

und wird in Kurve I veranschaulicht. Herr R. N. Ghosh hat im hiesigen Laboratorium die Abhängigkeit der Ionisierungsspannungen von der äusseren Struktur ausführlich studiert und er kommt zum Schlusse, dass sie mit zunehmender Anzahl der Gruppen-elektronen immer zunehmen. Wenn ein Niveau ganz besetzt ist, erreicht die Ionisierungsspannung ein Maximum. Wenn es eine statische $M_{32} M_{33}$ -Spaltung gibt, muss die Ionisierungsspannung bei Erfüllung der M_{32} -Niveau, also bei Cr oder Mn , ein Maximum erreichen. Zur Illustration fügen wir die folgende Kurve bei, die der Arbeit von R. N. Ghosh entnommen ist.

Es erhellt aus dieser Kurve, dass für Elemente wie O und Fl , für welche das Niveau ungefähr voll besetzt ist, die Ionisierungsspannung sehr gross ist; und diese Elemente nehmen teichter ein oder zwei neue Elektronen auf, als dass sie eines abgeben. Sie haben die negativen Valenzen zwei und eins. Zu positiver Valenz sind sie unfähig. Bei Ne ist die Schale ganz erfüllt, also es ist sehr schwer von Ne ein Elektron abzureissen oder anzuregen, und noch schwerer, ein neues Elektron dort anzuheften. Es ist weder zu positiver noch auch zu negativer Valenz fähig.

In allen Elementen, von B bis Fl , haben wir optische Terme, die zur Kombination

$$L_1(x+1)L_2 \text{ (normal } 2L_1xL_2\text{)}$$

gehören. Das L_1 -Elektron kann leicht zu L_2 übergehen.

Übergangsgruppe II, III, IV. Ihr Aufbau ist ganz analog der Gruppe Sc bis N . Aber die optische Analyse zeigt kleine Unterschiede. In Gruppe I ist die Struktur des äusseren Niveaus

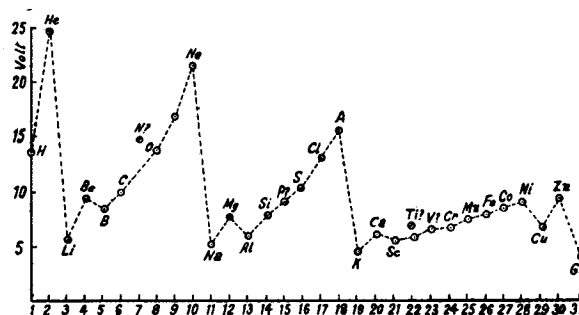


Fig. 4. Ionisierungsspannungs-Kurve.

$$\left. \begin{matrix} xM_2N_1 \\ (x-1)M_32N_1 \end{matrix} \right\}$$

In Gruppe II ist es bei einigen Elementen

$$\left. \begin{matrix} (x+1)M_3 \\ xM_3N_1 \end{matrix} \right\}$$

Vergleicht man z. B. Ni und Pd

$$\left. \begin{matrix} Ni & \dots & 8M_32N_1 \\ Ni & \dots & 9M_3N_1 \end{matrix} \right\} \quad \left. \begin{matrix} Pd & \dots & 9N_3O_1 \\ Pd & \dots & 10N_3 \end{matrix} \right\}$$

Ag^+ ist palladiumähnlich, der tiefstliegende Term rührt von $10 N_3$ her, daher überschreitet für Ag der normale $10 N_3O_1$ in seinem Energiewert das $9N_32O_1$, wenn es existiert, bedeutend. Daher ist Ag gegen Cu immer einwertig.

Auch für die seltenen Erden und die Übergangsgruppe III kann man Strukturen angeben; aber die Untersuchung ihrer optischen Spektren ist nur teilweise durchgeführt, und deshalb sind die Strukturen hier nicht gegeben.

Allahabad (Indien), 7. April 1927.

