

effect in the case of many metals and alloys are subject to variations as great as an octave and more. This difficulty is all the more real in that as yet we are not in a position to determine what influences on and in the extremely thin bounding surface of the metal in which the light absorption takes place are the determining factors in this displacement.

Berlin, Physikalisches Institut  
der Universität, July 1913.

### XCIII. *The High-Frequency Spectra of the Elements.*

By H. G. J. MOSELEY, M.A.\*

[Plate XXIII.]

**I**N the absence of any available method of spectrum analysis, the characteristic types of X radiation, which an atom emits when suitably excited, have hitherto been described in terms of their absorption in aluminium †. The interference phenomena exhibited by X rays when scattered by a crystal have now, however, made possible the accurate determination of the frequencies of the various types of radiation. This was shown by W. H. and W. L. Bragg ‡, who by this method analysed the line spectrum emitted by the platinum target of an X-ray tube. C. G. Darwin and the author § extended this analysis and also examined the continuous spectrum, which in this case constitutes the greater part of the radiation. Recently Prof. Bragg || has also determined the wave-lengths of the strongest lines in the spectra of nickel, tungsten, and rhodium. The electrical methods which have hitherto been employed are, however, only successful where a constant source of radiation is available. The present paper contains a description of a method of photographing these spectra, which makes the analysis of the X rays as simple as any other branch of spectroscopy. The author intends first to make a general survey of the principal types of high-frequency radiation, and then to examine the spectra of a few elements in greater detail and with greater accuracy. The results already obtained show that such data have an important bearing on the question of

\* Communicated by Prof. E. Rutherford, F.R.S.

† Cf. Barkla, *Phil. Mag.* xxii. p. 396 (1911).

‡ *Proc. Roy. Soc. A.* lxxxviii. p. 428 (1913).

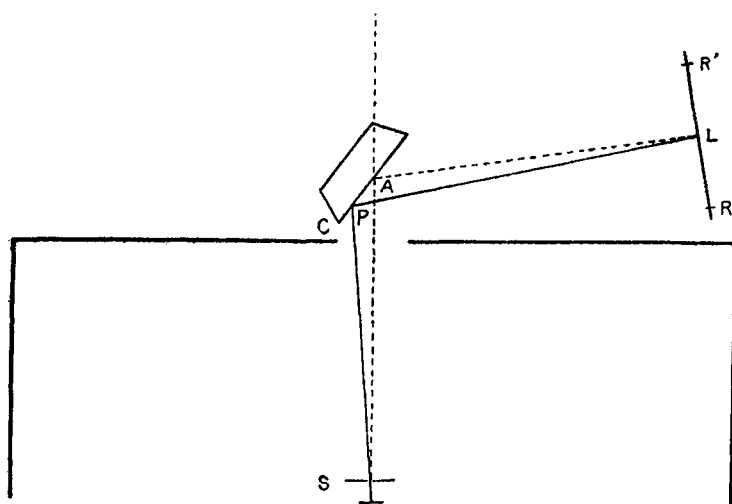
§ *Phil. Mag.* xxvi. p. 210 (1913).

|| *Proc. Roy. Soc. A.* lxxxix. p. 246 (1913).

the internal structure of the atom, and strongly support the views of Rutherford\* and of Bohr†.

Kaye‡ has shown that an element excited by a stream of sufficiently fast cathode rays emits its characteristic X radiation. He used as targets a number of substances mounted on a truck inside an exhausted tube. A magnetic device enabled each target to be brought in turn into the line of fire. This apparatus was modified to suit the present work. The cathode stream was concentrated on to a small area of the target, and a platinum plate furnished with a fine vertical slit placed immediately in front of the part bombarded. The tube was exhausted by a Gaede mercury pump, charcoal in liquid air being also sometimes used to remove water vapour. The X rays, after passing through the slit marked S in fig. 1,

Fig. 1.



emerged through an aluminium window  $\cdot 02$  mm. thick. The rest of the radiation was shut off by a lead box which surrounded the tube. The rays fell on the cleavage face, C, of a crystal of potassium ferrocyanide which was mounted on the prism-table of a spectrometer. The surface of the crystal was vertical and contained the geometrical axis of the spectrometer.

