



# CXV. On the spectra of X-rays and the theory of atomic structure

D. Coster

**To cite this article:** D. Coster (1922) CXV. On the spectra of X-rays and the theory of atomic structure , Philosophical Magazine Series 6, 43:258, 1070-1107, DOI: [10.1080/14786442208633964](https://doi.org/10.1080/14786442208633964)

**To link to this article:** <http://dx.doi.org/10.1080/14786442208633964>



Published online: 08 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 9



View related articles [↗](#)



Citing articles: 31 View citing articles [↗](#)

light particle, the two would have parted company before other light particles had impinged upon the rear of the first one. The heavy particle would, in fact, be charged not successively by single light particles, but by battalions of them in column. Equilibrium would be reached when, on an average, the columns were of mass equal to that of the heavy particle. The equilibrium could occur even though the velocities of the heavy particles were of the same order of magnitude as that of the lighter particles.

Under those conditions the law of final partition of energy would be entirely different from that which would result merely by making  $N$  large in the formula for gases.

Whether this would give a credible picture of the æther which would conform with other facts, it is not the intention here to discuss.

It would seem to imply a medium which would not be quite like æther, a gas, or a liquid, or a rigid solid, but having some of the properties of each.

The only point insisted on here is that such a thing is conceivable, and, although the Newtonian laws are assumed, there would not be that frittering down of all energy into the smallest movements. One exception alone is all that is necessary to disprove the generality of the argument that the Newtonian laws must always lead to this conclusion about dissipation of energy.

Conceptions of the æther on these lines may have been thought of before. Novelty is not claimed, but the writer is not aware that the bearing of such a conception on the theory of partition of energy has been pointed out.

CXV. *On the Spectra of X-rays and the Theory of Atomic Structure.* By D. COSTER\*.

[Plate XXIII.]

PART I.

*Introduction.*

§1. ACCORDING to Bohr's theory of spectra the frequencies of the lines in the X-ray spectrum of an element may be represented by the difference of two terms which correspond to the energies of the atom before and after the emission. Following Barkla's original notation for the different kinds of characteristic X-radiation, the various

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

groups of energy-levels whose existence may be inferred from the X-ray spectrum are usually denoted as K, L, M, N... levels. As pointed out by Kossel, these levels may be assumed to be connected with the different groups of electrons in the atom, in such a way that the various energy terms correspond to the work required for the removal of an electron from one of these groups. The various groups of electrons of the atom are in consequence often termed the K-, L-, M-, N- ... shells. This interpretation of the levels affords an explanation of the laws governing the absorption in the X-ray region: it is well known that this absorption is not connected with the single lines in the spectrum but extends over spectral regions which are sharply limited by the so-called absorption edges, the frequencies of which correspond to the energies of the levels concerned. Corresponding to the different ways in which the removal of an electron from a shell may take place we obtain several levels for each shell.

As has been pointed out by Sommerfeld, part at any rate of this complexity in the groups of levels may be connected with the complexity of the ensemble of the stationary states of the hydrogen atom. According to Sommerfeld's theory of the fine structure of the hydrogen lines, the stationary states of an atom containing one electron are characterized by two quantum numbers. One of these numbers, which we shall term the total quantum number  $n$ , is the same as that occurring in Bohr's interpretation of the simple formula for the hydrogen spectrum. The other number is the so-called "azimuthal" quantum number, which determines the value of the angular momentum of the electron round the nucleus, and which we shall denote by  $k$ .

§2. In his recent publications\* Bohr has developed a theory of atomic structure which contains certain essentially new features, and which seems to give a natural interpretation of the periodic system and at the same time to offer an explanation of the results of Kossel and Sommerfeld on the X-ray spectrum. According to Bohr's theory, the orbits of the electrons in the different groups of the atom are characterized by different total quantum numbers, this number being equal to 1 for the innermost group (K-shell), 2 for the next group (L-shell), and so on, every time increasing by one unit until the surface of the atom is reached. Within each group the electrons are again divided into sub-groups, corresponding to different types of orbits and characterized by different values of  $k$ . A survey of the gradual development

\* 'Nature,' March 1921 and October 1921. See also for a fuller account, *Zeitschrift f. Physik*, ix, p. 1 (1922).

of these groups and sub-groups with increasing atomic number is illustrated by the following table, which indicates the proposed constitution of the atoms of the inert gases.

Element.		Number of electrons in $n_k$ orbits.																				
		1 <sub>1</sub>	2 <sub>1</sub>	2 <sub>2</sub>	3 <sub>1</sub>	3 <sub>2</sub>	3 <sub>3</sub>	4 <sub>1</sub>	4 <sub>2</sub>	4 <sub>3</sub>	4 <sub>4</sub>	5 <sub>1</sub>	5 <sub>2</sub>	5 <sub>3</sub>	5 <sub>4</sub>	5 <sub>5</sub>	6 <sub>1</sub>	6 <sub>2</sub>	6 <sub>3</sub>	6 <sub>4</sub>	6 <sub>5</sub>	6 <sub>6</sub>
Helium	2 ...	2																				
Neon	10 ...	2	4	4																		
Argon	18 ...	2	4	4	4	4	—															
Krypton	36 ...	2	4	4	6	6	6	4	4	—	—											
Xenon	54 ...	2	4	4	6	6	6	6	6	6	—	4	4	—	—	—						
Niton	86 ...	2	4	4	6	6	6	8	8	8	8	6	6	6	—	—	4	4	—	—	—	—

§ 3. In previous papers\* I have been able to show that nearly all the lines of the X-ray spectra of the heavier elements can be arranged in a simple scheme, involving the existence of one K-level, three L-levels, five M-levels, and seven N-levels†, and that in continuation of the work of Sommerfeld it is possible to characterize every level in a definite way by means of two quantum numbers  $n$  and  $k$  as defined above. Further, the appearance of the observed X-ray lines was found to be governed by two simple "rules of selection." According to the first rule only those combinations between two levels will appear, for which the quantum number  $k$  remains unaltered or changes by one unit. The second rule‡ states that the levels may be divided

\* *Zeitschrift f. Physik*, v. p. 139 (1921), denoted in the following by I., and vi. p. 185 (1921), (denoted by II). Compare also: A. Smekal, *Zeitschr. f. Phys.* v. p. 91 (1921), and v. p. 121 (1921); A. Dauvillier, *C. R.* clxxii. p. 1350 (1921), *C. R.* clxxiii. p. 35 (1921), *C. R.* clxxiii. p. 647 (1921); G. Wentzel, *Zeitschr. f. Phys.* vi. p. 84 (1921); A. Sommerfeld and G. Wentzel, *Zeitschr. f. Phys.* vii. p. 86 (1921).

† This also suggests that we must expect the existence of one K-, three L-, five M-, and seven N-absorption edges. These absorption edges have actually been found in the K- and L-series, by several authors for different elements, and recently I have been able to establish the existence of five absorption edges in the M-series for U and Th. (See *Phys. Rev.* II. xix. p. 20, 1922.)

‡ This rule of selection has been stated independently by Sommerfeld and Wentzel in another way. They introduce a third quantum-number, "Grundquantenzahl." This number is equal to or one unit larger than the azimuthal quantum number. The transitions are subject to the condition that this "Grundquantenzahl" must change by one unit. As we do not yet know the physical meaning of this "Grundquantenzahl," it seemed to me better to state this rule of selection in the same way as it was first suggested to me by Mr. H. A. Kramers.

Downloaded by [NUS National University of Singapore] at 04:25 29 October 2015

Handwritten musical score for 24 staves, labeled P through K. The notation includes various notes, rests, and accidentals. The staves are grouped into several sections: P, Q, N, M, L, and K. The right side of the score shows the corresponding notes for each staff, such as a6, b6, a5, b5, etc. The bottom right corner has the text "b 1".

\* It should be mentioned that some very weak lines have been observed which represent a transition  $b \rightarrow b$ . They are the transition  $L_3-K$  observed only for W by Duane and Stenström and the lines  $L_{\beta_3}$  (transition  $M_1-L_3$ ) and  $L_{\beta_{10}}$  (transition  $M_2-L_2$ ) observed by several authors for various elements. (See *Zeitschr. f. Phys.* ii. p. 200, table 9.)

*Phil. Mag.* S. 5. Vol. 43. No. 258. June 1922. 3 Z

on measurements for elements of atomic number preceding or following that of niton (86)\*.

Comparing this diagram with the above table representing the results of Bohr's theory, we see that it has been possible to characterize the levels by the same quantum-numbers as those which in the niton atom characterize the different groups and subgroups. We may now assume that the existence of the levels indicated in diagram I. is connected with the appearance of the various subgroups of electrons in the atom. Further, we may assume that in those cases where more than one level is characterized by the same quantum numbers, we witness different processes of removal of an electron from the same subgroup, the remaining electrons in the group arranging themselves afterwards in different ways.

§4. These conclusions obtain strong support from an inspection of the way in which the energy differences of the levels corresponding to the various values of  $n$  and  $k$  vary with the atomic number  $N$  of the element. The considerations in question rest upon a comparison with the theory of the stationary states of an atom consisting of a single electron revolving round a positive nucleus. In the first approximation, where the motion of the electron is calculated according to Newtonian mechanics, the energy necessary to remove the electron from one of these states to an infinite distance from the nucleus depends only on the total quantum number  $n$ . This energy is given by Bohr's formula,

$$W = N^2 \frac{hcR}{n^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $N$  is the number of unit charges on the nucleus,  $h$  Planck's constant,  $c$  the velocity of light, and  $R$  a universal constant appearing in the theory of spectra and called the Rydberg constant. The theoretical value of the latter constant is given by the relation

$$R = \frac{2\pi^2 e^4 m}{h^3 c} = 109737, \text{ (number of wave-lengths per cm.)},$$

where  $e$  is the charge of the electron and  $m$  its mass for velocities small compared with the velocity of light.

\* As to the nomenclature of the lines, which often differs very much with different authors, I have in this paper in general used that proposed by Prof. Siegbahn. Still, for a theoretical discussion it may be advantageous to use sometimes another nomenclature analogous to that used for the visible region. According to this latter one, *e. g.*, the lines  $K\alpha_2$  and  $L\gamma_2$  may be called  $KL_2$  and  $L_3N_5$  respectively.

Taking into account the variation of mass with velocity required by the theory of relativity, the energy necessary for the removal of the electron from one of the stationary states is, to a first approximation, given by Sommerfeld's formula,

$$W = \frac{N^2 hc R}{n^2} + \frac{N^4 hc R \alpha}{n^4} \left( \frac{n}{k} - \frac{3}{4} \right), \quad . . . \quad (2)$$

where  $k$  is the azimuthal quantum number and  $\alpha$  a numerical constant small compared with unity, the theoretical value of which is given by

$$\alpha = \left( \frac{2\pi e^2}{hc} \right)^2 = 5.30 \cdot 10^{-5}.$$

Formula (1) gives an interpretation of the general laws which had been revealed by Moseley's fundamental discoveries. According to these laws the energies of the observed levels are closely proportional to the square of the atomic number, the energies of the K-, L-, and M-levels being approximately represented by the formulæ

$$W_K = Rhc(N - a_K)^2, \quad W_L = \frac{Rhc(N - a_L)^2}{4}, \quad W_M = \frac{Rhc(N - a_M)^2}{9}, \quad . . . \quad (3)$$

where  $a_K$ ,  $a_L$ , and  $a_M$  are constants which are different for the different levels. The appearance of these constants in formula (3) is simply explained by taking into consideration the interaction of the electrons in the atom; the main effect of these is virtually to reduce the attractive influence of the nucleus on the electron whose removal corresponds to the level under consideration. The constant  $a$  is therefore often termed the "screening-constant" belonging to the level; and the quantity  $(N - a)$  may be called the effective nucleus charge.