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38. ON THE DETAILED EXPLANATION OF SPECTRA OF THE METALS OF THE SECOND GROUP*

(*Phil. Mag., Sr. VII, 3, 1265, 1927*)

The explanation of the spectra of elements is now making very rapid strides, thanks to the work on the arrangement of electrons inside the atom on the one hand, and development of the principles of non-mechanical vector addition of quantum numbers on the other hand, which we owe to Landé, Russell, Pauli, Heisenberg, Hund¹, and others. The latter authors have so far confined their attention to the fundamental levels of the atom, though in some papers the higher levels have been accounted for on similar lines. In the present paper, an attempt has been made to show that these principles can be extended for finding out all

the higher terms, and in the case of metals of the second group all details of their spectra are explained in a very satisfactory way. The following is a brief sketch of the method of working:—In accordance with Pauli's Principle, we assign to each electron the characteristics of a doublet spectrum. Applied to alkalis, the explanation of the spectrum is very easy. The vibrating electron always comes after a sublevel has been completely closed, hence the atomic residue contributes nothing towards the resultant spectrum. The electron may be supposed to run through all the higher levels, beginning from X_1 . We thus get 2S , 2P , 2D , ... terms,—i.e. a completely developed doublet spectrum. The higher terms arise when the electrons run through the possible higher levels. In the case of alkaline

* Communicated by the Author.

¹ For a complete bibliography, see a paper by Otto Laporte, *Journ. Opt. Soc. Amer.*, July, 1926.

earths, there are two outermost electrons. In the normal case, both are in some X_1 -level. But when the atom is excited, one may be supposed to be at rest; the other runs through all the higher levels. The spectrum observed is due to the combination of the orbits of these two electrons. The rules for combination of orbits were first given by Pauli and developed by Hund and Heisenberg. For the sake of lucidity, I have attached a complete structure diagram. The rules of addition of quantum numbers are also summarized below. It may be added that I claim no originality in this paper except the method of representation, which I have found to be very convenient.

Principles of Orbit Combination

The principles which have so far been developed may be thus briefly summarized:—

Each spectral term may be denoted by the symbol n^r_{kj} (Landé), where r denotes the multiplicity $r=(1, 2, 3, \dots$ for singlets, doublets, triplets, etc.), k =azimuthal quantum number (1, 2, 3, ... for s, p, d, f, \dots), j =inner quantum number which is the vector sum of r and k . But for purposes of addition, we do not use r, k as they occur above, but have to use certain associated numbers. Different authors use different symbols with different values: thus Landé uses R, K, J ; Sommerfeld uses j_s, j_a, j ; and Pauli uses $[i, j, k]$. A comparison between the different systems of

symbols is given in a recent paper by Otto Laporte, who finds that the Sommerfeld system is superior to the other two. In the following we adopt the Sommerfeld systems with a slight change. We shall write

i_r , in place of Sommerfeld's j_s ,

i_k , in place of Sommerfeld's j_a

i_j , to denote the effective inner quantum number.

Thus

$i_r=0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ for singlets, doublets, triplets, etc.

$i_k=k-1, 0, 1, 2, 3$, for s, p, d, f, \dots

i_j is calculated from the rule:—

i_j =Vector sum of i_k and i_r in the quantum sense—

i.e. it must have all successive whole or half-numbered values lying between $|i_r+i_k|$ and

$|i_r-i_k|$.

For purposes of description, Landé's notation n^r_{kj} may be retained.

Table I. contains a full chart of (i_r, i_j, i_k) values for different systems.

The corresponding magnetic quantum number $i_m = \pm i_j, \pm i_j-1, \pm i_j-2$, and thus i_m is the vector sum of i_{mr} and i_{mk} , where

