LXXX. *The High-Frequency Spectra of the Elements.* Part II. *By* H. G. J. Moseley, *M.A.*[*]

THE first part[†] of this paper dealt with a method of photographing X-ray spectra, and included the spectra of a dozen elements. More than thirty other elements have now been investigated, and simple laws have been found which govern the results, and make it possible to predict with confidence the position of the principal lines in the spectrum of any element from aluminium to gold. The present contribution is a general preliminary survey, which claims neither to be complete nor very accurate.

A somewhat different method of photographing these spectra has been developed independently by de Broglie[‡] and by Herveg[§]. The latter closely confirms the angles given by Moseley and Darwin[‖] for reflexion of Pt rays from selenite. De Broglie finds less satisfactory agreement for the reflexion from rocksalt. De Broglie has also examined the spectra of W and Au, and has obtained for Cu and Fe results similar to those given in Part I.

The general experimental method has remained unaltered, and need not be again described. The same crystal of potassium ferrocyanide has been used as analyser throughout. The sharpness of the lines of short wave-length has

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[*] Communicated by the Author.

[†] Moseley, Phil. Mag. xxvi. p. 1024 (1913).

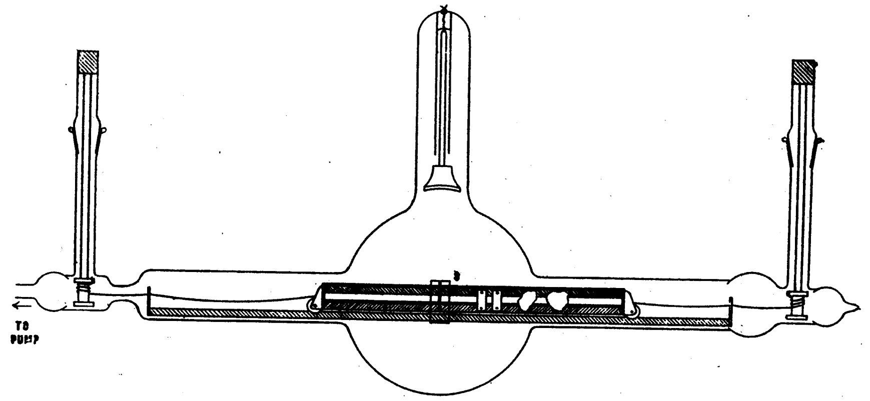
[‡] De Broglie, *C. R.* 17 Nov., 22 Dec., 1913, 19 Jan., 2 Feb., 2 March, 1914.

[§] Herveg, *Verh. d. D. Phys. Ges.* xvi. p. 73, Jan. 1914.

[‖] Moseley & Darwin, Phil. Mag. xxvi. p. 210 (1913).

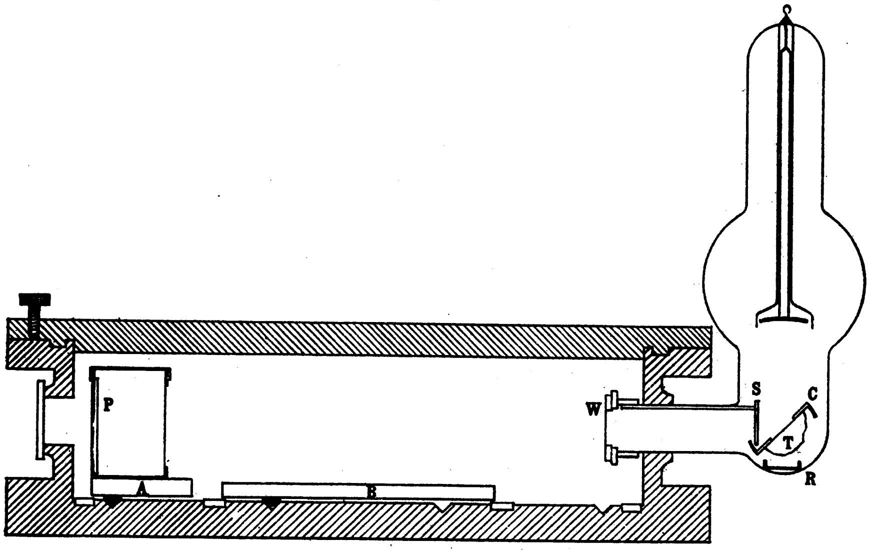
been much improved by reducing the breadth of the defining slit to about 0·2 mm. The most convenient type of X-ray tube is drawn to scale in fig. 1. The aluminium trolley which carries the targets can be drawn to and fro by means of silk fishing-line wound on brass bobbins. An iron screen S fastened to the rails is furnished with a fine vertical slit which defines the X-ray beam. The slit should be fixed exactly opposite the focus-spot of the cathode-stream, though a slight error can be remedied by deflecting the cathode rays with a magnet. The X rays escape by a side-tube $2\frac{1}{2}$ cm. diameter closed by an aluminium window 0·022 mm. thick. The X-ray tube, which has a capacity of over 3 litres, was exhausted with a Gaede mercury-pump, for the loan of which I am indebted to Balliol College.