From formula (2) we obtain an explanation of the circumstance that certain pairs of energy-levels corresponding to the same value of  $n$  vary to a close approximation as the fourth power of the atomic number. Following the notation of Sommerfeld, such pairs of levels may be termed "relativity doublets," since the energy-difference between the two orbits is due to the differential effect of the relativity modification on orbits having the same value of  $n$  but different values of  $k$ . In the diagrams these pairs of levels are denoted by  $\{$ .

As stated above, for levels having the same values of  $n$  and  $k$  we should expect that differences in the energy necessary

to remove an electron from the atom would arise from different orientations of the orbits of the remaining electrons within the group concerned. In such levels it may be said that the remaining electrons can have different screening effects. This offers a simple explanation of a fact revealed by an inspection of the measurements, that the energy-differences between two such levels to a close approximation vary linearly with the atomic number. Such a pair of levels may therefore be termed "screening doublets"\*.

In this connexion, however, it must be pointed out, that the numerical values of the screening constants for the different levels calculated from the relativity doublets do not agree with those calculated from the screening doublets †. This is just what we might expect from Bohr's theory of atomic structure. According to this theory the electrons of the outer shells come during their revolution round the nucleus wholly inside the orbits of the inner shells, so that they are moving in a varying field of force. Now it is easily seen, that the effect of the relativity change of mass on the orbit of the electron is mainly due to that part of the orbit which lies close to the nucleus, and where the velocity is very great. We thus understand that the screening constant for these electrons appearing in the relativity term of formula (2) has another value than that appearing in the main term which in first approximation gives the whole energy of the orbit.

§ 5. In general, corresponding to a given pair of values for  $n$  and  $k$  there exist two levels, of which one is of the type denoted in the above diagram as an  $a$ -level, the other a  $b$ -level. For the largest value of  $k$  corresponding to any given value of  $n$  there appears, however, only one level. I am indebted to Prof. Bohr for the remark that this circumstance may be brought in suggestive connexion with his theory of atomic structure, which rests upon a consideration of the way in which an atom may be formed by the successive binding of the electrons by the nucleus. In fact, in such a process the subgroups corresponding to the highest value of  $k$  will correspond to the electrons bound during the last stage of formation of the group, and, in contrast to the removal of an electron from subgroups corresponding to

\* Sommerfeld divides the doublets into "regular" and "irregular" doublets. As the screening doublets show no irregularity at all, these names seem not to be well chosen.

† Compare Sommerfeld and Wentzel, *Zeitschrift für Physik*, vii. p. 86 (1921).



smaller values of  $k$ , the removal of an electron from this sub-group may therefore be expected to represent a simple and well-defined reversal of a step in the process of formation of the group.

In this connexion it must be pointed out that the proposed explanation of the origin of these levels requires that the screening constants for a pair of levels corresponding to a relativity doublet should have approximately the same value. No simple explanation of this, however, is offered in the present state of the theory.

§ 6. Though there still remain some difficulties, we may say that the X-ray spectra are built up in a simple manner and that there exist many analogies between these spectra and the series spectra in the visible region. There are also, however, some striking differences. In the visible spectrum, transitions in which the azimuthal quantum number remains the same do not occur under ordinary conditions. In the X-ray spectrum, however, there are several lines for which  $k$  remains constant. A few of them are fairly intense lines (*e. g.*, in the case of the heavier elements  $L\beta_4$  and  $L\beta_3$  and also  $L\gamma_2$  and  $L\gamma_3$  are of about the same intensity). Recently I have found that there is another difference between the X-ray spectrum and the visible spectrum. In the latter there exist also transitions for which the total quantum number  $n$  does not change at all. To these belong for instance the first line of the principal series of the alkali metals. From this we might expect that the transition  $L_1-L_3$  would give rise to a line in the X-ray spectrum which might easily be detected. An investigation with a tungsten anticathode showed, however, that this line does not exist at all, or at any rate must be very weak. Experimental particulars are given in Part II.

These various differences between X-ray spectra and optical spectra need not be surprising in view of the fundamental differences which exist (in spite of analogies) between the origins of the two types of spectra. This difference is due to the fact that in the emission of the optical spectrum we have to do with the change of the motion of an electron whose orbit is characterized by higher quantum numbers than the orbits of the other electrons in the atom. In the emission of the X-ray spectrum, however, we meet with a change in the motion of an electron which must be expected to be in intimate interaction with the electrons of the same shell moving in orbits with the same quantum numbers\*.

\* Compare Bohr, *Zeitschr. f. Physik*, ix. p. 1 (1922).

## PART II.

*The New Measurements of the L-series in the X-ray Spectra of the Elements from Rb to Ba* \*.

§ 1. As mentioned above, the results indicated by diagram I. have a direct bearing only on elements of atomic number comparable with that of niton. We should expect a change in this diagram for elements with lower atomic number, since the formation of new shells in the outer region of the atom with increasing atomic number must be accompanied by the appearance of new levels in the energy diagram which find their expression in the appearance of new lines.

My previous work was based on an investigation of the L-series of most of the elements from W to U †, which I carried out in the laboratory of Prof. Siegbahn. In view of a comparison with the theory of atomic structure, it was desirable to extend this investigation to elements of lower atomic number. In continuation of the former work I have therefore undertaken in the same laboratory an examination of the L-series of such elements. Though this work is not yet finished, the results already obtained seem to be sufficiently interesting to justify publication. In the present paper only the results obtained for the elements Rb–Ba will be discussed.

§ 2. The apparatus used for the experiments consisted of an X-ray vacuum-spectrograph, and the metal X-ray tube of the Coolidge type described by Prof. Siegbahn ‡. The tube was driven by two similar induction-coils of medium size. The primaries of the coils were connected in series to a source of alternating current of 50 cycles. As the tube itself acts as a current rectifier, no other rectifier was used in the secondary circuit. For most of the work the secondaries of the coils were connected in series. In this way a current of about 30 m.a. with a maximum tension of about 30 k.v. could easily be obtained. This tension is at the same time about the highest which can be sustained by this tube.

The tension was estimated by an adjustable parallel spark-gap. If the vacuum is not very good, the discharges through the tube give rise to great fluctuations in the tension. Under these circumstances no simple relation exists between the maximum tension measured by the spark-gap and the mean value. For a very high vacuum, which could be obtained easily with the molecular pump, the maximum tension was

\* Part of these experimental results have recently been published in *Archives Néerlandaises* (Serie III. A, tome vi., 1<sup>re</sup> livraison, p. 76.)

† *Zeitschr. f. Physik*, iv. p. 178 (1921), and *Zeitschr. f. Phys.* I. and II.

‡ *Phil. Mag.* xxxvii. p. 601 (1919).

about 1.4 times the mean tension. Up to 10 k.v. a Braun electrometer was used. At times it was necessary to work with a rather low tension. In this case the secondaries were connected in parallel, so that a larger current could be obtained. In photographing the absorption discontinuities of silver a maximum tension of not more than 5400 v. was used, and with this tension the influence of the "space charge" in limiting the magnitude of the maximum current could readily be observed. As is known, this effect has been experimentally and theoretically studied by Langmuir\*, who clearly showed that in an extremely high vacuum the charge due to the electrons moving in the field between the hot wire cathode and the anode diminishes the rate at which electrons may escape from the hot wire and enter the field. For every tension there exists a maximum "saturation current" which depends on the dimensions of the tube and is independent of the temperature of the hot wire, if once a certain temperature has been surpassed. In this experiment the saturation current was less than 10 m.a. for a tension of about 5400 volt. As with this small current a very long exposure is required, it was desirable to get rid of the space-charge effect. This may be done by working with a somewhat lower vacuum, as in this case the positive ions of the gas neutralize the influence of the electrons in the field. Fortunately I was able to reduce the vacuum just sufficiently by an imperfectly sealed join in the tube. Otherwise it would have been necessary to lower the vacuum by regulating the speed of the molecular pump. Under these circumstances it was possible to get a current of about 50 m.a. at a tension of 5400 v.

As fairly long wave-lengths were measured, it was necessary to have also a vacuum in the spectrograph. The spectrograph was exhausted by a Gaede pump which gave a pressure of about 0.1 to 0.2 mm. The slit of the X-ray tube, which was immediately connected with the spectrograph, was covered with goldbeater's skin in order to separate the high vacuum from the low vacuum. This goldbeater's skin was coloured with erythrosine to prevent the visible light as much as possible from entering the spectrograph. The tube itself was exhausted by a molecular pump in series with the low vacuum pump. The pumps were able to give a very good vacuum in about 10 minutes. The time of exposure for one plate varied from  $\frac{1}{2}$  to  $1\frac{1}{2}$  hour.

§ 3. To get also the fainter lines of the spectrum, it appeared to be advantageous to use tensions several times higher than the critical exciting tension. Thus in several cases the maximum tension obtainable with the apparatus

\* Phys. Rev. II, ii. p. 450 (1913).

was used. On the other hand, the high tension gave some trouble in identifying the lines, as several lines due to other elements appeared in higher orders on the plates (*e.g.*, on many plates taken with a gypsum crystal, Cu K-lines and W L-lines were obtained in as high as the 5th order). In general, the best plates were obtained when the element could be placed in the form of a metallic sheet on the anticathode. For this reason Sb, Sn, In, and Cd were melted in a fairly pure state on the copper anticathode, while the elements Ag, Pd, and Rh were attached with solder; Mo was pressed in a copper ring which was soldered on to the anticathode. There was no particular difficulty in obtaining good plates with these elements.

The other elements examined on this occasion (*i.e.*, Ba, Cs, Te, Ru, Nb, Zr, Y, Sr, and Rb) were used in the form of salts or oxides, which were pressed into the roughened surface of a copper plate soldered on to the anticathode. For every element this copper plate was renewed. As the salts are sputtered from the anticathode somewhat quickly, it appeared to be better not to use the highest energy which could be obtained from the apparatus. In general, for these elements the best plates were obtained with a maximum tension of about 20–25 k.v. and a current of not more than 15 m.a. For each element from 6 to 10 different plates were taken through the whole region of the spectrum. Between two exposures the tube was opened and a fresh quantity of salt was brought on the anticathode. Very often it was necessary to take several plates of the same part of the spectrum before a good one was obtained.

§4. The distances of the lines on the plates were measured under the microscope, and from this the wave-lengths of the new lines could be measured relatively to the lines  $\alpha_1$ ,  $\beta_1$ , and  $\gamma_1$  which have previously been determined with great precision by Hjalmar\*. The other lines mentioned by Hjalmar ( $\alpha_2$ ,  $\alpha_3$ ,  $\beta_4$ ,  $\beta_3$ ,  $\beta_2$ , and in a few cases  $\gamma_2$ ,  $\gamma_3$ ,  $\gamma_4$ ) were usually determined by this author either relatively to  $\alpha_1$ ,  $\beta_1$ ,  $\gamma_1$ , or from the old measurements of Friman, a correction having been applied.

In the following tables the lines determined by Hjalmar by the precision method as well as those measured relatively to them on his own plates have been taken from this author without change. These comprise nearly all the lines whose wave-lengths appear in his tables to one or two decimal places. The other lines have been determined in the present investigation.