$$i_{mr} = \pm i_r, \quad \pm i_r - 1,$$

$$i_{mk} = \pm i_k, \quad \pm i_k - 1.$$

TABLE I

Showing values of i_r, i_k, i_j

| ODD MULTIPLETS | | | | | | | EVEN MULTIPLETS | | | | | | | |
|----------------|---|---|---|---|-----------------------------|---|-----------------|---------------|---------------|---------------|---------------|----------------|-----------------------------|---------|
| i i_k | 0 | 1 | 2 | 3 | 4 | 5 | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | $\frac{9}{2}$ | $\frac{11}{2}$ | i_j i_k | |
| $s = 0$ | 0 | | | | Singlet i_r | 0 | $\frac{1}{2}$ | | | | | | Doublet $i_r = \frac{1}{2}$ | $s = 0$ |
| $p = 1$ | | 1 | | | | | $\frac{1}{2}$ | $\frac{3}{2}$ | | | | | | $p = 1$ |
| $d = 2$ | | | 2 | | | | | $\frac{3}{2}$ | $\frac{5}{2}$ | | | | | $d = 2$ |
| $f = 3$ | | | | 3 | | | | | $\frac{5}{2}$ | $\frac{7}{2}$ | | | | $f = 3$ |
| $s = 0$ | | 1 | | | Triplet $i_r = \frac{3}{2}$ | | | $\frac{3}{2}$ | | | | | Quartet $i_r = \frac{3}{2}$ | $s = 0$ |
| $p = 1$ | 0 | 1 | 2 | | | | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | | | | | $p = 1$ |
| $d = 2$ | | 1 | 2 | 3 | | | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | | | | $d = 2$ |
| $f = 3$ | | | 2 | 3 | 4 | | | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | $\frac{9}{2}$ | | | $f = 3$ |
| $s = 0$ | | | 2 | | Quintet $i_r = \frac{5}{2}$ | | | | $\frac{5}{2}$ | | | | Sextet $i_r = \frac{5}{2}$ | $s = 0$ |
| $p = 1$ | | 1 | 2 | 3 | | | | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | | | | $p = 1$ |
| $d = 2$ | 0 | 1 | 2 | 3 | 4 | | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | $\frac{9}{2}$ | | | $d = 2$ |
| $f = 3$ | | 1 | 2 | 3 | 4 | 5 | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | $\frac{9}{2}$ | $\frac{11}{2}$ | | $f = 3$ |

The change in energy level in weak fields is given by

$$\frac{E}{Oh} = (i_{mr} + i_{mk})g,$$

where

g =Landé's splitting-up factor,

$$O = \text{Larmor's precession factor} = \frac{eH}{4\pi cm}$$

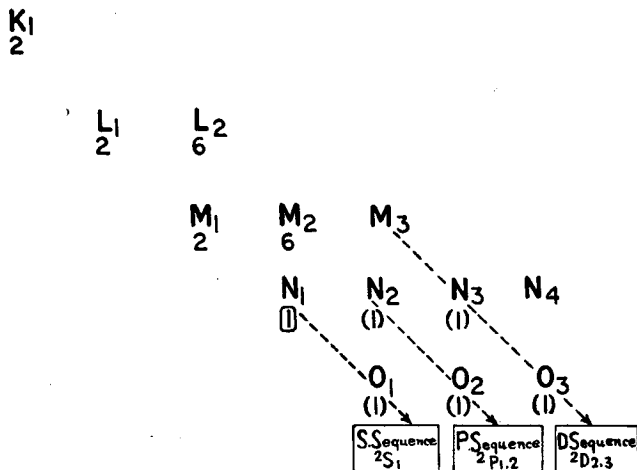
The change in strong fields is given by

$$\frac{E}{Oh} = 2i_{mr} + i_{mk}$$

We shall have no occasion to use the strong field or weak field magnetic quantum numbers².

The doublet spectrum is supposed to be the fundamental spectrum from which all other complicated spectra can be synthesized. When the constitution is such that there is only one electron left after a sublevel is closed, this electron as it runs through the following levels gives rise to the corresponding doublet terms. Thus we have for Potassium:

STRUCTURE DIAGRAM OF POTASSIUM (19)



ORIGIN OF NORMAL TERMS IN THE SPECTRUM OF K

Russell and Saunders' symbol has been used throughout (*vide* Ap. Journ. vol. lxi. p. 38). (1) denotes the running electron.

Thus the alkali spectrum is most simply explained on the assumption that it is due to the movement of the running electron in the successive higher levels.

[RULES OF SYNTHESIS.]

Alkaline Earths.