Fig. 1.



The radiations of long wave-length cannot penetrate an aluminium window or more than a centimetre or two of air. The photographs had therefore in this case to be taken inside an exhausted spectrometer. Fig. 2 gives a vertical section to scale of the X-ray tube and spectrometer. The former consists of a bulb containing the cathode, joined by a very large glass T-piece to a long tube of 4 cm. diameter, in which are the rails R and the carriage C. S is the defining-slit and W a window of goldbeaters' skin which separates the tube from the spectrometer. This material, which is usually air-tight, though sometimes it may require varnishing, is extremely transparent to X rays. A circular window of 2 cm. diameter will easily withstand the pressure of the atmosphere if left undisturbed. In these experiments, however, the pressure was relieved every time the spectrometer was exhausted, and under such conditions the goldbeaters' skin had frequently to be renewed. The spectrometer, which was specially designed for this work, consists of a strong circular iron box of 30 cm. inside diameter and 8 cm. high, closed by a lid which, when the flange is greased, makes an air-tight joint. Two concentric grooves are cut in the floor of the box. The table A, which carries the plate-holder, rests on three steel balls, of which two run in the outer groove, while the third rests on the floor of the box. The position of the crystal-table B is controlled in like manner by the inner groove. This geometrical construction for a spectrometer is well known. The scales are fixed to the box and the verniers to the tables. For these very soft rays the absorption by the black paper front of the plate-holder became serious, and two sheets of black tissue-paper were used instead. Lumps of the pure elements, usually several millimetres thick, were used as targets in the case of Mg, Al, Si, Mo, Ru, Pd, Ag, Sb, Ta. Foils such as Rh, W, Au were either silver-soldered or brazed onto copper. Os was used in the form of a thin chemical deposit on copper. The alloys used were ZrNi (70 per cent.), WFe (50 per cent.), NbTa (50 per cent.), and SnMn (50 per cent.). KCl and the oxides of the rare-earth elements were rubbed onto the surface of

Fig. 2.



nickel plates roughened with coarse emery-powder. The only serious difficulty in the experiments is caused by the heat produced by the cathode ray bombardment, and the consequent liberation of gas and destruction of the surface of the target. This makes it necessary to use the element in a form which is not too volatile and prevents the employment of a very powerful discharge. The total time of an exposure, including rests, varied from three minutes for a substance such as ruthenium, which could safely be heated, to thirty minutes for the rare earth oxides. The importance of using an efficient high-tension valve may again be mentioned.

The oxides of Sa, Eu, Gd, Er were given me by Sir William Crookes, O.M., to whom I wish to express my sincere gratitude. For the loan of the Os and a button of Ru I am indebted to Messrs. Johnson Matthey. The alloys were obtained from the Metallic Compositions Co., and the oxides of La, Ce, Pr, Nd, and Er from Dr. Schuchardt, of Görlitz.

Almost every line was photographed in two different orders, and the double angles of reflexion measured as before to within 0°·1 and sometimes 0°·05. In some sets of experiments a small error caused by the crystal surface not being exactly on the spectrometer-axis gave rise to a systematic discrepancy in the results obtained from reflexion in different orders. It was found that this error, which never changed the reflexion-angle by more than 0°·05, could be measured more accurately from the amount of the discrepancy than from direct observation of the crystal. A more serious correction was necessary when using the long wave-length apparatus. In this case the slit and photograph are not equidistant from the crystal, and the position of the spectrum-lines on the plate is no longer independent of the angle at which the crystal is set. The necessary corrections were calculated geometrically, and verified by photographing the same line for both right-handed and left-handed reflexions and with the crystal set at various angles.