\* *Phil. Mag.* xxi. p. 669 (1911).

† *Phil. Mag.* xxvi. pp. 1, 476, & 857 (1913).

‡ *Phil. Trans. Roy. Soc. A.* ccix. p. 123 (1909).

Now it is known\* that X rays consist in general of two types, the heterogeneous radiation and characteristic radiations of definite frequency. The former of these is reflected from such a surface at all angles of incidence, but at the large angles used in the present work the reflexion is of very little intensity. The radiations of definite frequency, on the other hand, are reflected only when they strike the surface at definite angles, the glancing angle of incidence  $\theta$ , the wave-length  $\lambda$ , and the "grating constant"  $d$  of the crystal being connected by the relation

$$n\lambda = 2d \sin \theta, \quad . . . . . (1)$$

where  $n$ , an integer, may be called the "order" in which the reflexion occurs. The particular crystal used, which was a fine specimen with face 6 cm. square, was known to give strong reflexions in the first three orders, the third order being the most prominent.

If then a radiation of definite wave-length happens to strike any part  $P$  of the crystal at a suitable angle, a small part of it is reflected. Assuming for the moment that the source of the radiation is a point, the locus of  $P$  is obviously the arc of a circle, and the reflected rays will travel along the generating lines of a cone with apex at the image of the source. The effect on a photographic plate  $L$  will take the form of the arc of an hyperbola, curving away from the direction of the direct beam. With a fine slit at  $S$ , the arc becomes a fine line which is slightly curved in the direction indicated.

The photographic plate was mounted on the spectrometer arm, and both the plate and the slit were 17 cm. from the axis. The importance of this arrangement lies in a geometrical property, for when these two distances are equal the point  $L$  at which a beam reflected at a definite angle strikes the plate is independent of the position of  $P$  on the crystal surface. The angle at which the crystal is set is then immaterial so long as a ray can strike some part of the surface at the required angle. The angle  $\theta$  can be obtained from the relation  $2\theta = 180^\circ - SPL = 180^\circ - SAL$ .

The following method was used for measuring the angle  $SAL$ . Before taking a photograph a reference line  $R$  was made at both ends of the plate by replacing the crystal by a lead screen furnished with a fine slit which coincided with the axis of the spectrometer. A few seconds' exposure to the X rays then gave a line  $R$  on the plate, and so defined on it

\* Moseley and Darwin, *loc. cit.*

the line joining S and A. A second line R' was made in the same way after turning the spectrometer arm through a definite angle. The arm was then turned to the position required to catch the reflected beam and the angles LAP for any lines which were subsequently found on the plate deduced from the known value of KAP and the position of the lines on the plate. The angle LAR was measured with an error of not more than  $0^{\circ}.1$ , by superposing on the negative a plate on which reference lines had been marked in the same way at intervals of  $1^{\circ}$ . In finding from this the glancing angle of reflexion two small corrections were necessary in practice, since neither the face of the crystal nor the lead slit coincided accurately with the axis of the spectrometer. Wave-lengths varying over a range of about 30 per cent. could be reflected for a given position of the crystal.

In almost all cases the time of exposure was five minutes. Ilford X-ray plates were used and were developed with rodinal. The plates were mounted in a plate-holder, the front of which was covered with black paper. In order to determine the wave-length from the reflexion angle  $\theta$  it is necessary to know both the order  $n$  in which the reflexion occurs and the grating constant  $d$ .  $n$  was determined by photographing every spectrum both in the second order and the third. This also gave a useful check on the accuracy of the measurements;  $d$  cannot be calculated directly for the complicated crystal potassium ferrocyanide. The grating constant of this particular crystal had, however, previously\* been accurately compared with  $d'$ , the constant of a specimen of rocksalt. It was found that

$$d = 3d' \frac{.1988}{.1985}.$$

Now W. L. Bragg † has shown that the atoms in a rock-salt crystal are in simple cubical array. Hence the number of atoms per c.c.

$$2 \frac{N\sigma}{M} = \frac{1}{(d')^3}:$$

$N$ , the number of molecules in a gram-mol., =  $6.05 \times 10^{23}$ , assuming the charge on an electron to be  $4.89 \times 10^{-10}$ ;  $\sigma$ , the density of this crystal of rocksalt, was 2.167, and  $M$  the molecular weight = 58.46.