\* *Zeitschr. f. Physik*, iii. p. 262 (1920), and vii. p. 341 (1921).

TABLE I.  
Wave-lengths in X.U. ( $10^{-11}$  cm.)

	$l$	$\eta$	$\alpha_2$	$\alpha_1$	$\beta_1$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_2$	$\gamma_5$	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$
37 Rb.....	.....	8029.0	.....	7302.7	7060.4	6302.8	6769.9	6967.5	.....	6738.6	.....	6028.2	.....	.....
38 Sr.....	7821	7505	.....	6347.8	6609.2	6385.5	6349.9	6503.0	.....	6278.8	.....	5629.4	.....	.....
39 Y.....	.....	.....	.....	6434.9	6198.4	6001.9	5967.8	.....	.....	.....	.....	.....	.....	.....
40 Zr.....	6898	6583.1	.....	6055.9	5822.8	5652.7	5618.2	5693.5	5573.4	5481.0	5373.0	4941.2	.....	.....
41 Nb.....	6509	6195	5717	5711.3	5479.6	5331.4	5285.9	5346.1	5225.3	.....	5024.1	4639	.....	.....
42 Mo.....	.....	5835	5400	5394.3	5165.8	5035.8	5000.2	.....	4909.2	4819.0	4711.1	4361.3	.....	.....
44 Ru.....	.....	.....	4843.67	4835.67	4611.00	4512.6	4476.4	4476.4	4361.9	4276.6	4172.82	3987.9	.....	.....
45 Rh.....	5207.0	4911.2	4595.56	4587.78	4364.00	4277.8	4241.3	4230.1	4122.1	4035.2	.....	3677.0	.....	.....
46 Pd.....	4939.6	4650.2	4366.60	4358.50	4137.30	4062.3	4025.7	4007.0	3900.7	3811.6	3716.36	3480.9	.....	.....
47 Ag.....	4697.6	4410.1	4153.82	4145.64	3926.64	3861.1	3824.45	3799.4	3693.83	3607.3	3514.85	3299.7	.....	.....
48 Cd.....	4471.3	4187.5	3956.36	3947.82	3730.08	3674.25	3636.42	3607.3	3506.4	3418.1	3328.00	3131.6	.....	.....
49 In.....	4259.3	3976.1	3772.42	3763.67	3547.83	3499.0	3461.9	3428.0	3331.2	3241.8	3155.29	2973.6	.....	2919.1
50 Sn.....	4063.3	3781.8	3601.08	3592.18	3377.92	3336.3	3298.9	3262.2	3167.9	3077.4	2994.93	2827.3	.....	2771.3
51 Sb.....	3890.3	3599.6	3440.75	3431.77	3218.36	3184.3	3145.14	3107.8	3016.6	2925.6	2845.07	2689.9	.....	2633.6
52 Te.....	3710.1	.....	3291.00	3281.99	3069.97	3040.0	3001.3	2961.4	2876.1	2783.1	2706.47	2564.9	.....	2505.7
55 Os.....	.....	2983.3	2895.60	2886.10	2677.84	2660.5	2622.93	2587.5	2506.4	2411.1	2342.52	2232.2	2227.0	2169.1
56 Ba.....	3128.7	2857.1	2779.02	2769.64	2562.24	2549.8	2511.0	2477.2	2399.3	2302.3	2236.60	2134.0	2129.5	2071.5

TABLE II.

	<i>l</i>	$\eta$	$\alpha_2$	$\alpha_1$	$\beta_1$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_2$	$\gamma_5$	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$
37 Rb.....		113.50	.....	124.78	129.06	135.96	134.61	130.75		135.23			151.17	
38 Sr.....	116.51	121.43	.....	133.07	137.87	142.71	143.51	140.13		145.13			161.88	
39 Y.....		.....	.....	141.61	147.01	151.83	152.70			.....			.....	
40 Zr.....	132.07	138.22	.....	150.47	156.50	161.21	162.20	160.05	163.50	166.26	169.63	181.42		
41 Nb.....	139.29	147.09	159.40	159.55	166.29	170.93	172.07	170.45	174.39	.....	181.38	196.43		
42 Mo.....		156.16	168.75	168.93	176.40	180.96	182.24	.....		189.10	193.42	208.94		
44 Ru.....		.....	188.13	188.44	197.62	201.94	203.57	203.57	208.91	213.08	218.38	234.38		
45 Rh.....	175.01	185.55	198.29	198.62	208.77	213.03	214.86	215.42	221.07	225.83	231.53	247.83		
46 Pd.....	184.48	195.96	208.69	209.07	220.25	224.32	226.36	227.42	233.62	239.08	245.19	261.80		
47 Ag.....	193.99	206.63	219.37	219.80	232.06	236.01	238.27	239.85	246.69	252.62	259.15	276.17		
48 Cd.....	203.80	217.61	230.32	230.82	244.29	248.00	250.59	252.62	259.89	266.60	273.81	291.00		312.18
49 In.....	213.95	229.18	241.55	242.12	256.84	260.43	263.22	265.84	273.55	281.10	288.79	306.46		328.82
50 Sn.....	224.27	240.96	253.05	253.67	269.76	273.13	276.24	279.34	287.66	296.11	304.26	322.31		346.01
51 Sb.....	234.86	253.16	264.84	265.53	283.13	286.18	289.73	293.22	302.08	311.48	320.29	338.90		363.69
52 Te.....	245.62	.....	276.89	277.65	296.83	299.75	303.61	307.41	316.84	327.44	336.69	355.28		420.11
55 Os.....		305.45	314.70	315.74	340.29	342.80	347.41	352.18	363.58	377.94	389.00	408.23	409.18	
56 Ba.....	291.26	318.95	327.90	329.01	355.64	357.38	362.89	367.86	379.80	395.81	407.42	427.03	427.92	439.91

TABLE III.  
 $\sqrt{\frac{\nu}{R}}$  (square roots of frequencies).

	$l$	$\eta$	$\alpha_2$	$\alpha_1$	$\beta_1$	$\beta_4$	$\beta_3$	$\beta_6$	$\beta_2$	$\gamma_6$	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$
37 Rb.....	.....	10 653	.....	11 170	11 360	11 574	11 602	11 436		11 629			12 285	
38 Sr.....	10 794	11 019	.....	11 536	11 742	11 946	11 979	11 888		12 047			12 723	
39 Y.....	.....	.....	.....	11 900	12 125	12 322	12 357	.....		.....			.....	
40 Zr.....	11 492	11 756	.....	12 267	12 510	12 697	12 736	12 651	12 787	12 894	13 030		13 580	
41 Nb.....	11 832	12 128	12 625	12 631	12 895	13 074	13 118	13 056	13 206	.....	13 468		14 015	
42 Mo.....	.....	12 497	12 990	12 998	13 282	13 452	13 500	.....	13 624	13 751	13 908		14 455	
44 Ru.....	.....	.....	13 716	13 727	14 058	14 211	14 268	14 268	14 454	14 597	14 778		15 309	
45 Rh.....	13 229	13 622	14 081	14 093	14 449	14 595	14 658	14 677	14 868	15 028	15 216		15 745	
46 Pd.....	13 582	13 999	14 446	14 459	14 841	14 978	15 045	15 080	15 285	15 462	15 658		16 180	
47 Ag.....	13 923	14 374	14 811	14 826	15 233	15 363	15 436	15 487	15 706	15 894	16 098		16 618	
48 Cd.....	14 277	14 752	15 176	15 193	15 630	15 748	15 830	15 894	16 121	16 328	16 547		17 059	
49 In.....	14 627	15 139	15 542	15 560	16 026	16 138	16 224	16 304	16 539	16 766	16 994		17 506	17 668
50 Sn.....	14 976	15 523	15 907	15 927	16 424	16 527	16 620	16 713	16 960	17 208	17 443		17 953	18 133
51 Sb.....	15 325	15 911	16 274	16 295	16 827	16 917	17 021	17 124	17 381	17 649	17 897		18 409	18 602
52 Te.....	15 672	.....	16 640	16 663	17 229	17 313	17 425	17 533	17 800	18 085	18 349		18 849	19 071
55 Cs.....	.....	17 477	17 740	17 769	18 447	18 504	18 639	18 767	19 068	19 440	19 723	20 211	20 228	20 497
56 Ba.....	17 066	17 859	18 108	18 139	18 858	18 904	19 050	18 180	19 488	19 895	20 185	20 655	20 687	20 974

Hjalmar and Friman found  $\beta_4$ ,  $\beta_3$ , and  $\beta_2$  as far down as Pd,  $\gamma_1$  appears for the last time for Mo in their tables, and the  $\eta$ - $l$  and  $\gamma_5$ - $\beta_6$  doublets were not observed at all in this region. But I could still detect  $\beta_4$  and  $\beta_2$  for Sr and Rb,  $\beta_2$  and  $\gamma_1$  were found as far down as Zr, although very faint (Hjalmar's value of  $\lambda = 5295.1$  for  $\text{Nb}\beta_2$  corresponds to my value of  $\lambda = 5295.9$  X.U. for  $\beta_2$  for the same element). The lines  $\gamma_2$ ,  $\gamma_3$ , and  $\gamma_4$  in this region had not been identified correctly by the former authors. The line  $\gamma_{2,3}$  ( $\gamma_2$  and  $\gamma_3$  could no longer be separated in this region) has still been observed for Rb and  $\gamma_4$  still for In. Both doublets  $\eta$ - $l$  and  $\gamma_5$ - $\beta_6$  could also be measured down to Rb and Sr.

The spectra of the elements Ba and Cs were taken with a rocksalt crystal, Te-Pd with calcite, Rh partly with calcite, partly with gypsum, and Ru-Rb with a gypsum crystal. For these elements the breadth of the lines was considerably greater than the width of the slit, implying that the lines represent a finite frequency interval. Strongly exposed lines obtained with a rocksalt or calcite crystal, especially, were diffuse at the edges, which obviously reduced the accuracy of the measurements. Extremely broad and diffuse were the lines,  $\eta$ ,  $l$ , and  $\gamma_{2,3}$ . For  $\beta_2$  for some elements a broadening could be observed at the short wave-length side. The lines  $\alpha_1$  and  $\beta_1$  were accompanied by satellites (see Part II. § 7), while for the lightest elements  $\alpha_2$  could not be separated from  $\alpha_1$ . All this reduced the accuracy of the measurements. Usually only reference measurements were made. The distance on the plate to the reference line was often fairly large, sometimes over 10 mm., and in a few cases even between 15 and 20 mm. Thus errors in the measurements of the line-distances and irregularities in the structure of the crystal may be quite appreciable here. In the case of the lines taken with a rocksalt or calcite crystal, however, the error in the wave-lengths must be in nearly all cases considerably smaller than one X.U. This is especially true of the lines lying in the neighbourhood of a reference line. In a few cases (sometimes for  $\eta$ ,  $l$ , and  $\gamma_{2,3}$ ) this error may be a little larger. Some lines could not be measured under a microscope and their distance was estimated with a millimetre scale. They stand in the tables without decimals in the wave-lengths. Their errors may be more than 2 X.U. Using gypsum as analysing crystal, we have on the one hand the disadvantage of the greater space-lattice constant, on the other hand the advantage of getting sharper lines, which usually lie nearer



together on the photographic plate. For the lines measured with a gypsum crystal we have to multiply the above given limits of error by  $1\frac{1}{2}$ –2. Thus far I have neglected the errors in the wave-length which are due to the remarkable fact detected by Stenström † that Bragg's relation  $n\lambda = 2d \sin \phi$  is only approximately true. Especially with a gypsum crystal the deviations are fairly large and may give rise to an error of several X-units, but as this error is nearly the same for wave-lengths of about the same value it does not affect the conclusions drawn in this paper. Tables I., II., III. contain only the lines which can be arranged in diagram I.