In the work on the very short wave-lengths, the reflexion of the general heterogeneous radiation gave some trouble. This is always an important part of the radiation from an X-ray tube, but with a hard tube it is analysed by reflexion mainly into constituents of very short wave-length, and so usually does not interfere with the line-spectra. It is only with an extremely soft tube, combined with precautions against absorption by the air, that constituents reflected at large angles become prominent. When examining such a spectrum as that of Ag in the K series, the general reflexion cannot be avoided. Unfortunately, when photographed it takes the form of irregular fringes, which effectually hide faint spectrum-lines. A change of target, with the position of slit and crystal unaltered, does not affect the appearance of the fringes, a fact which proves that they are due to the general heterogeneous radiation. It is easy to show that the fringes are merely a very foreshortened pattern of patches on the crystal surface which reflect exceptionally well. The way in which they move and spread out laterally as the crystal is turned provides a proof of this, and so does Barkla's [*] observation that when the crystal is moved sideways the fringes move with it. It is easy to devise methods for getting rid of the fringes. In the first place, narrowing the slit or increasing the distance from the crystal will diminish their intensity compared with that of the line-spectrum. In the second place, turning the crystal will move and blur the fringes, but leave the sharpness of the lines unaffected provided the slit and photograph are equidistant from the reflecting surface [†]. The quantitative measurements of Moseley and Darwin [‡] on the reflexion of the general radiation must have been little affected by these fringes, as the incident beam was restricted to a very narrow pencil which always impinged on the same part of the crystal.

The results obtained for radiations belonging to Barkla's K series are given in Table I., and for convenience the figures already given in Part I. are included. The wave-length λ has been calculated from the glancing angle of reflexion θ by means of the relation $n\lambda=2d\sin\theta$, where d has been taken to be $8{\cdot}454\times10^{-8}$ cm. As before, the strongest line is called α and the next line β. The square root of the frequency of each line is plotted in fig. 3, and the wave-lengths can be read off with the help of the scale at the top of the diagram.

The spectrum of Al was photographed in the first order only. The very light elements give several other fainter lines, which have not yet been fully investigated, while the results for Mg and Na are quite complicated, and apparently depart from the simple relations which connect the spectra of the other elements. In the spectra from yttrium onwards only the α line has so far been measured, and further results in these directions will be given in a later paper. The

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[*] Barkla and Martyn, Proc. Phys. Soc. London (1913).

[†] Moseley, *loc. cit.* p. 1025. See also W. H. and W. L. Bragg, Proc. Roy. Soc. A, lxxxviii. p. 428 (1913).

[‡] Moseley and Darwin, *loc. cit.*

TABLE I.

	α line. $\lambda\times10^8$ cm.	Q_K.	N. Atomic Number.	β line. $\lambda\times10^8$.
Aluminium	8·364	12·05	13	7·912
Silicon	7·142	13·04	14	6·729
Chlorine	4·750	16·00	17	......
Potassium	3·759	17·98	19	3·463
Calcium	3·368	19·00	20	3·094
Titanium	2·758	20·99	22	2·524
Vanadium	2·519	21·96	23	2·297
Chromium	2·301	22·98	24	2·093
Manganese	2·111	23·99	25	1·818
Iron	1·946	24·99	26	1·765
Cobalt	1·798	26·00	27	1·629
Nickel	1·662	27·04	28	1·506
Copper	1·549	28·01	29	1·402
Zinc	1·445	29·01	30	1·306
Yttrium	0·838	38·1	39	......
Zirconium	0·794	39·1	40	......
Niobium	0·750	40·2	41	......
Molybdenum.........	0·721	41·2	42	......
Ruthenium	0·638	43·6	44	......
Palladium	0·584	45·6	46	......
Silver	0·560	46·6	47	......

spectra both of K and of Cl were obtained by means of a target of KCl, but it is very improbable that the observed lines have been attributed to the wrong elements. The α line for elements from Y onwards appeared to consist of a very close doublet, an effect previously observed by Bragg* in the case of rhodium.

The results obtained for the spectra of the L series are given in Table II. and plotted in fig. 3. These spectra contain five lines, α, β, γ, δ, ϵ, reckoned in order of decreasing wave-length and decreasing intensity. There is also always a faint companion α' on the long wave-length side of α, a rather faint line ϕ between β and γ for the rare earth elements at least, and a number of very faint lines of wave-length greater than α. Of these, α, β, ϕ, and γ have been systematically measured with the object of finding out how the spectrum alters from one element to another. The fact that often values are not given for all these lines merely indicates the incompleteness of the work. The spectra, so far as they have been examined, are so entirely similar that without doubt α, β, and γ at least always exist. Often γ was

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* Bragg, 'Nature,' March 12, 1914.