\* Moseley & Darwin, *loc. cit.*

† Proc. Roy. Soc. A. lxxxix. p. 248 (1913).

TABLE I.

Element.	Line.	$\theta_2$ .	$\lambda$ .	$\theta_3$ .	$\lambda$ .	$\lambda$ .	$\lambda_d/\lambda_\beta$ .	$Q = (\nu/\lambda\nu_0)^{\frac{5}{2}}$ .	N atomic number.	Atomic weight.
CALCIUM.	$\alpha$ ...	23.4°	$3.357 \times 10^{-8}$	36.7°	$3.368 \times 10^{-8}$	1.089	19.00	20	40.09	
	$\beta$ ...	21.4	3.085	33.3	3.094	...	...	21	44.1	
SCANDIUM.	...	...	...	...	...	...	...	...	...	
TITANIUM.	$\alpha$ ...	19.1	2.766	29.3	2.758	1.093	20.99	22	48.1	
	$\beta$ ...	17.4	2.528	20.6	2.524	1.097	21.96	23	51.06	
VANADIUM.	$\alpha$ ...	17.35	2.521	26.55	2.519	1.100	22.98	24	52.0	
	$\beta$ ...	15.8	2.302	24.05	2.297	1.101	23.99	25	54.93	
CHROMIUM.	$\alpha$ ...	15.75	2.295	24.1	2.301	1.103	24.99	26	55.85	
	$\beta$ ...	14.3	2.088	21.8	2.083	1.104	26.00	27	56.97	
MANGANESE.	$\alpha$ ...	14.5	2.117	22.0	2.111	1.104	27.04	28	58.68	
	$\beta$ ...	13.15	1.923	19.9	1.918	1.105	28.01	29	63.57	
IRON.	$\alpha$ ...	13.3	1.945	20.2	1.946	1.106	29.01	30	65.37	
	$\beta$ ...	12.05	1.765	18.25	1.765	...	...	...	...	
COBALT.	$\alpha$ ...	12.25	1.794	18.6	1.798	1.104	26.00	27	58.97	
	$\beta$ ...	11.15	1.635	16.8	1.629	1.104	27.04	28	58.68	
NICKEL.	$\alpha$ ...	11.35	1.664	17.15	1.662	1.105	28.01	29	63.57	
	$\beta$ ...	10.25	1.504	15.5	1.506	1.106	29.01	30	65.37	
COPPER.	$\alpha$ ...	10.55	1.548	15.95	1.549	...	...	...	...	
	$\beta$ ...	9.55	1.403	14.4	1.402	...	...	...	...	
ZINC.	$\alpha$ ...	9.85	1.446	14.85	1.445	...	...	...	...	
	$\beta$ ...	not found	found	13.4	1.306	...	...	...	...	

This gives  $d' = 2.814 \times 10^{-9}$  and  $d = 8.454 \times 10^{-8}$  cm. It is seen that the determination of wave-length depends on  $e^{\frac{1}{2}}$ , so that the effect of uncertainty in the value of this quantity will not be serious. Lack of homogeneity in the crystal is a more likely source of error, as minute inclusions of water would make the true density greater than that found experimentally.

Twelve elements have so far been examined. The ten given in Table I. were chosen as forming a continuous series with only one gap. It was hoped in this way to bring out clearly any systematic results. The inclusion of nickel was of special interest owing to its anomalous position in the periodic system. Radiations from these substances are readily excited, and the large angles of reflexion make it easy to measure the wave-lengths with accuracy. Calcium alone gave any trouble. In this case, owing to the high absorption coefficient of the principal radiation—about  $1200 \text{ cm.}^{-1}$  in aluminium—the X-ray tube was provided with a window of goldbeaters' skin and the air between the crystal and the photographic plate displaced by hydrogen. The layer of lime which covered the surface of the metal gave off such a quantity of gas that the X rays could only be excited for a second or two at a time. Brass was substituted for zinc to avoid volatilization by the intense heat generated at the point struck by the cathode rays. Ferro-vanadium (35 per cent. V) and ferro-titanium (23 per cent. Ti), for which I am indebted to the International Vanadium Co., proved convenient substitutes for the pure elements, which are not easily obtained in the solid form.