In the case of the next group of elements, viz. the alkalis, a second electron is added. If we take Mg, we have the constitution:—

$$\text{Mg} = \left(\begin{array}{cccc} \text{K} & \text{L} & \text{M}_1 & \text{M}_2 \dots \\ 2 & 8 & 1, (1) \rightarrow (1) & \end{array} \right)$$

The optical spectrum is due to the two outer electrons shown under M₁. In most cases, one electron remains fixed at M₁, the other runs through the successive levels. The level observed is the vector sum of the levels of these two electrons. As mentioned above, these rules have been developed by Russell, Pauli, Heisenberg, and Hund. Let N^R_{KJ} denote the resultant levels, and let I stand for the Sommerfeld quantum numbers. Then to get a complete knowledge of N^R_{KJ}, we must have a knowledge of the corresponding values of I_K, I_J, I_R. We have

$$I_R = \text{vector sum of } (i_r)_1 \text{ and } (i_r)_2;$$

$$I_K = \text{vector sum of } (i_k)_1 \text{ and } (i_k)_2.$$

The determination of I_J presents the most formidable difficulties. It cannot be defined as the vector sum of (i_j)₁ and (i_j)₂. We have to write out all the possible magnetic levels for each of the components (1) and (2) and then add them, taking one from each group. Thus:—

The magnetic levels of electron (1) are

$$(i_m)_2 = \pm(i_1)_1, \pm(i_1)_1 - 1, \pm(i_1)_1 - 2, \dots$$

The magnetic levels of electron (2) are

$$(i_m)_2 = \pm(i_2)_2, \pm(i_2)_2 - 1, \pm(i_2)_2 - 2 \dots$$

Thus the above procedure, without any further restriction, would give us

$$\{2(i_j)_1 + 1\} \{2(i_j)_2 + 1\} \text{ values of } I_m.$$

After arranging these values symmetrically, we have to obtain the values of I_J. This will completely define the resultant term I_J.

Applying this rule to Mg, when we have both electrons in the M₁ orbit,

| | | | | |
|-------------------|-------------------|-------|---------------|------------------------------|
| | i_r | i_k | i_j | i_m |
| for electron (1): | $\frac{1}{2}$ | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ $-\frac{1}{2}$ |
| " " (2): | $\frac{1}{2}$ | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ $-\frac{1}{2}$ |
| Resultant: | 0 $\frac{2}{2}$ | 0 | 0 | |
| | I_R | I_K | $I_J = 0$ | $I_J = 1$ |

The resultant orbit has therefore I_R=0 and $\frac{2}{2}$, i.e. it belongs to a singlet or triplet system. I_K=0, i.e. K=1. It is an s-orbit I_J=0, 1. It has the inner quantum number =0 or 1.

Since ³S₁ is not observed, Pauli lays down a principle which excludes it, viz.: no two electrons in a closed orbit can have identical values of i_m.

This rule excludes ³S₁, for it arises from (i_m)₁= $\frac{1}{2}$, (i_m)₂= $\frac{1}{2}$, or both = $-\frac{1}{2}$.

From this principle also follows Stoner's rule: The number of electrons in a closed group =2 [j used in Landé's sense]. For the resultant magnetic moment due to the component electrons = 0, and this can take place if we assign to each the different possible value of (i_m) for a subgroup. The number = 2j or (2i_j+1), and to every

²The preliminary introduction is taken from Laporte's article in the Journ. Opt. Soc. America, July 1926.

positive value there is a corresponding negative value. Hence the resultant = 0, when there are $2j$ electrons, and each is contained in a different magnetic level. But I do not think that Stoner's subdivision of each higher level L_2 or M_2 into $L_{21} L_{22} M_{21} M_{22}$ is quite justified. See a paper by Saha and Ray in the *Physikalische Zeitschrift*.

Origin of Higher Terms.

But Pauli's principle cannot be applied where the electrons are in different levels. Thus let electron (1) be in the M_1 -orbit, electron (2) in the N_1 -orbit. Here Pauli's rule will not hold; we shall get 2^1S_0 , 2^3S_1 -terms. Similarly, as the electron (2) runs through the higher X_{11} levels it gives rise to the higher members of the 1^1S_0 and 3^1S_1 series, viz. 2^1S_0 , 2^3S_1 , etc.

Combination of M_1 and M_2 Levels.