Fig. 3.

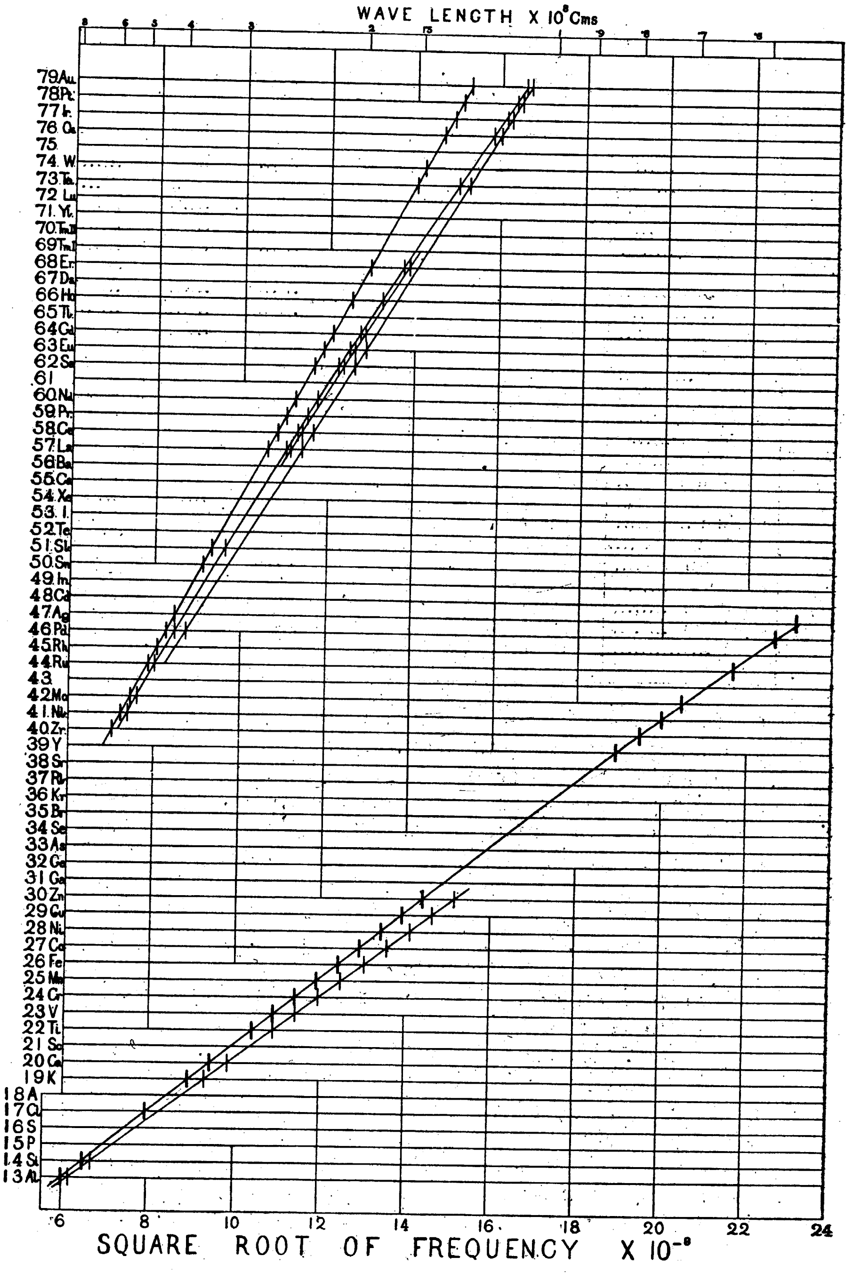
WAVE LENGTH X 10⁸ Cms
8
6
5
4
3
2
1.5
1
.9
.8
.7
.6
79Au
78Pt
77Ir
76Os
75
74 W
73Ta
72Lu
71Yt
70TmII
69TmI
68Er
67Ds
66Ho
65Tb
64Gd
63Eu
62Sa
61
60Nd
59Pr
58Ce
57La
56Ba
55Cs
54Xe
53 I
52Te
51Sb
50Sn
49In
48Cd
47Ag
46Pd
45Rh
44Ru
43
42Mo
41Nb
40Zr
39Y
38Sr
37Rb
36Kr
35Br
34Se
33As
32Ge
31Ga
30Zn
29Cu
28Ni
27Co
26Fe
25Mn
24Cr
23V
22Ti
21Sc
20Ca
19K
18A
17Cl
16S
15P
14Si
13Al
6
8
10
12
14
16
18
20
22
24
SQUARE ROOT OF FREQUENCY X 10⁻⁸

TABLE II.