§ 5. The right classification of the lines often gives trouble. Some indications were supplied by the relativity L-doublets, which are given in Table IV. Down to Ag the  $\gamma_1$ - $\beta_2$  doublet

TABLE IV.  
Relativity L-doublets.

	$\eta$ - $l$ .	$\beta_1$ - $\alpha_2$ .	$\gamma_5$ - $\beta_6$ .	$\gamma_1$ - $\beta_2$ .	$L_1$ - $L_2$ .
37 Rb .....	...	4.28*	4.48		
38 Sr .....	4.92	4.80*	5.00		
39 Y .....	...	5.40*	...		
40 Zr .....	6.15	6.03*	6.21	6.13	
41 Nb .....	7.10	6.89	...	6.99	
42 Mo .....	...	7.70	...	7.80	
44 Ru .....	...	9.49	9.53	9.47	
45 Rh .....	10.54	10.48	10.41	10.46	
46 Pd .....	11.48	11.56	11.66	11.57	
47 Ag .....	12.64	12.69	12.77	12.46	12.68
48 Cd .....	13.81	13.97	13.98	13.92	
49 In .....	15.23	15.29	15.26	15.24	
50 Sn .....	16.69	16.71	16.77	16.60	
51 Sb .....	18.31	18.29	18.26	18.21	
52 Te .....	...	19.94	20.03	19.85	
55 Cs .....	...	25.59	25.76	25.42	(25.8)
56 Ba .....	27.69	27.74	27.95	27.61	28.00

\* As  $\alpha_2$  could not be measured for this element, the value  $\beta_1$ - $\alpha_1$  has been used. This value is smaller than  $\beta_1$ - $\alpha_2$ .

difference is apparently smaller than the other ones ‡, lower down this "doublet defect" disappears in the accidental errors. The cause of this defect will be seen from diagram I. The pairs of lines  $\eta$ - $l$ ,  $\beta_1$ - $\alpha_2$ , and  $\gamma_5$ - $\beta_6$  come each from the same initial level, whereas  $\gamma_1$  and  $\beta_2$  come from different initial levels. I have never observed the transition  $N_4$ - $L_1$ ,

† Stenström, Dissertation, Lund, 1919; Hjalmar, *Zeitschr. f. Phys.* i. p. 439 (1920); Siegbahn, *Comptes Rendus*, clxxiii. p. 1350 (1922).

‡ Compare also *Zeitschr. f. Phys.* II. table 3, p. 191.

which might be supposed to exist by analogy with the transition  $M_2-L_1$ , which gives rise to the line  $\alpha_2$ .

Pairs of lines the frequencies of which show a relativity doublet difference occur very often in the X-ray spectrum, but those which would form a screening doublet do not occur at all in virtue of the  $a-b$  rule (see diagram I.). But we may find lines the frequency difference of which is either the sum or the difference of two screening doublets. To the former class belong  $\beta_4-\eta$  and  $\gamma_2-\gamma_5$ , to the latter  $\beta_3-\beta_1$  and  $\gamma_3-\gamma_1$ . As the screening doublets are approximately proportional to the effective nucleus charge of the atom, the differences of the

TABLE V.  
Differences in  $\sqrt{\frac{\nu}{R}}$ .

	$\beta_4-\eta$	$\gamma_2-\gamma_5$	$\beta_3-\beta_1$	$\gamma_3-\gamma_1$
37 Rb .....	0.921	0.666	0.242	
38 Sr .....	927	676	237	
39 Y .....	...	...	232	
40 Zr .....	941	686	226	0.550
41 Nb .....	946	...	223	547
42 Mo .....	955	704	218	547
44 Ru .....	...	712	210	531
45 Rh .....	973	715	209	527
46 Pd .....	979	718	204	522
47 Ag .....	989	724	203	520
48 Cd .....	996	731	200	512
49 In .....	999	740	198	512
50 Sn .....	1004	745	196	510
51 Sb .....	1006	760	194	511
52 Te .....	...	756	196	510
55 Cs .....	1027	771	192	505
56 Ba .....	1045	770	192	502
74 W .....	1136	822	202	517
83 Bi .....	1200	910	224	495

square roots of the frequencies of these lines are easily seen to be nearly constant for the different elements. These differences are shown in Table V. This table in connexion with Table IV. most strongly supports the identification of the lines which has been proposed by the author. The differences  $\beta_4-\eta$  and  $\gamma_2-\gamma_5$  increase slowly with increasing atomic number. This is due to the fact, that in every line-frequency the screening constant of the initial as well as that of the final level is involved, and these screening constants in general will be different. For the heaviest elements the relativity correction here also plays a part.

The values which I have given for  $\gamma_3$  may be verified

by some measurements in the K-series. As is seen from diagram I. the following relation must hold for the frequencies :

$$K\beta_2 - K\beta_1 = L\gamma_3 - L\beta_3.$$

Table VI. gives some numerical values.

TABLE VI.

	$L\gamma_3 - L\beta_3.$	$K\beta_2 - K\beta_1.$
Cd .....	40.41	39.0
Pd .....	35.44	32.4
Rh .....	32.97	34.7
Mo .....	26.70	26.5

The values for the K-lines of Rh and Mo are calculated from the wave-lengths given by Duane\* ( $K\beta_2$  is called  $K\gamma$  by Duane). The values for Cd and Pd have been kindly furnished me by Mr. A. B. Leide, who has measured some K-lines in this laboratory. As an error of 0.5 X.U. in one of the K-lines involves an error of more than 4 per cent. in the differences under consideration, we may say that the agreement is very good.

The line  $\beta_6$  crosses  $\beta_4$  and  $\beta_3$  twice, a circumstance which in the beginning gave rise to some difficulties in the identification of these lines.  $\beta_6$  crosses  $\beta_4$  once for Pt and  $\beta_3$  for Dy and crosses both lines again between Rh and Mo. In this region the  $\beta_6$ -curve is nearly a straight line in the Moseley-diagram, whereas the  $\beta_3$ - and  $\beta_4$ -lines are noticeably curved.

§ 6. As regards the intensities of the different lines, it has been found that for the elements U-W the lines  $\beta_3$  and  $\beta_4$  are not much different in intensity, but in the region Ba-Rb  $\beta_3$  is much more intense than  $\beta_4$ . An illustration of this fact is given by figs. 1 and 2 (Pl. XXIII.) †. Fig. 1 gives

\* Phys. Review, II. xiv. p. 373 (1919).

† The reproductions are about twice the natural size. The black lines in the original photographs are represented as white lines in the reproductions.

the lines of the  $\beta$ -group for Pb taken with a rocksalt crystal; fig. 2 gives nearly the whole L-spectrum of Rh\* taken with a gypsum crystal. For the lines  $\gamma_2$  and  $\gamma_3$  the case is much similar: for the heaviest elements they are approximately of equal intensity; for Ta  $\gamma_3$  seems to be prominent; for Ba and Cs  $\gamma_3$  is still fairly strong, whereas  $\gamma_2$  can scarcely be perceived. This fact may imply that the disturbances of the inner atomic field which give rise to  $\beta_4$  and  $\gamma_2$  (the azimuthal quantum number does not change for these lines) are less important for the lighter elements. But the change of relative intensity of  $\beta_3$  and  $\beta_4$  must partly be accounted for as a change in the intensity of  $\beta_3$ . This line seems to correspond to a transition less probable for the heavier elements than for the lighter ones.

In the case of  $\eta$ - $l$  and  $\gamma_5$ - $\beta_6$  doublets a corresponding change of the intensities could not be observed. For all elements  $l$  is about 2-3 times as strong as  $\eta$  and  $\beta_6$  2-3 times as strong as  $\gamma_5$ . The lines  $\eta$  and  $\gamma_5$  like  $\beta_4$  and  $\gamma_2$  correspond to transitions for which the azimuthal quantum number does not change; the lines  $l$  and  $\beta_6$  correspond to transitions for which the azimuthal quantum number decreases, whilst the lines  $\beta_3$  and  $\gamma_3$  correspond to transitions for which it increases.

§ 7. Another interesting result of this investigation of the L-spectra of the lighter elements was the discovery that the two most intense lines of this spectrum,  $\alpha_1$  and  $\beta_1$ , show a complicated structure, which has not been observed for the heavier elements, or is at any rate much less pronounced. Both lines in question show a broadening on the short wave-length side. This cannot be ascribed to any peculiarity in the experimental conditions, as it has a very regular structure which is independent of the time of exposure. On the other hand, the line  $\beta_3$  which on several long exposed plates was very intense showed no such structure, appearing merely somewhat diffuse on both sides. For the  $\alpha_1$ -line this broadening ends fairly abruptly, so that the edge could be measured with sufficient accuracy. From this the wave-length corresponding to this edge could be calculated. (A correction must be made for the half width of the slit.) In the following tables this wave-length has been called  $\alpha_1'$ . This must be

\* The satellites of  $\alpha_1$  and  $\beta_1$  (see Part III. § 7) have not been well reproduced on this plate. They were more easily visible on the original photograph. On the reproduction Sn La stands erroneously for Fe K $\alpha$  2nd order.

understood to mean that there is an emission-band extending from  $\alpha_1$  to  $\alpha_1'$ . When one passes from Cd to Ag this band suddenly changes. For Ag two new lines could be detected: one, which is within this emission-band, is called  $\alpha_3$ , the other, a short distance outside, is called  $\alpha_4$  \*. The intensity of the line  $\alpha_3$  changes very little from Ag, where it is found for the first time, down to Rb. The line  $\alpha_4$  seems to become somewhat stronger for the lighter elements †.

The satellites of  $\beta_1$  take a different course. The proximity of  $\beta_4$  makes it impossible to study these satellites for the elements Ba and Cs, but from Sb (where they were observed for the first time) down to Rb they do not essentially change. Firstly there is an emission band, the short wave-length-edge of which has been denoted by  $\beta_1'$ . This band is fainter than the  $\alpha_1$ -band and not so sharply limited. Furthermore, outside the band a line has been found, denoted by  $\beta_{13}$ , which is faint for the elements Sb–Rh, but becomes more intense for the elements Mo–Rb.

It is a well known fact that the human eye does not always form a correct judgment of the blackening of a photographic plate. In particular a sudden change in the *gradient* of the blackening gives the impression of a white or a black line. It therefore seemed to be advisable to study the  $\alpha_1$ - and  $\beta_1$ -satellites with the photometer also ‡. It must be borne in mind, however, that even the photometer does not give a wholly correct impression of the blackening of the plate. With this photometer part of the photographic plate is projected by a microscope-objective on the slit of the thermopile. In these measurements 0.03 mm. on the photographic plate corresponds to the breadth of the slit. Further, it is impossible to have a sharp image for the

\* (Note added during the proof.)—Recently, however, by taking some other powerfully exposed plates, I was able to establish the existence of the lines  $\alpha_3$  and  $\alpha_4$  for Cd also, but for this element they are very faint. For In the existence of these lines remains very uncertain, for Sn no trace of them could be observed. In this connexion it might be of interest to remark that the appearance of these satellites is within wide limits independent of the tension used on the tube.