We have

| | | | | | |
|-------------------|---------------|---------------|------------------------------|---|-------------------------------|
| | $i_r.$ | $i_k.$ | $i_j.$ | $i_m.$ | |
| for electron (1): | $\frac{1}{2}$ | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ |
| „ „ (2): | $\frac{1}{2}$ | 1 | $(\frac{1}{2}, \frac{3}{2})$ | $(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{3}{2})$ | $(\frac{1}{2}, -\frac{1}{2})$ |
| | 0 | $\frac{3}{2}$ | 1 | 0 | $I_j=0$ |
| | I_r | I_k | | 1 0 $\bar{1}$ | $I_j=1$ |
| | | | | 2 1 0 1 $\bar{2}$ | $I_j=2$ |
| | | | | 1 0 $\bar{1}$ | $I_j=1$ |

The resultant orbit will be 1^1P_1 , $3^1P_{0,1,2}$. The number of magnetic levels for these terms is $3+(1+3+5)=12$. The possible numbers of combinations of $(i_m)_1$ and $(i_m)_2$ are 2 and 6, and if we write them out, and add for the resultant I_m , and write out the corresponding values of J , we get the P terms ($2^1S_{\frac{1}{2}}$, $2^1P_{\frac{1}{2}}$) give us 1^1P_1 , 3^1P_0 , and ($2^3S_{\frac{1}{2}}$, $2^3P_{\frac{3}{2}}$) give us 3^1P_1 , 3^1P_2 .

Combination of N_1 and N_3 Levels.³

We need not repeat the summation for i_r . Now $I_k=2$, or the resultant are D-terms, 1^1D_2 , $3^1D_{1,2,3}$. The values of i_j are $\frac{1}{2}$ and $(\frac{3}{2}, \frac{3}{2})$ respectively. $(\frac{1}{2})$, $(\frac{3}{2})$ give us 1^1D_2 , 3^1D_1 , and $(\frac{1}{2})$, $(\frac{3}{2})$ give us $3^1D_{2,3}$. In this way we get by combination with levels N_2 the higher Rydberg terms of 1^1P_1 and $3^1P_{0,1,2}$. Combination with N_4 gives us the first F-terms.

We thus get a general explanation of the regular term-sequences in the spectrum of Mg, and *mutatis mutandis* for Ca, Sr, and Ba as well. But the procedure is capable of yielding still further results. It is known to spectroscopists that, in spite of the similarity amongst the spectra of these elements, there are certain outstanding differences. For the spectrum of Mg, the highest value for the sequence $D=15268.7$, while the highest D-values for Ca, Sr, and

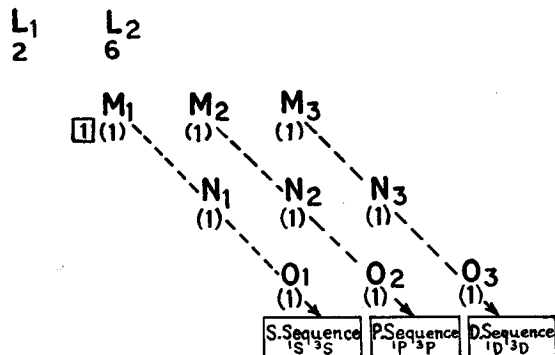
Ba are much higher; in fact they sometimes exceed the P-values, as the following table shows:—

| | D. | | P. | |
|----|----------|---------|----------|---------|
| Mg | 1^1D_2 | 15268.7 | 1^1P_1 | 26620.7 |
| | 3^1D_2 | 13714.7 | 3^1P_1 | 39801.4 |
| Ca | 1^1D_2 | 27455.3 | 1^1P_1 | 25652.4 |
| | 3^1D_2 | 28955.2 | 3^1P_1 | 34094.6 |
| Sr | 1^1D_2 | 25786.8 | 1^1P_1 | 24238.1 |
| | 3^1D_2 | 27717.7 | 3^1P_1 | 31432.2 |
| Ba | 1^1D_2 | 30634.1 | 1^1P_1 | 23969.2 |
| | 3^1D_2 | 32814.1 | 3^1P_1 | 29392.8 |

These large D-values can be easily explained if we compare the Structure Diagrams of Mg and Ca.