	α line. $\lambda\times10^8$ cm.	Q_L.	N. Atomic Number.	β line. $\lambda\times10^8$.	ϕ line. $\lambda\times10^8$.	γ line. $\lambda\times10^8$.
Zirconium	6·091	32·8	40	......	......	......
Niobium	5·749	33·8	41	5·507	......	......
Molybdenum......	5·423	34·8	42	5·187	......	......
Ruthenium	4·861	36·7	44	4·660	......	......
Rhodium	4·622	37·7	45	......	......	......
Palladium	4·385	38·7	46	4·168	......	3·928
Silver	4·170	39·6	47	......	......	......
Tin	3·619	42·6	50	......	......	......
Antimony	3·458	43·6	51	3·245	......	......
Lanthanum	2·676	49·5	57	2·471	2·424	2·313
Cerium	2·567	50·6	58	2·360	2·315	2·209
Praseodymium ...	(2·471)	51·5	59	2·265	......	......
Neodymium	2·382	52·5	60	2·175	......	......
Samarium	2·208	54·5	62	2·008	1·972	1·893
Europium	2·130	55·5	63	1·925	1·888	1·814
Gadolinium	2·057	56·5	64	1·853	1·818	......
Holmium	1·914	58·6	66	1·711	......	......
Erbium	1·790	60·6	68	1·591	1·563	......
Tantalum	1·525	65·6	73	1·330	......	1·287
Tungsten	1·486	66·5	74	......	......	......
Osmium	1·397	68·5	76	1·201	......	1·172
Iridium	1·354	69·6	77	1·155	......	1·138
Platinum	1·316	70·6	78	1·121	......	1·104
Gold	1·287	71·4	79	1·092	......	1·078

not included in the limited range of wave-lengths which can be photographed on one plate. Sometimes lines have not been measured, either on account of faintness or of the confusing proximity of lines due to impurities.

Lines due to impurities were frequently present, but caused little trouble except in the rare earth group. Here two extreme cases occurred. The X-ray spectrum of the praseodymia showed that it consisted roughly of 50 per cent. La, 35 per cent. Ce, and 15 per cent. Pr. Unfortunately the position expected for the α line of Pr coincides with the known position of the β line of La, but the β line of Pr was quite conspicuous, and had precisely the wave-length anticipated. Two specimens of erbia were used. The specimen purchased contained 50 per cent. Er and 50 per cent. of another element, of which the X-ray spectrum coincides with the spectrum calculated for Ho. The erbia given by Sir William Crookes was evidently nearly pure, but showed the α and β lines of Ho quite faintly, and also faint lines agreeing with α and β of Ds and α of Tm I and of Tm II. The Nd was free from La, Ce, and Pr, but contained a fair proportion of Sm. The Sm, Eu, and Gd appeared to be pure. I hope soon to complete the examination of the spectra of this group.

Conclusions.

In fig. 3 the spectra of the elements are arranged on horizontal lines spaced at equal distances. The order chosen for the elements is the order of the atomic weights, except in the cases of A, Co, and Te, where this clashes with the order of the chemical properties. Vacant lines have been left for an element between Mo and Ru, an element between Nd and Sa, and an element between W and Os, none of which are yet known, while Tm, which Welsbach has separated into two constituents, is given two lines. This is equivalent to assigning to successive elements a series of successive characteristic integers. On this principle the integer N for Al, the thirteenth element, has been taken to be 13, and the values of N then assumed by the other elements are given on the left-hand side of fig. 3. This proceeding is justified by the fact that it introduces perfect regularity into the X-ray spectra. Examination of fig. 3 shows that the values of $\nu^{\frac{1}{2}}$ for all the lines examined both in the K and the L series now fall on regular curves which approximate to straight lines. The same thing is shown more clearly by comparing the values of N in Table I. with those of

$$Q_K = \sqrt{\frac{\nu}{\frac{3}{4}\nu_0}},$$

ν being the frequency of the α line and ν_0 the fundamental Rydberg frequency. It is here plain that $Q_K = N-1$ very approximately, except for the radiations of very short wavelength which gradually diverge from this relation. Again, in Table II. a comparison of N with

$$Q_L = \sqrt{\frac{\nu}{\frac{5}{36}\nu_0}},$$

where ν is the frequency of the L α line, shows that $Q_L = N-7{\cdot}4$ approximately, although a systematic deviation clearly shows that the relation is not accurately linear in this case.