† I have previously observed the broadening of  $\alpha_1$  for the elements Ta–U, but have interpreted it erroneously. See *Zs. f. Phys.* II. p. 191.

‡ This photometer has been described by M. Siegbahn, *Ann. der Physik*, (4) xlii. p. 689 (1913), and A. E. Lindh, *Zs. f. Phys.* vi. p. 303 (1921), See also W. J. H. Moll, *Proceedings Phys. Soc. London*, vol. xxxiii. part 4, p. 207 (1921).

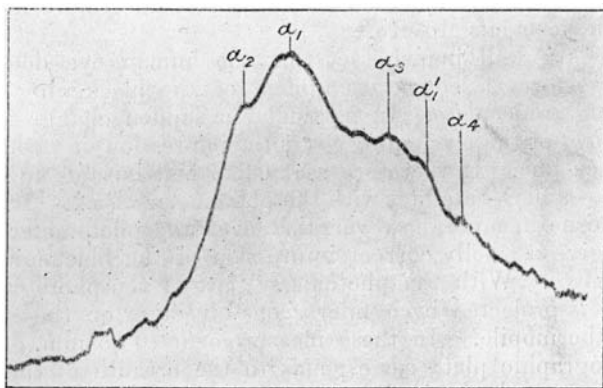
visible and the infra-red light at the same time. Hence a blackening, which may be represented thus :  $\square$  is regis-

tered by the photometer thus :  $\wedge$  \*.

Small irregularities of the plate which are not readily noticed by the eye are registered by the photometer. Most of the small abrupt changes of the curves must be explained in this way. As a rule the more continuous changes correspond to changes in the blackening of the plate. This may be verified by comparing photometer-curves taken across the plate at different heights.

Fig. 1 gives a typical curve for Rh (taken in the opposite

Fig. 1.



Rhodium  $L\alpha_1$  with satellites (calcite crystal).

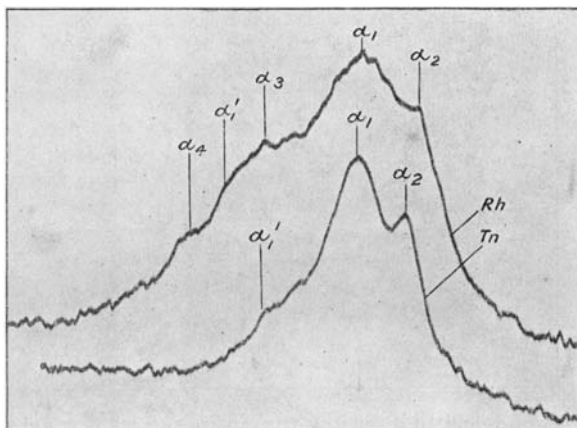
direction as compared with the other curves). Fig. 2 shows the great difference between the Rh  $\dagger \alpha_1$  and the In  $\alpha_1$  line. Fig. 3 clearly demonstrates that this difference suddenly appears between Cd and Ag. (The numerous accidental

\* Another question is, whether the blackening of the plate really gives a correct impression of the emission-spectrum. It might be supposed, that for these strongly exposed lines the secondary radiation in the photographic plate has some effect in broadening the lines, but as the breadth of the lines largely depends on the space-lattice constant of the analysing crystal (with gypsum rather sharp lines were obtained) we may conclude that this influence cannot be very great.

† This curve is taken at a height different from that in fig. 1. In figs. 2, 3, and 4 *Tn* stands for *In*.

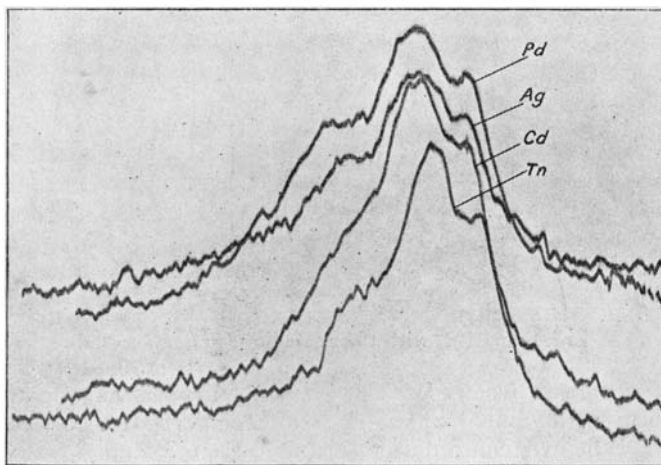
irregularities in the latter curves must be ascribed to some mechanical disturbance.) Fig. 4 gives the  $\beta_1$  curves for Ag

Fig. 2.



Rh  $La_1$  and In  $La_1$  with their satellites (calcite crystal).

Fig. 3.



The  $La_1$  lines of Pd, Ag, Cd, and In, with their satellites (calcite crystal).

and In;  $\beta_1'$  and  $\beta_{1\beta}$  are much less pronounced than the  $\alpha_1$  satellites. No sudden change is here observed for Ag.

Fig. 5 shows  $\alpha_1$  and  $\beta_1$  with their satellites for Zr, taken at two different heights of the plate. On the plates of the elements Mo-Rb taken with a gypsum crystal,  $\alpha_3$  could not

Fig. 4.

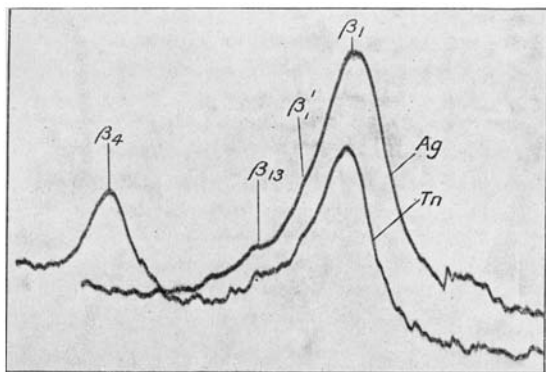
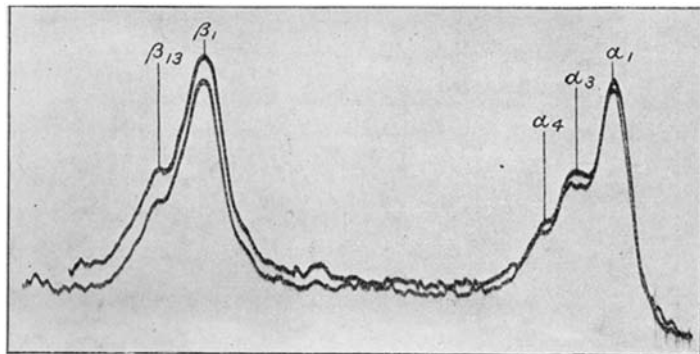
Ag  $L\beta_1$  and In  $L\beta_1$  with their satellites (calcite crystal).

Fig. 5.

Zr  $L\alpha_1$  and  $L\beta_1$  with their satellites (gypsum crystal).

be separated from  $\alpha_1'$ . This gives a somewhat asymmetrical form to this line.  $\alpha_2$  and  $\beta_1'$ , which could be detected easily with the eye, could not be separated from  $\alpha_1$  and  $\beta_1$  with the photometer. Fig. 3 (Pl. XXIII.) gives a reproduction of the  $\alpha_1$ - and  $\beta_1$ -lines of Rb.

The wave-lengths and frequencies of the  $\alpha_1$ - and  $\beta_1$ -satellites are given in Tables VII., VIII., and IX. The wave-lengths of  $\alpha_3$  for Mo-Rb are probably too great, since this line



TABLE VII.

	$\beta_{13}$			$\beta_1'$		
	$\lambda$	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\beta_{13}}}{R}} - \sqrt{\frac{\nu_{\beta_1}}{R}}$	$\lambda$	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\beta_1'}}{R}} - \sqrt{\frac{\nu_{\beta_1}}{R}}$
37 Rb .....	7022.4	129.77	0.032	7041	129.42	0.016
38 Sr .....	6573.4	138.63	32	6590	138.28	17
40 Zr .....	5793.3	157.30	32	5807	156.93	17
41 Nb .....	5449.7	167.21	36	5465	166.76	18
42 Mo .....	5138.4	177.34	35	5150	176.95	20
45 Rh .....	4342.5	209.85	37	4351	209.45	23
46 Pd .....	4117.1	221.33	36	4125	220.91	22
47 Ag .....	3906.9	233.24	39	3914	232.84	26
48 Cd .....	3711.6	245.52	39	3719	245.04	24
49 In .....	3530.4	258.12	40	3539	257.48	20
50 Sn .....	3360.7	271.15	43	3367	270.64	27
51 Sb .....	3202.6	284.54	41	3210	283.91	23

TABLE VIII.

	$\alpha_4$			$\alpha_3$		
	$\lambda$	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\alpha_4}}{R}} - \sqrt{\frac{\nu_{\alpha_1}}{R}}$	$\lambda$	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\alpha_3}}{R}} - \sqrt{\frac{\nu_{\alpha_1}}{R}}$
37 Rb .....	7248.8	125.71	0.042	7271.0	125.33	0.025
38 Sr .....	6797.3	134.06	43	6818.3	133.64	24
40 Zr .....	6013.2	151.54	43	6029.1	151.14	27
41 Nb .....	5671.1	160.68	45	5684.9	160.30	30
42 Mo .....	5356.4	170.13	45	5370.3	169.68	28
45 Rh .....	4558.8	199.89	45	4571.3	199.34	26
46 Pd .....	4330.9	210.41	46	4342.7	209.84	27
47 Ag .....	4119.4	221.21	47	4131.0	220.39	26

TABLE IX.

	$\alpha_1'$		
	$\lambda$	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\alpha_1'}}{R}} - \sqrt{\frac{\nu_{\alpha_1}}{R}}$
45 Rh .....	4564.9	199.62	0.036
46 Pd .....	4336.2	210.15	38
47 Ag .....	4125.4	220.90	36
48 Cd .....	3928.8	231.95	37
49 In .....	3744.7	243.35	40
50 Sn .....	3574.0	254.97	41
51 Sb .....	3413.8	266.94	43
55 Cs .....	2870.8	317.43	47
56 Ba .....	2755.1	330.76	48

could not be separated from  $\alpha_1'$ . The last columns give the difference between the square root of the frequency of  $\alpha_1$  or  $\beta_1$  and that of a satellite. These differences are nearly constant but decrease slowly with decreasing atomic number.

§ 8. Two very remarkable lines are the new lines  $\beta_{11}$  and  $\beta_{12}$ . They may be seen on fig. 2 (Pl. XXIII.). For Ba, Cs, Te, these lines probably do not occur; they could be detected for the first time for Sb. From In down to Mo they are fairly strong lines which could be easily measured under the microscope. They could be detected also for Nb and Zr, although for these elements they nearly coincide with  $\gamma_5$ , which is a much sharper line in this region. For Sr and Rb they are very faint or perhaps they do not occur at all. Apparently these lines have nothing to do with the lines  $\beta_7$ ,  $\beta_8$ ,  $\beta_9$ , and  $\beta_{10}$  which I have previously measured for the heavier elements\*.