Plate XXIII. shows the spectra in the third order placed approximately in register. Those parts of the photographs which represent the same angle of reflexion are in the same vertical line. The actual angles can be taken from Table I. It is to be seen that the spectrum of each element consists of two lines. Of these the stronger has been called  $\alpha$  in the table, and the weaker  $\beta$ . The lines found on any of the plates besides  $\alpha$  and  $\beta$  were almost certainly all due to impurities. Thus in both the third and second order the cobalt spectrum shows Ni  $\alpha$  very strongly and Fe  $\alpha$  faintly. In the third order the nickel spectrum shows Mn  $\alpha_2$  faintly. The brass spectra naturally show  $\alpha$  and  $\beta$  both of Cu and of Zn, but Zn  $\beta_2$  has not yet been found. In the second order the ferro-vanadium and ferro-titanium spectra show very intense third-order Fe lines, and the former also shows Cu  $\alpha_3$  faintly. The Co contained Ni and 0.8 per cent. Fe, the Ni 2.2 per cent. Mn,

and the V only a trace of Cu. No other lines have been found; but a search over a wide range of wave-lengths has been made only for one or two elements, and perhaps prolonged exposures, which have not yet been attempted, will show more complex spectra. The prevalence of lines due to impurities suggests that this may prove a powerful method of chemical analysis. Its advantage over ordinary spectroscopic methods lies in the simplicity of the spectra and the impossibility of one substance masking the radiation from another. It may even lead to the discovery of missing elements, as it will be possible to predict the position of their characteristic lines.

It will be seen from Table I. that the wave-lengths calculated from the two orders are in good agreement. The third order gives the stronger reflexion, and as the angles dealt with are the larger these results are the more accurate. The similarity of the different spectra is shown by the fact that the two lines  $\alpha$  and  $\beta$  remain approximately constant, not only in relative intensity but also in relative wave-length. The frequency of  $\beta$  increases, however, slightly faster than that of  $\alpha$ . The same two lines  $\alpha$  strong and  $\beta$  weak constitute the rhodium spectrum examined by Bragg\*, and they are obviously in some way closely related. One or two photographs taken with the radiation from platinum gave results in good agreement with those obtained by the electrical method, and no trace of the elaborate system of bands described by de Broglie † in the reflexion from rock-salt was encountered. The three lines found by Herveg ‡ in the reflexion from selenite doubtless represent part of the Pt spectrum in the second order. The actual breadth of the lines and certain minute details in their structure will not be considered here, as discussion would take too much space and more experiments are needed. The only other element examined was tantalum. In this case the radiation belongs to the L series, and the spectrum consists of a strong line of wave-length  $1.525 \times 10^{-8}$  cm., two others of less intensity at  $1.330$  and  $1.287 \times 10^{-8}$  cm., and probably some very faint lines also.

A discussion will now be given of the meaning of the wave-lengths found for the principal spectrum-line  $\alpha$ . In Table I. the values are given of the quantity

$$Q = \sqrt{\frac{\nu}{\frac{3}{4}\nu_0}}$$

\* Proc. Roy. Soc. A. lxxxix. p. 277 (1913).

† *Le Radium*, x. pp. 186 & 245 (1913).

‡ *Deutsch. Phys. Ges. Verh.* xv. 13, p. 555 (1913).

$\nu$  being the frequency of the radiation  $\alpha$ , and  $\nu_0$  the fundamental frequency of ordinary line spectra. The latter is obtained from Rydberg's wave-number,  $N_0 = \frac{\nu}{c} = 109,720$ .