Now if either the elements were not characterized by these integers, or any mistake had been made in the order chosen or in the number of places left for unknown elements, these

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[*] Welsbach, *Monatsh.* xxxii. p. 373 (1911).

regularities would at once disappear. We can therefore conclude from the evidence of the X-ray spectra alone, without using any theory of atomic structure, that these integers are really characteristic of the elements. Further, as it is improbable that two different stable elements should have the same integer, three, and only three, more elements are likely to exist between Al and Au. As the X-ray spectra of these elements can be confidently predicted, they should not be difficult to find. The examination of keltium [*] would be of exceptional interest, as no place has been assigned to this element.

Now Rutherford[†] has proved that the most important constituent of an atom is its central positively charged nucleus, and van den Broek [‡] has put forward the view that the charge carried by this nucleus is in all cases an integral multiple of the charge on the hydrogen nucleus. There is every reason to suppose that the integer which controls the X-ray spectrum is the same as the number of electrical units in the nucleus, and these experiments therefore give the strongest possible support to the hypothesis of van den Broek. Soddy [§] has pointed out that the chemical properties of the radio-elements are strong evidence that this hypothesis is true for the elements from thallium to uranium, so that its general validity would now seem to be established.

From the approximate linear relation between $\nu^{\frac{1}{2}}$ and N for each line we obtain the general equation

$$\nu = \mathrm{A}\,(\mathrm{N}-b)^2,$$

where A and b are constants characteristic of each line. For the K α line

$$\mathrm{A}=\left(\frac{1}{1^2}-\frac{1}{2^2}\right)\nu_0 \quad \text{and} \quad b=1.$$

For the L α line approximately

$$\mathrm{A}=\left(\frac{1}{2^2}-\frac{1}{3^2}\right)\nu_0 \quad \text{and} \quad b=7{\cdot}4.$$

The fact that the numbers and arrangement of the lines in the K and the L spectra are quite different, strongly suggests that they come from distinct vibrating systems, while the fact that b is much larger for the L lines than for the K lines

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[*] Urbain, *C.R.* clii. p. 141 (1911).

[†] Rutherford, Phil. Mag. xxi. p. 669 (1911), and xxvii. p. 488 (1914).

[‡] Van den Broek, *Phys. Zeit.* xiv. p. 32 (1913), and 'Nature,' Nov. 27, Dec. 25, 1913, March 5, 1914.

[§] Soddy, *Jahrbuch Rad. und. Elect.* x. p. 193 (1913); 'Nature,' Dec. 4, Dec. 18 (1913).

suggests that the L system is situated the further from the nucleus.

It was shown in Part I.[*] that the linear relation between $\nu^{\frac{1}{2}}$ and $N-b$ was most naturally explained if the vibrating system was a ring of electrons rotating round the central nucleus with an angular momentum which was the same for the different elements. This view has been analysed and put in a more generalised form in a letter to 'Nature'[†], written in answer to criticisms made by Lindemann[‡].

Summary.

1. Every element from aluminium to gold is characterized by an integer N which determines its X-ray spectrum. Every detail in the spectrum of an element can therefore be predicted from the spectra of its neighbours.
2. This integer N, the atomic number of the element, is identified with the number of positive units of electricity contained in the atomic nucleus.
3. The atomic numbers for all elements from Al to Au have been tabulated on the assumption that N for Al is 13.
4. The order of the atomic numbers is the same as that of the atomic weights, except where the latter disagrees with the order of the chemical properties.
5. Known elements correspond with all the numbers bebetween 13 and 79 except three. There are here three possible elements still undiscovered.
6. The frequency of any line in the X-ray spectrum is approximately proportional to $A(N-b)^2$, where A and b are constants.

I wish to thank Prof. J. S. Townsend, F.R.S., for providing me with every facility for carrying on this work, which has been greatly assisted by a grant from the Institut International de Physique Solvay.

Electrical Laboratory,
Oxford.

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[*] *Loc. cit.* p. 1032.

[†] Moseley, 'Nature,' Jan. 15 (1914).

[‡] F. A. Lindemann, 'Nature,' Jan. 1, Feb. 5, 1914.