On the short wave-length side of  $\gamma_1$  a new line ( $\gamma_7$ ) could be detected. This line is weaker than  $\beta_{11}$  and  $\beta_{12}$  and could be observed as early as Ba. It might be supposed that this line forms a relativity-L-doublet with  $\beta_{11}$  or  $\beta_{12}$ . The differences, however, between the frequency-differences  $\gamma_7 - \beta_{11}$

TABLE X.

	Wave-lengths.			Frequencies.			Differences $\sqrt{\frac{\nu}{R}}$		
	$\beta_{11}$	$\beta_{12}$	$\gamma_7$	$\beta_{11}$	$\beta_{12}$	$\gamma_7$	$\beta_{11} - \beta_2$	$\beta_{12} - \beta_2$	$\gamma_7 - \gamma_1$
41 Nb.....	5161		.....	176.56		.....	0.081		
42 Mo.....	4859.7	4841.7	.....	187.52	188.21	.....	0.071	0.095	
45 Rh.....	4084.8	4072.5	5896.8	223.09	223.76	233.85	68	91	0.076
46 Pd.....	3867.6	3856.7	3676	235.61	236.28	247.87	65	86	86
47 Ag.....	3663.3	3653.7	3479.5	248.76	249.40	261.89	66	87	85
48 Cd.....	3477.5	3468.4	3302	262.05	262.73	275.98	67	88	66
49 In.....	3304.0	3295.9	3125	275.81	276.48	291.57	68	89	81
50 Sn.....	3142.6	3134.7	2968.5	289.97	290.69	306.98	69	90	78
51 Sb.....	2993.4	2985.8	.....	304.43	305.20	.....	67	89	
56 Ba.....	.....		2218	.....		410.82	.....		84

or  $\gamma_7 - \beta_{12}$  and the  $\beta_1 - \alpha_2$  doublet are in most cases greater than the limits of experimental error. As is seen from the last columns of Table X.,  $\beta_{11}$  and  $\beta_{12}$  form a screening-doublet, also  $\beta_{12}$  and  $\beta_2$ . The same is true for  $\gamma_7$  and  $\gamma_1$ . Some other

\* (Note added during the proof.)—From a paper recently published by Mr. Wentzel (*Annalen der Physik*, lxxvi. p. 437 (1921)), however, we are inclined to suppose that the lines  $\beta_{11}$  and  $\beta_{12}$  might be connected with the line  $\beta_3$  of the heavier elements.

new lines, which possibly may exist for some elements (one between  $\beta_6$  and  $\beta_2$  and one between  $\alpha_1$  and  $\beta_1$ ) will be studied in connexion with an investigation of the elements Ta-Ba and Rb-Cu.

§ 9. Tables XI. and XII. give the characteristic absorption discontinuities in the L-region for Ba, Cs and Ag, and the

TABLE XI.  
Wave-lengths.

	$L_1$	$\beta_2$	$L_2$	$\gamma_1$	$L_3$	$\gamma_3$	$\gamma_4$
56 Ba .....	2356·7 (2348)	2399·3	2198 (2194)	2236·60	(2063)	2129·5	2071·5
55 Cs .....	2466 (2459)	2506·4	(2299)	2342·52	(2157)	2227·1	2169·4
47 Ag .....	3684·4	3693·83	3504·7	3514·85	3260·5	3299·7	

TABLE XII.  
Frequencies  $\frac{\nu}{R}$ .

	$L_1$	$\beta_2$	$L_2$	$\gamma_1$	$L_3$	$\gamma_3$	$\gamma_4$
56 Ba .....	386·67 (388·1)	379·80	414·67 (415·3)	407·42	(441·7)	427·92	439·91
55 Cs .....	369·50 (370·6)	363·58	(396·4)	389·00	(422·5)	409·18	420·11
47 Ag ... ..	247·33	246·69	260·01	259·15	279·48	276·17	

shortest wave-lengths of the emission spectrum which belong to each of them. The absorption wave-lengths of Ba and Cs were accidentally found on the same plates on which the emission spectra were taken. They were obviously due to the selective absorption of the heterogeneous radiation of the copper anticathode, in the Ba and Cs salt used on the anticathode. Hertz's values \* are added in parenthesis. They differ from ours by about 7 X.U. in the mean. The absorption spectrum of Ag is determined with a gypsum crystal,

\* *Zeitschr. für Physik*, iii. p. 19 (1920).

making use of the increased absorption in the silver of the photographic plate. For this region of wave-lengths, especially if the rather faint discontinuity  $L_3$  is to be photographed, it is desirable to exclude totally the spectra of higher order. For this reason the maximum tension on the tube should be not more than twice the critical exciting tension. Therefore in taking the  $L_3$  absorption the mean tension on the tube, as read with the Braun electrometer, was fixed at about 5400 volts. As a fairly large current was used (50 m.a.) a very good plate was obtained in four hours. The discontinuities  $L_1$  and  $L_2$  were both found on one plate after an exposure of about three hours.

§ 10. As has been stated in Part I. § 6, I have tried to obtain some experimental information about the existence of the line  $L_3L_1$ , *i. e.*, the transition  $L_1-L_3$ . For tungsten this line should lie in the M-region, between the lines  $M\beta$  and  $M\gamma$  which have been measured by Stenström. We may calculate the wave-length of this line for W from the following data. The frequency of the line  $L_3L_1$  is equal to the frequency difference of the absorption discontinuities  $L_1^*$  and  $L_3^*$ . These have been measured by Duane and Patterson. They found 1213.6 and 1024 X.U. respectively. From this we find for the frequency difference  $L_3-L_1$  139.07 in multiples of the Rydberg number, from which we may calculate the required wave-length as 6553 X.U. Taking into account the limits of experimental error given by Duane and Patterson, we find that the error in the wave-length in question must be less than 3 per cent. We may calculate the same wave-length with somewhat greater accuracy in the following way. From diagram I. we see that the following relation must hold between the frequencies :

$$L\beta_2 + (L_3 - L_1) = L\beta_3 + M\gamma.$$

Putting into this formula the frequencies measured by Siegbahn for  $L\beta_2$  and  $L\beta_3$  and the value for  $M\gamma$  measured by Stenström, we find for the same frequency difference  $L_3-L_1$  139.05, giving the same wave-length 6553 X.U. Taking into account the limits of error of the  $M\gamma$  line and of the L-lines, which can be measured with greater accuracy than the discontinuities, we find that the error in this value is less than 0.3 per cent.

We should expect that this line would only arise if an electron is removed from the L-shell in such a way that the

\* By these symbols the levels as well as the absorption-discontinuities corresponding to these levels are denoted.

remaining electrons form a configuration corresponding to a  $L_3$ -level. Using a tungsten anticathode, the tension on the tube must according to Einstein's relation be more than 12000 volt. As the expected line might not be very strong, it is desirable to work with a tension which is at least twice as great. The tube was therefore driven with the maximum tension which could be obtained. With this tension a very strong L-spectrum in the first order was obtained in ten minutes. As analysing crystal a gypsum crystal was used; the time of exposure was one hour. Besides the lines  $M\beta$  and  $M\gamma$  several other lines which could not be identified at first sight were found on the plate. Now the lines in the M-series have a very typical structure, being rather diffuse and broadened on the short wave-length side. Therefore no doubt could arise as to the identification of these lines. As to the new line  $L_3L_1$ , however, we should expect that it would be distinctly different, and especially that it would be fairly sharp for W. For a right interpretation of the plate it was therefore desirable to exclude all the lines which appeared on the plate in higher order. This could be done in the following simple way. A new plate was exposed under the same conditions. Half of this plate was covered with an aluminium sheet of  $7\mu$  thickness. By this sheet wave-lengths of more than 6000 X.U. are totally absorbed. Fig. 4 (Pl. XXIII.) gives a reproduction of the spectrum obtained in this way. Most of the lines are not appreciably absorbed by the aluminium, but the lines  $M\beta$  and  $M\gamma$  have been totally absorbed. Copper and tungsten lines were found in 4th and 5th order. Between the  $L\beta_2$  and  $L\beta_1$  line of W the line  $L\beta_3$  was seen on the plate also in 5th order. This line comes from the  $L_3$  level. As  $L\beta_3$  is not a very strong line for W, it was very faint on the plate, and it cannot be seen on the reproduction. Further the Ca K absorption line in the second order may be seen as a dark line quite near the  $M\gamma$  line of W. This line is due to the selective absorption in the Ca of the crystal\*. From the appearance of the tungsten lines in such high order we may conclude that the experimental conditions were such as to excite the  $L_3$  level quite sufficiently to give rise to the line  $L_2L_1$ , unless this transition is very improbable. The place where we should expect the line is marked with a  $\uparrow$  on the reproduction. In the neighbourhood of this place only one very faint line was seen on the plate. This line, however, was not appreciably absorbed

\* In general, absorption discontinuities are obtained in a very easy manner if the absorbing element forms part of the analysing crystal.

by the aluminium sheet (the reproduction does not give a very good impression of this fact). It is quite possible that it is the tungsten  $L\gamma_1$  in the 6th order.

In the same way I was able to show that the transition  $L_2L_1$  does not exist; this, however, is what we should already expect from the  $a-b$  rule.

### PART III.

#### *Discussion of Results.*

§ 1. As has been stated in Part II. § 1, the object of this paper is to compare the changes in the characteristic X-ray spectrum as the atomic number decreases with the changes in the structure of the atom as given by Bohr's theory, of which a brief account has been given in Part I. In order to do this, we will deal with the diagrams of the energy levels of the inert gases, which are based upon measurements of the elements preceding or following the inert gases in the periodic table. For niton the diagram has already been given in Part I. of this paper.

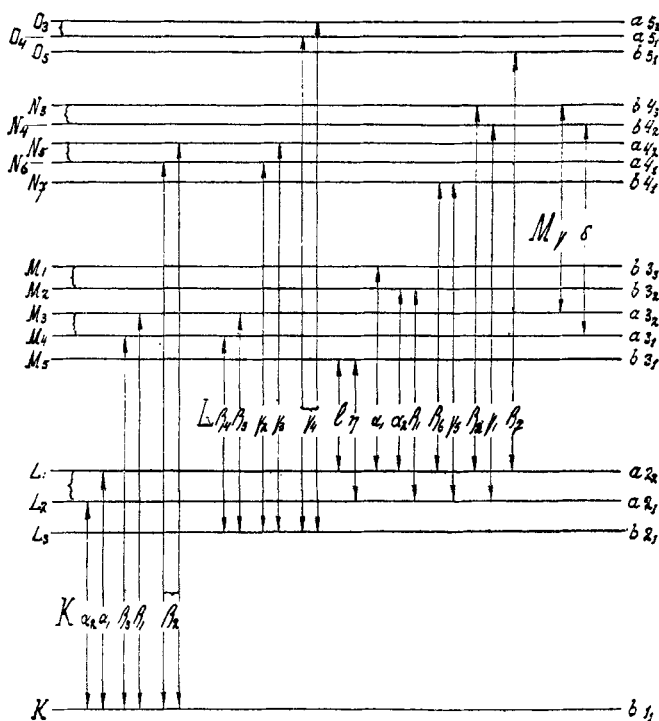
As regards this diagram, the following remarks may here be made. Only the lines belonging to the L-series have been systematically investigated for the elements in the neighbourhood of niton\*. The complexity of the line  $L_4$  which is suggested by analogy with the appearance of the pairs of lines  $L\beta_3-L\beta_4$  and  $L\gamma_3-L\gamma_2$  could not be proved experimentally, because of the small difference of energy between the levels  $O_3$  and  $O_4$ . The energy-difference between the levels  $O_1$  and  $O_2$  could not be obtained experimentally for the same reason. As yet there is no experimental evidence for the existence of the three P-levels inserted in the diagram. Perhaps the line 568.9 found by Dauvillier† in the spectrum of U represents a transition  $P_1 \rightarrow L_3$ . But since in general it is very dangerous to draw conclusions from the measurements of only one element, it seems better to postpone a discussion of the P-levels until a thorough investigation of the X-ray spectrum of the radioactive elements has been made. The K-spectrum of the elements in the region of high atomic number has been measured with sufficient accuracy for W only. But also different measurements of the K-series, made by several authors for elements of lower atomic number, support the arrangement of lines

\* See D. Coster, *Zeitschrift f. Physik*, iv. p. 178 (1921) and I. and II. In I. and II. the arguments are given in favour of the arrangement of the lines in the diagram 1.

