad . \quad . \; 1.11$$

This formula, known as Thomson's formula, is proved in Appendix I (§ 1).

An atom consists of a nucleus surrounded by electrons. *The nucleus plays no part in the scattering of X-rays*, because of its high mass, as may be seen from the Thomson formula. There will be interference between the waves scattered by the various electrons. A calculation, which we give in appendix I (§ 4), shows that the amplitude of the wave scattered by the atom is equal to

$$A = f \, . \, A_e$$

and that the scattered intensity, measured by the square of the amplitude is

$$I = f^2 I_e \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; 1.12$$

A_e is the amplitude of the wave scattered by a single electron and its intensity given by the formula 1.11; f is known as the atomic structure factor or the atom factor; it depends on the angle of scattering and the wavelength. For very small angles it approaches the number of electrons in the atom, or the atomic number Z. In fact, the Z scattered waves are then all in phase and their amplitudes add up. The intensity is, then Z^2I_e. As the scattering angle increases, *f* decreases.

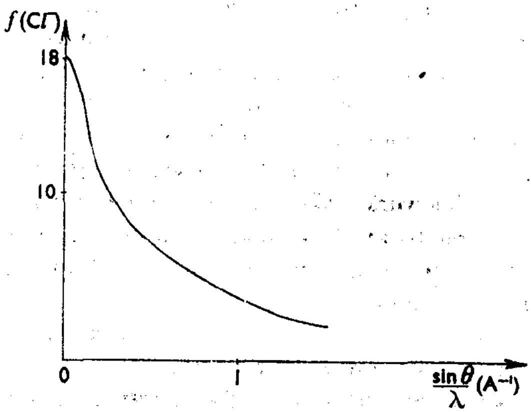

Fig. 5. *f* as a function of (sin θ)/λ for the ion Cl⁻

The calculation reproduced in appendix I (§ 4) shows that

$$f=\int_0^\infty u(a)\,\frac{\sin\left(4\pi\dfrac{\sin\theta}{\lambda}\,a\right)}{4\pi\dfrac{\sin\theta}{\lambda}\,a}\,da \qquad \ldots\ldots\ldots\ 1.13$$

$u(a)da$ represents the number of electrons contained between spheres, having the nucleus as centre, of radii a and $a+da$; 2θ is the scattering angle and λ the wavelength of the primary beam. *f* is a function of $\dfrac{\sin\theta}{\lambda}$ only*. It is possible to calculate $u(a)$ from theories of atomic structure (Thomas 1927, Fermi 1928, Hartree 1928). Fig. 5 represents the variation of *f* as a function of (sin θ)/λ for the ion Cl⁻. In Appendix III we give values of *f* for the more common ions and atoms. These theoretically calculated values have been confirmed experimentally.

In general, for a given value of (sin θ)/λ, the atom factor is independent of the wavelength. However, when the latter is in the neighbourhood of the absorption discontinuity, λ_K, of the atom an anomaly occurs: the atom factor is then less, by some units, than its theoretical value. In Chap. IX para. 1 we shall see an interesting application of this phenomenon.

8. Incoherent scattering or Compton effect. The other scattering phenomenon is easily understood in terms of the corpuscular representa-

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* We shall see later that $\dfrac{\sin\theta}{\lambda}$ plays a very important part in the theory of diffraction by crystals. This ratio is equal to $\dfrac{1}{2d}$, d being the spacing of the grating planes which reflect the wavelength λ at the angle θ. For reflection by a given plane, *f* is independent of λ.