STRUCTURE DIAGRAM OF Mg (12)

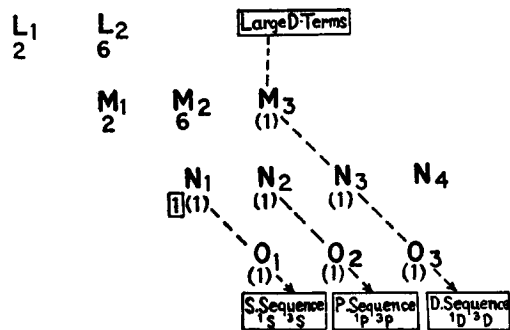
K_1
2



ORIGIN OF NORMAL TERMS IN MAGNESIUM

STRUCTURE DIAGRAM OF CALCIUM (20)

K_1
2



ORIGIN OF NORMAL TERMS IN THE SPECTRUM OF Ca

A comparison of the two structure diagrams shows that the successive positions of the running electron in Mg are M_1 (1^1S_0), M_2 (1^1P and 3^1P), M_3 (1^1D and 3^1D), and we have approximately $1^1P = \frac{N}{2^2}$, $1^1D = \frac{N}{3^2}$. But in Ca the positions

³Fowler, Report on Series in Line Spectra, ch. xiv.

| K ₁ 2 | | | | | | Transitional group I. | Transitional group II. | Rare earths I. | Transitional group III. |
|--|--|--|----------------|----------------|----------------|---|---|-------------------------|---|
| 1 H | | | | | | 21 Sc M ₂ 2N ₁ 2M ₂ N ₁ | 39 Y 2N ₂ O ₁ N ₂ 2O ₁ | 57 La | 71 Lu |
| 2 He 2K ₁ | | | | | | 22 Ti 2M ₂ 2N ₁ 3M ₂ N ₁ | 40 Zr 3N ₂ O ₁ 2N ₂ 2O ₁ | 58 Ce 59 Pr 60 Nd | 72 Hf 2O ₂ 2P ₁ 3O ₂ P ₁ |
| 3 Li 2K ₁ L ₁ | | | L ₁ | L ₂ | | 23 V 3M ₂ 2N ₁ 4M ₂ N ₁ | 41 Nb 4N ₂ O ₁ 3N ₂ 2O ₁ | 62 Sm | 73 Ta 3O ₂ 2P ₁ 4O ₂ P ₁ |
| 4 Be 2L ₁ 2L ₂ | | | 2 | 6 | | 24 Cr 5M ₂ N ₁ 4M ₂ 2N ₁ | 42 Mo 5N ₂ O ₁ 4N ₂ 2O ₁ | 63 Eu | 74 W 4O ₂ 2P ₁ 5O ₂ P ₁ |
| 5 B 2L ₁ L ₂ | | | | | M ₁ | 25 Mn 5M ₂ 2N ₁ 6M ₂ N ₁ | 43 Ma 6N ₂ O ₁ 5N ₂ 2O ₁ | 64 Gd | 75 Re 5O ₂ 2P ₁ 6O ₂ P ₁ |
| 6 C 2L ₁ 2L ₂ | | | | | 2 | 26 Fe 6M ₂ 2N ₁ 7M ₂ N ₁ | 44 Ru 7N ₂ O ₁ 6N ₂ 2O ₁ | 65 Tb | 76 Os 6O ₂ 2P ₁ 7O ₂ P ₁ |
| 7 N 3L ₂ | | | | | M ₂ | 27 Co 7M ₂ 2N ₁ 8M ₂ N ₁ | 45 Rh 8M ₂ O ₁ 7M ₂ 2O ₁ | 66 Dy | 77 Ir 7 O ₂ 2P ₁ 8 O ₂ P ₁ |
| 8 O 4L ₂ | | | | | 6 | 28 Ni 8M ₂ 2N ₁ 9M ₂ N ₁ | 46 Pd 10N ₂ 9N ₂ O ₁ | 67 Ho | 78 Pt 9O ₂ 2P ₁ 9O ₂ P ₁ |
| 9 F 5L ₂ | | | | | M ₃ | | | 68 Er | |
| 10 Ne 6L ₂ | | | | | 10 | | | 69 Tu | |
| 11 Na 6L ₂ M ₁ | | | | | | | | 70 Yb | |
| 12 Mg 6L ₂ 2M ₁ | | | | | M ₁ | | | | |
| 13 Al 2M ₁ M ₂ | | | | | 2 | | | | |
| 14 Si 2M ₂ M ₃ | | | | | 6 | | | | |
| 15 P 3M ₂ | | | | | | | | | |
| 16 S 4M ₂ | | | | | | | | | |
| 17 Cl 5M ₂ | | | | | | | | | |
| 18 A 6M ₂ | | | | | | | | | |
| 19 K 6M ₂ N ₁ | | | | | | | | | |
| 20 Ca 6M ₂ 2N ₁ | | | | | | | | | |
| 21 Sc 6M ₂ 2N ₁ | | | | | | | | | |
| 22 Ti 6M ₂ 2N ₁ | | | | | | | | | |
| 23 V 6M ₂ 2N ₁ | | | | | | | | | |
| 24 Cr 6M ₂ 2N ₁ | | | | | | | | | |
| 25 Mn 6M ₂ 2N ₁ | | | | | | | | | |
| 26 Fe 6M ₂ 2N ₁ | | | | | | | | | |