† *Comptes Rendus*, clxii. p. 1350 (1921).

given in the diagram. The line  $K\beta_3$  has been detected by de Broglie \* only for the elements tungsten and rhodium. The frequency-difference found by de Broglie for the lines  $K\beta_1$  and  $K\beta_3$  agrees very well with that for the lines  $L\beta_3$  and  $L\beta_4$ . The complexity of the line  $K\beta_2$  could not be observed but is suggested by analogy with the pairs of lines  $K\beta_1$ - $K\beta_3$ ,  $L\beta_3$ - $L\beta_4$ , and  $L\gamma_3$ - $L\gamma_2$ . In any case it is probable that most of the energy of this line is due to the transition  $N_5 \rightarrow K$ . The lines in the M-region have been measured by Stenström and Karcher for different elements. It is highly probable that there exist further transitions in this region, other than those detected by Stenström.

Diagram II.—XENON.

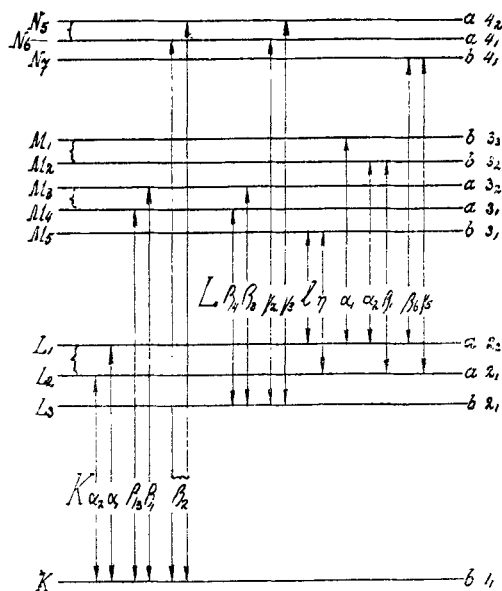


§ 2. The diagrams II. and III. for the inert gases, xenon and krypton, are derived from the experimental results given in Part II. of this paper. As for the L-series we see from the tables in Part II. that all the lines inserted in the

\* *Comptes Rendus*, clxx. p. 1053 (1920) and clxx. p. 1245 (1920).

diagrams were actually measured for the elements with higher atomic numbers than xenon or krypton respectively. The single exception is the line  $L\beta_7$ . Though there are some indications that this line has been found for Ba and Cs, its identification is not quite certain. An investigation of the rare-earth metals, as yet unfinished, will possibly settle the question. The lines  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$  and  $\beta_2$  of the K-series have been measured by several authors for different elements

Diagram III.—KRYPTON.



in this region; the line  $\beta_3$ , which lies at a very small wave-length distance from  $\beta_1$ , has been measured only for Rh, by de Broglie, as stated above. The lines  $M\gamma$  and  $M\delta$  have only been inserted in the xenon diagram for the sake of completeness. They have only been found for the elements U, Th, Bi, Pb, Au, and Pt\* and they have not yet been studied systematically. It will be very difficult to measure them in this region, as even for Ba they should have wave-lengths of about 13000 and 12000 X.U. respectively. The largest wave-length hitherto measured with the aid of crystal reflexion is the line  $L\alpha$  for copper (13309 X.U.).

\* See Stenström, Dissertation, Lund, 1919; Karcher, Phys. Rev. II. xv. p. 285 (1920). These lines have been called  $M\gamma_1$  and  $M\gamma_2$  by Karcher.



On the other hand, we may see from a comparison of the diagrams I. and II. and the tables of Part II. that the lines, which according to the diagrams should fall out between niton and xenon (*i. e.* in the L-series  $\beta_5$  and  $\gamma_6$ ) were actually not found for the elements in the neighbourhood of xenon. In the same way we may see from the diagrams II. and III. compared with the tables of Part II. that the lines  $L\gamma_4$ ,  $L\beta_2$  and  $L\gamma_1$ , which according to the diagrams should fall out between xenon and krypton, were not observed for Rb and Sr.

§ 3. We will now proceed to a closer comparison of Bohr's theory of the development of groups of electrons in the atom with the experimental results as regards the first appearance of the lines in the X-ray spectra.

Starting from niton the lines which first disappear are  $\beta_5$  and  $\gamma_6$ . For the elements in the neighbourhood of niton both the lines  $\beta_5$  and  $\gamma_6$  are fairly strong; in the neighbourhood of the Pt metals their intensity decreases very appreciably; for W, and especially for Ta, which elements both gave very good plates, they belong to the faintest known lines in the X-ray spectra. In the rare-earth metals and for Ba and Cs not the slightest trace of these lines has as yet been found. On several plates, however, I found white lines on a dark background in the place where we should expect to find  $\beta_5$  or  $\gamma_6$ . As mentioned in II. § 9, these white lines are the characteristic absorption lines\*  $L_1$  and  $L_2$  due to the absorption of the Cu radiation in the salts which were used upon the anticathode. Though even this is not an absolute proof† that the lines  $\beta_5$  and  $\gamma_6$  do not exist, it seems on the whole to be very probable that these lines disappear for the rare-earth metals. This is in agreement with the theory. According to this  $5_3$  orbits probably appear for the first time for La (57)‡, but in the rare earths the electrons moving in these orbits are very loosely bound in the form of valency electrons, which are hardly present in the salts used in the experiments. It is only in Ta (73) and the following elements, that a  $5_3$  electron can first be expected to be present under the conditions of the experiments and to correspond to a binding sufficiently strong for the  $5_3$  level to be detected.

\* On carefully exposed photographs of an absorption edge usually a white line may be seen. This white line implies that the electron "prefers" the absorption of a frequency which is just able to bring it outside the atom.

† In studying the  $L_1$  and  $L_2$  absorption edges of tungsten, Duane and Patterson have also made use of the absorption in the tungsten of the anticathode. (See Proc. Nat. Ac. Sci. Washington, Sept. 1920.)

‡ Compare N. Bohr, *Zeitschr. f. Physik*, ix. p. 1 (1922).

We should expect the line  $M\epsilon$  to disappear at the same time as the lines  $L\beta_5$  and  $L\gamma_6$ , as the existence of this line is also bound to a  $5_3$  subgroup of electrons. This line has as yet not been studied systematically. It has been measured by Stenström \* for U and Th and by Karcher † for the elements Bi, Au, and Pt.

§ 4. The appearance of the lines  $M\alpha_1$ ,  $M\alpha_2$ , and  $M\beta$  is connected with the existence of  $4_4$  electrons in the N-shell. According to Bohr, these electrons occur for the first time in the rare earths. For the elements Dy (66) there must already be electrons present in  $4_4$  orbits, as the appearance of the lines  $M\alpha$  ( $\alpha_1$  and  $\alpha_2$  could not be separated for the elements with lower atomic number than Tl) and  $M\beta$  has been established by Stenström for this element. The wave-lengths of these lines are respectively 9509 and 9313 X.U. It would be of interest to try to find these lines also for elements with lower atomic number than Dy.

§ 5 The existence of the line  $L\gamma_4$  depends on the presence of  $5_2$  electrons in the O-shell. As pointed out to me by Professor Bohr, it appears from comparison with the optical spectra of Cd and In, that  $5_2$  orbits appear for the first time in the neutral atom of the latter element. The experimental results seem to indicate that for the line  $\gamma_4$  there are certain complications. The very striking changes in the intensities of the pairs of lines  $\beta_5-\gamma_6$  (see Part III. § 3) and  $\beta_2-\gamma_1$  (see Part III. § 6) cannot be questioned. But usually it is very difficult to make any definite assertions concerning changes of the relative intensity of the lines with different elements, as we are not certain that they have been exposed under the same conditions. However, there is evidently a considerable change in the intensity of the line  $L\gamma_4$  between the elements Sb and Sn. Down to In (49), this line could be measured but here it had become very faint. For Cd, where we according to Bohr should expect  $\gamma_4$  to disappear, no certain information about this line could be obtained from the experiments. Extrapolating according to Moseley's law we find for the wave-length of  $\gamma_4$  for Cd about 3081 X.U., which is at the same time about twice the wave-length of the copper  $K\alpha_2$  line. Using an X-ray tube of brass and working with a fairly high tension which appeared to be necessary in photographing the very weak lines, it is impossible to avoid wholly the characteristic Cu-radiation. Actually the copper

\* Stenström, Dissertation, Lund, 1919.

† Karcher, Phys. Rev. II. xv. p. 285 (1920). The line  $M\epsilon$  has been called  $M\gamma_3$  by Karcher.

$K\alpha_1$  and  $K\alpha_2$  lines though very faint were in second order observed on the plate. From a thorough examination of the plates, however, we are inclined to conclude that the line  $\gamma_4$  does not exist for Cd or at any rate must be still weaker than in the case of In. For the next element (Ag) we are troubled by the increased absorption in the photographic plate ( $L_3$  discontinuity), so that for this element nothing can be stated about the existence of  $\gamma_4$ . A complication showed in the photographs of the Pd (46) and Rh (45) spectra. Besides a very faint line at 3450 X.U. for Pd and at 3651 X.U. for Rh, which might be considered to be  $\gamma_4$ , another line of the same appearance was found for both elements. (For Pd  $\lambda=3433$  and for Rh  $\lambda=3631$ .) These lines, however, have shorter wave-lengths than the extrapolated values of the respective  $L_3$  discontinuities.

§ 6. The lines  $\beta_2$  and  $\gamma_1$  depend on the existence of the  $4_3$  electrons in the N-shell, which electrons according to Bohr are found for the first time in the neutral atom of Y (39). Relatively to the other lines of the L-spectrum  $\beta_2$  and  $\gamma_1$  have their ordinary intensity as far down as Mo. For Nb however they are considerably weaker compared with the other lines, for Zr they are both very faint. For Y,  $\beta_2$  and  $\gamma_1$  were not visible, but here the plates were not especially good. For Sr and Rb, for which the plates were quite good,  $\gamma_1$  had wholly disappeared. If we extrapolate  $\beta_2$  according to Moseley's law, this line almost coincides with  $\beta_4$  in the case of Sr, while for Rb it should lie on the long-wave-length side of  $\beta_4$ . A faint line was actually found in this place. On different plates, however (taken with different Rb salts), the relative intensity of this line seemed to show considerable variations. This could easily be understood if the line were due to some other element. Thus it seems to be most probable that  $\beta_2$  disappears at the same time as  $\gamma_1$  between Zr (40) and Sr (38). The lines  $M\gamma$  and  $M\delta$  should disappear at the same time as  $L\beta_2$  and  $L\gamma_1$ . As these lines must have a wave-length of about 37 A.U. for Nb, they cannot be studied in this region in the present state of spectroscopy.