The reason for introducing this particular constant will be given later. It is at once evident that  $Q$  increases by a constant amount as we pass from one element to the next, using the chemical order of the elements in the periodic system. Except in the case of nickel and cobalt\*, this is also the order of the atomic weights. While, however,  $Q$  increases uniformly the atomic weights vary in an apparently arbitrary manner, so that an exception in their order does not come as a surprise. We have here a proof that there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus, of the existence of which we already have definite proof. Rutherford has shown, from the magnitude of the scattering of  $\alpha$  particles by matter, that this nucleus carries a + charge approximately equal to that of  $\frac{A}{2}$  electrons, where  $A$  is the atomic weight. Barkla, from the scattering of X rays by matter, has shown that the number of electrons in an atom is roughly  $\frac{A}{2}$ , which for an electrically neutral atom comes to the same thing. Now atomic weights increase on the average by about 2 units at a time, and this strongly suggests the view that  $N$  increases from atom to atom always by a single electronic unit. We are therefore led by experiment to the view that  $N$  is the same as the number of the place occupied by the element in the periodic system. This atomic number is then for H 1 for He 2 for Li 3 . . . for Ca 20 . . . for Zn 30, &c. This theory was originated by Broek † and since used by Bohr ‡. We can confidently predict that in the few cases in which the order of the atomic weights  $A$  clashes with the chemical order of the periodic system, the chemical properties are governed by  $N$ ; while  $A$  is itself probably a complicated function of  $N$ . The very close similarity between the X-ray spectra of the different elements shows that these radiations originate inside the atom, and have no direct connexion with the complicated light-spectra and chemical properties which are governed by the structure of its surface.

\* Cf. Barkla, *Phil. Mag.* xiv. p. 408 (1907).

† *Phys. Zeit.* xiv. p. 32 (1913).

‡ *Loc. cit.*



We will now examine the relation

$$Q = \sqrt{\frac{\nu}{\frac{3}{4}\nu_0}}$$

more closely. So far the argument has relied on the fact that  $Q$  is a quantity which increases from atom to atom by equal steps. Now  $Q$  has been obtained by multiplying  $\nu^{\frac{3}{2}}$  by a constant factor so chosen as to make the steps equal to unity. We have, therefore,

$$Q = N - k,$$

where  $k$  is a constant. Hence the frequency  $\nu$  varies as  $(N - k)^2$ . If  $N$  for calcium is really 20 then  $k = 1$ .

There is good reason to believe that the X-ray spectra with which we are now dealing come from the innermost ring of electrons\*. If these electrons are held in equilibrium by mechanical forces, the angular velocity  $\omega$  with which they are rotating and the radius  $r$  of their orbit are connected by

$$m\omega^2 r = \frac{e^2}{r^2} (N - \sigma_n),$$

where  $\sigma_n$  is a small term arising from the influence of the  $n$  electrons in the ring on each other, and  $\sigma_2 = 0.25$ ,  $\sigma_4 = 0.96$ ,  $\sigma_6 = 1.83$ ,  $\sigma_8 = 2.81$ . In obtaining this simple expression the very small effect of other outside rings has been neglected. If then, as we pass from atom to atom, the number of electrons in the central ring remains unaltered,

$$(\omega^2 r^3)_{N+1} - (\omega^2 r^3)_N \text{ remains constant;}$$

but these experiments have shown that

$$\nu_{N+1}^{\frac{3}{2}} - \nu_N^{\frac{3}{2}} \text{ is also constant,}$$

and therefore

$$\frac{\omega^2 r^3}{\nu^{\frac{3}{2}}} \text{ is constant.}$$

For the types of radiation considered by Bohr, provided the ring moves from one stationary state to another as a whole, and for the ordinary transverse vibrations of the ring, provided the influence of outer rings can be neglected,  $\nu$  is proportional to  $\omega$ .

This gives  $\omega^{\frac{3}{2}} r^3$  and therefore  $m\omega r^2$ , the angular momentum of an electron, the same for all the different atoms. Thus we

\* J. J. Thomson, *Phil. Mag.* xxiii. p. 456 (1912).

have an experimental verification of the principle of the constancy of angular momentum which was first used by Nicholson \*, and is the basis of Bohr's theory of the atom.