| 27 Co 6M ₂ 2N ₁ | | | | | | | | | |
| 28 Ni 6M ₂ 2N ₁ | | | | | | | | | |
| 29 Cu 6M ₂ 2N ₁ | | | | | | | | | |
| 30 Zn 6M ₂ 2N ₁ | | | | | | | | | |
| 31 Ga 6M ₂ 2N ₁ | | | | | | | | | |
| 32 Ge 6M ₂ 2N ₁ | | | | | | | | | |
| 33 As 6M ₂ 2N ₁ | | | | | | | | | |
| 34 Se 6M ₂ 2N ₁ | | | | | | | | | |
| 35 Br 6M ₂ 2N ₁ | | | | | | | | | |
| 36 Kr 6M ₂ 2N ₁ | | | | | | | | | |
| 37 Rb 6N ₂ O ₁ | | | | | | | | | |
| 38 Sr 6N ₂ 2O ₁ | | | | | | | | | |
| 39 Y 6N ₂ 2O ₁ | | | | | | | | | |
| 40 Zr 6N ₂ 2O ₁ | | | | | | | | | |
| 41 Nb 6N ₂ 2O ₁ | | | | | | | | | |
| 42 Mo 6N ₂ 2O ₁ | | | | | | | | | |
| 43 Ma 6N ₂ 2O ₁ | | | | | | | | | |
| 44 Ru 6N ₂ 2O ₁ | | | | | | | | | |
| 45 Rh 6N ₂ 2O ₁ | | | | | | | | | |
| 46 Pd 6N ₂ 2O ₁ | | | | | | | | | |
| 47 Ag 6N ₂ 2O ₁ | | | | | | | | | |
| 48 Cd 6N ₂ 2O ₁ | | | | | | | | | |
| 49 In 6N ₂ 2O ₁ | | | | | | | | | |
| 50 Sn 6N ₂ 2O ₁ | | | | | | | | | |
| 51 Sb 6N ₂ 2O ₁ | | | | | | | | | |
| 52 Te 6N ₂ 2O ₁ | | | | | | | | | |
| 53 I 6N ₂ 2O ₁ | | | | | | | | | |
| 54 Xe 6N ₂ 2O ₁ | | | | | | | | | |
| 55 Cs 6O ₂ P ₁ | | | | | | | | | |
| 56 Ba 6O ₂ 2P ₁ | | | | | | | | | |
| 57 La 6O ₂ 2P ₁ | | | | | | | | | |
| 58 Ce 6O ₂ 2P ₁ | | | | | | | | | |
| 59 Pr 6O ₂ 2P ₁ | | | | | | | | | |
| 60 Nd 6O ₂ 2P ₁ | | | | | | | | | |
| 61 Pm 6O ₂ 2P ₁ | | | | | | | | | |
| 62 Sm 6O ₂ 2P ₁ | | | | | | | | | |
| 63 Eu 6O ₂ 2P ₁ | | | | | | | | | |
| 64 Gd 6O ₂ 2P ₁ | | | | | | | | | |
| 65 Tb 6O ₂ 2P ₁ | | | | | | | | | |
| 66 Dy 6O ₂ 2P ₁ | | | | | | | | | |
| 67 Ho 6O ₂ 2P ₁ | | | | | | | | | |
| 68 Er 6O ₂ 2P ₁ | | | | | | | | | |
| 69 Tu 6O ₂ 2P ₁ | | | | | | | | | |
| 70 Yb 6O ₂ 2P ₁ | | | | | | | | | |
| 71 Lu 6O ₂ 2P ₁ | | | | | | | | | |
| 72 Hf 6O ₂ 2P ₁ | | | | | | | | | |
| 73 Ta 6O ₂ 2P ₁ | | | | | | | | | |
| 74 W 6O ₂ 2P ₁ | | | | | | | | | |
| 75 Re 6O ₂ 2P ₁ | | | | | | | | | |
| 76 Os 6O ₂ 2P ₁ | | | | | | | | | |
| 77 Ir 6O ₂ 2P ₁ | | | | | | | | | |
| 78 Pt 6O ₂ 2P ₁ | | | | | | | | | |
| 79 Au 6O ₂ 2P ₁ | | | | | | | | | |
| 80 Hg 6O ₂ 2P ₁ | | | | | | | | | |
| 81 Tl 6O ₂ 2P ₁ | | | | | | | | | |
| 82 Pb 6O ₂ 2P ₁ | | | | | | | | | |
| 83 Bi 6O ₂ 2P ₁ | | | | | | | | | |
| 84 Po 6O ₂ 2P ₁ | | | | | | | | | |
| 85 Rad 6O ₂ 2P ₁ | | | | | | | | | |
| 86 Nt 6O ₂ 2P ₁ | | | | | | | | | |
| 87 Eka Cs 6Q ₂ | | | | | | | | | |
| 88 Ra 6Q ₂ | | | | | | | | | |