§ 7. As for the line  $L\beta_7$  it was not possible to identify it in the region under consideration. This line is also for the heaviest elements a rather faint line. For Pt and the elements with higher atomic number it seems to be a double line. This is difficult to explain in the light of our present knowledge of the X-ray spectrum. As has also been observed by Dauvillier, it is a single line for W, and I was able to

observe the same thing for Ta. It will be very difficult to investigate  $\beta_7$  in the region Ba-Rb, as it must coincide for several elements with  $\beta_{11}$  or  $\beta_{12}$  (see Part II. § 8). According to Bohr's theory we must expect that this line may perhaps occur as early as Rb, as for this element 5<sub>1</sub> electrons appear for the first time.

§ 8. It is a very important feature of Bohr's theory of atomic structure, that within the region of the rare-earth metals the N-shell is developed from a shell containing 3 subgroups of 6 electrons each with the quantum symbols 4<sub>1</sub>, 4<sub>2</sub>, 4<sub>3</sub>, into a shell containing 4 subgroups of 8 electrons each with the quantum symbols 4<sub>1</sub>, 4<sub>2</sub>, 4<sub>3</sub>, and 4<sub>4</sub> respectively. In favour of this view the following experimental facts may be considered. As is seen from the diagrams the energy difference between the N<sub>3</sub> level and the region outside the atom is given by the frequency difference of the  $L\beta_2$  line and the  $L_1$  discontinuity. This difference corresponds to a volt difference of 420 for Bi (83), 170 for W (74), 90 for Ba (56), and less than 10 for Ag (47). This means that in the region from Ba to W the binding of the 4<sub>3</sub> electrons increases much more slowly than in the regions from Ag to Ba and from W to Bi. This is just what we should expect from theoretical considerations. Within the region of the rare earths not only do the three subgroups of 4<sub>1</sub>, 4<sub>2</sub>, and 4<sub>3</sub> electrons increase by two electrons each, but also a new subgroup of eight 4<sub>4</sub> electrons is built up. As part of the orbits of the 4<sub>3</sub> electrons lies outside the orbits of the 4<sub>4</sub> electrons, and as a 4<sub>3</sub> electron during its revolution spends most of its time in this part where its velocity is smallest, the 4<sub>4</sub> electrons must be assumed to contribute appreciably to the total screening effect on the 4<sub>3</sub> electrons.

New measurements of the absorption discontinuities of the elements Ba-Sb which recently have been made by Mr. Lindsay in this laboratory give also a strong support to Bohr's theory. From the values of the  $L_2$ -discontinuities of these elements which Mr. Lindsay has kindly put at my disposal and my values of the wave-lengths of the line  $L\gamma_4$  for the same elements, we are able to calculate the energy difference between the C<sub>3</sub>-level and the outside of the atom. This difference, the value of which most probably corresponds to 30-40 volts for W (74), is still 30-25 volts for Ba (56) and Cs (55), but decreases to less than 10 volts for Te (52) and less than 6 volts for Sb (51). From this it appears very clearly that the outmost shells of the atom (O- and P-shell) do not change very much for the elements from W

to Ba, but that these shells materially change for the elements with lower atomic number than Ba.

My researches in the L-series of the rare earths above quoted seem also to offer strong arguments in favour of Bohr's theory. The lines in the L-series, which are connected with N-levels, are :  $\beta_2$ ,  $\gamma_1$ ,  $\gamma_3$ ,  $\gamma_2$ ,  $\beta_6$  and  $\gamma_5$ . Now for some of these lines remarkable anomalies of a new type were found. For both the lines  $\beta_2$  and  $\gamma_1$  rather faint satellites were observed at some distance on the long wave-length side \*. Though we cannot yet account for this phenomenon, we should according to the theory expect some irregularities just in this region, accompanying the gradual transformation of the N-shell during the completion of the electronic configuration of 4-quantum orbits. For the lines  $\gamma_2$  and  $\gamma_3$  an analogous phenomenon was observed. As these lines lie very near to one another, it is somewhat difficult to interpret the photographs. The lines  $\beta_6$  and  $\gamma_5$  however, which are not very strong, seem to show no irregularities at all. More experimental data will soon be published.

§ 9. It is a fact well known to every one who has worked some time in X-ray spectroscopy, that on nearly every photograph taken of the X-ray spectrum of a single element there are found some lines which cannot be classified. It is probable that in most cases these lines are due to some other element, and very often this may actually be proved. The lines in the K-series of elements of higher atomic number, however, have not yet systematically been measured. If these lines appear in higher order on the plate, the identification will be impossible.

On the other hand, we must reckon with the possibility that some of the "unknown" lines really belong to the investigated element in question. In this case we must assume that the appearance of these non-systematic lines depends on special conditions, which are only fulfilled for one or very few elements. It appears from these considerations that conclusions which are based upon measurements of only one element have no great value for other elements.

There are several lines which cannot be inserted in such simple diagrams as I, II, and III, but which are found for

\* The other lines which cannot be inserted in a simple diagram lie always on the short wave-length side of a line with which they seem to be in some way connected.

several elements and can be classified according to Moseley's law. In the L-series these are the line  $\beta_8$ , which has been found on the short wave-length side of  $\beta_2$  for a great number of the elements Ta-U \*, and the lines which are dealt with in Part II. §§ 7 and 8 of this paper. In the K-series of the lighter elements similar lines have been found by Hjalmar †. Most of these non-diagram lines seem to disappear again for elements with higher atomic number. Another characteristic feature of these lines is that they always lie on the short wave-length side of a very strong diagram line with which they seem to be connected in some way ‡. Usually their frequency difference from this line is roughly proportional to the atomic number of the emitting element.

In order to explain the appearance of the non-diagram lines we might suppose that under certain conditions a subgroup of electrons from which one electron has been removed may give rise to more energy-levels than have been inserted in the diagrams. If this really is the case, these new levels must evidently play a different part from those which appear in the diagrams. As yet they have not been detected in the absorption spectra § : furthermore, they each seem to be connected with one line only and they usually disappear again for atoms of higher atomic number.

Again, part of these new levels might be attributed to a more complicated excitation of the atom. Suppose that when a high-speed  $\beta$ -particle collides with the atom, under certain conditions two electrons are removed at the same time. If then an electron were to fall back into the atom, this transition would give rise to a new line in the X-ray spectrum which would lie on the short wave-length side of a diagram line connected with the removal of only one electron. In this case we should expect to find a great difference between a characteristic X-ray spectrum excited by the impact of high-speed  $\beta$ -particles (primary radiation) and a spectrum excited by absorption of X-rays (secondary radiation). For the latter we should expect that no such non-diagram lines would appear. As some of these lines are quite strong,

\* *Zeitschrift f. Physik*, II. p. 191.

† *Zeitschrift f. Physik*, i. p. 439 (1920).

‡ The new lines recently detected for the rare-earth metals (see Part III. § 8) are an exception to this rule.

§ In this connexion it may be of interest to state that the structure found by Hertz (*Zeitschr. f. Phys.* iii. p. 19 (1920)) for the  $L_1$ - and  $L_2$ -discontinuities seems to be not directly connected with that which I have found for the  $L-\alpha$  and  $L-\beta_1$  lines respectively.

we hope it may be possible to settle this question by experiment\*.

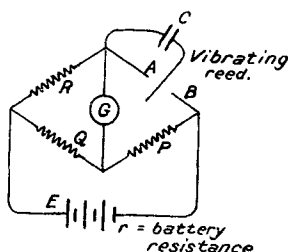
It gives me great pleasure to express my best thanks to Prof. M. Siegbahn of Lund and Prof. N. Bohr of Copenhagen, for the great interest they have shown in my work. I am also much indebted to my friend Mr. H. A. Kramers for his valuable help in reading the manuscript.

CXVI. *On a Development of Maxwell's Capacity Bridge.*

By V. A. BAILEY, M.A., *The Queen's College, Oxford*†.

IT is well known that one of the most accurate and convenient methods for determining Capacity in E.M. Units is that devised by Clerk Maxwell, shown in fig. 1.

Fig. 1.



One side of the condenser is made to touch A and B alternately  $n$  times per second by means of an electrically-driven tuning-fork or (as in the experiments of Thompson and Searle) by means of a rotating commutator. The galvanometer shows no deflexion when the following relation holds:—

$$nC = \frac{Q[(P+r)(Q+R+G) + Q(R+G)]}{[R(P+Q) + r(Q+R)][P(Q+R+G) + QG]},$$

$P$ ,  $Q$ ,  $R$ , and  $r$  being the resistances of the conductors as indicated in the diagram, and  $G$  the capacity of the condenser.

\* (Note added during the proof.)—In this connexion attention may be called to a very interesting paper recently published by Mr. Wentzel (*Annalen der Physik*, lxvi. p. 937 (1921)). In this paper Mr. Wentzel clearly showed that most of the non-diagram lines arise in an atom which has lost more than one electron. I intend to deal in particular with the non-diagram lines of the L-series in another paper.

† Communicated by Prof. J. S. Townsend, F.R.S.

FIG. 1.

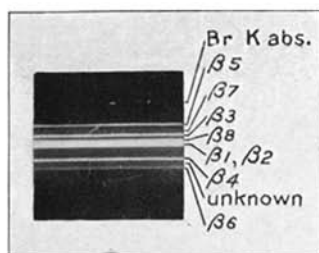
**Pb  $L\beta$**  (rocksalt crystal).

FIG. 3.

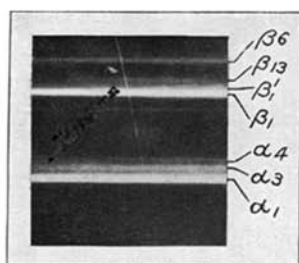
**Rb  $L\alpha_1$  and  $L\beta_1$**  with their satellites (gypsum crystal).

FIG. 2.

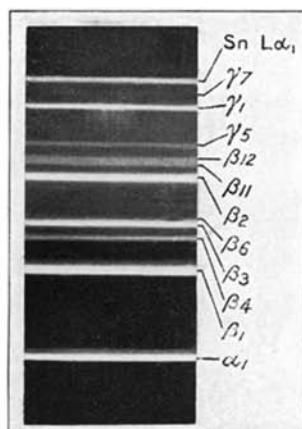
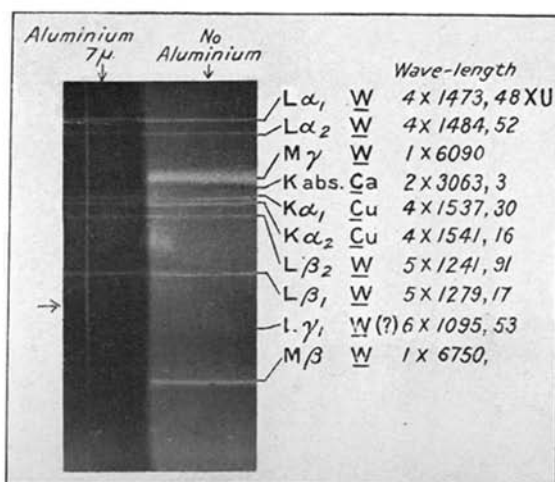
**Rh L-spectrum** (gypsum crystal).

FIG. 4.

**W L and M spectrum** (gypsum crystal).