It is evident that  $k = \sigma_n$ . If then  $k = 1$ , it is suggested that the ring contains 4 electrons, for  $\sigma_4 = 0.96$ .

We are now justified in making a quantitative comparison between the frequency of  $\alpha$  and that of the fundamental radiation from such a ring calculated from the theory of Bohr.

We have obtained the experimental result,

$$\nu = \frac{3}{4} \nu_0 (N - \sigma_n)^2.$$

On his theory, making the assumption that the ring moves as a whole from stationary state 2 to state 1, the frequency of the principal radiation emitted is

$$\nu = \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \frac{2\pi^2 e^4 m}{h^3} (N - \sigma_n)^2,$$

where  $e$  is the charge on an electron,  $m$  its mass, and  $h$  Planck's constant.

The numerical agreement between these two constants  $\nu_0$  and  $\frac{2\pi^2 e^4 m}{h^3}$  is known to be very close, while Bohr's explanation of the Balmer series for hydrogen assumes them to be identical. This numerical agreement between the experimental values and those calculated from a theory designed to explain the ordinary hydrogen spectrum is remarkable, as the wave-lengths dealt with in the two cases differ by a factor of about 2000. The assumption that the whole ring takes part in the radiation introduces, however, a grave difficulty from energy considerations, while no explanation of the faint line  $\beta$  has been forthcoming. Probably further experiments will show that the theory needs some modification.

The results hitherto obtained for the radiations of the L series are too meagre to justify any explanation. As before, the line of longest wave-length is the most prominent, a result similar to that found in ordinary light-spectra. The wave-lengths found for this line in the case of tantalum and platinum suggest that possibly the frequency is here

$$\nu = \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \nu_0 (N - \sigma_n)^2.$$

Here  $N$  and  $\sigma_n$  are unknown, but it is evident from the periodic system that  $N_{Pt} - N_{Ta} = 5$ , while probably  $\sigma_n$  remains

\* Monthly Notes Roy. Astr. Soc. June 1912.

the same for all elements in the same column. The actual value found for  $\nu_{\text{Pt}}^{\frac{1}{2}} - \nu_{\text{Ta}}^{\frac{1}{2}}$  is  $1.08 \times 10^8$ , and the calculated value is  $1.07 \times 10^8$ . Whether this relation really holds good can only be decided by further experiment.

In conclusion I wish to express my warm thanks to Prof. Rutherford for the kind interest which he has taken in this work.

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XCIV. *Ionization of Gases by Collision with Low Electric Forces.* By F. W. WHEATLEY, B.A., B.Sc. (Adelaide), Lincoln College, Oxford\*.

[Plate XXIV.]

**P**ROFESSOR TOWNSEND in his book 'The Theory of Ionization of Gases by Collision' has shown that the process of ionization by collision between the ions and molecules of a gas may be examined by investigating the currents between parallel plate electrodes when ultraviolet light falls on the negative electrode or when the gas is ionized by Röntgen or Becquerel rays.

In the determinations which have already been made, the effect of the electrons for values of the ratio  $X/p$  larger than 60 has been obtained.

The experiments described in this paper were undertaken with a view to finding the effects obtained by collision with smaller forces, and for that purpose it is necessary to measure the currents between plates at various distances apart to a high degree of accuracy. A very constant source of radiation is therefore required for the experiments, and it would be practically impossible to obtain reliable results either with ultraviolet light or with Röntgen rays.

The source of radiation used was polonium. The results show that the ionization produced by  $\alpha$  rays is identical with that produced by Röntgen or Becquerel rays or by ultraviolet light, and has this advantage that it produces a constant current.

The apparatus which was used is shown in the accompanying figure and consisted of two parallel brass plates B and C inside an airtight bell-jar A. The bell-jar was provided with two outlets D and E. Through D a wire passed connecting the lower plate C to a source of potential V. The opening E led to a Töpler pump, an open manometer and a MacLeod gauge, and could also be connected

\* Communicated by Prof. J. S. Townsend, F.R.S.