(Explanation of the Chart.)

[The chart is a modification of the earlier schemes of Bohr and Stoner. The L₂₁ and L₂₂ levels of Stoner are compounded into one L₂-level. (For explanation, see a paper by Saha and Ray in the *Physikalische Zeitschrift*.) The chart explains the formation of (1) the regular groups, (2) the transitional groups, (3) the rare earths, and gives the electronic composition of the outer shells of the electrons, as obtained from Hund's interpretation of complex spectra (*Zs. j. Phys.*, vols. xxxiii & xxxiv.). The same chart explains

the periodic classification, and the spectra of elements. The distinctive nature of the small groups of two, consisting of an alkali and alkaline earth, is clearly brought out. They are formed when any X₁-level (X=K, L, M, N...) is filled, just as the regular groups are obtained when X₂ is filled, transitional groups when X₃ is being filled, as rare earths when X₄ (X=N) is being filled.

For the explanation of spectra with the same chart, see the text.]

are N_1 (1S_0), N_2 (1P , 3P), and then M_3 , not N_3 , which is on a higher level. Now the 1D -term corresponding to N_3 has the normal value, *i.e.* $Ca \frac{N}{3^2}$, but the 1D -term corresponding to M_3 must have a higher value, *i.e.* $Ca \frac{N}{2^2}$. This diagram, therefore, symbolically explains the origin of the large D -terms in Ca and also in Sr and Ba . In the spark spectrum of Ca^+ , it explains why the first of 2D -terms is larger than 2P , while in the spectrum of Mg^+ , 2P is $> ^2D$.

Concluding Remarks.

The foregoing work shows that the above scheme of electron arrangement, which is a modification of Stoner's scheme, combined with the rules of synthesis of complicated spectra from the elementary component doublet spectra, gives a very satisfactory explanation of the fundamental as well as of all the higher terms regular and anomalous, of the alkaline earths. Even the detailed differences (*e.g.* occurrence of large D -terms in Ca , Ba , Cr , and its absence in Mg) are readily explained. But the theory goes still further. It gives us a clue to the origin of dashed terms. They arise when the stationary electron is in the metastable orbit, and the running electron is in the same orbit or in the higher homologous orbit. We can also obtain some clue

regarding the term values. If the orbit arises when both electrons are in the same shell, or the running electron in the previous unclosed shell, the values are large. No matter whether we get S , P , D , F , or G terms, the order of the value will be the same, when the origin of these terms is common. The origin of dashed terms is taken in a subsequent paper.

Thus note that when both electrons in Ca are in M_3 -levels, we get 3F , 3P , 1G , 1D , 1S_0 terms. Their order of value is the same.

But if the running electron is in a higher shell, it will give rise to higher Rydberg terms; the values will decrease

approximately as $\frac{N}{m^2}$, $m=1, 2, 3$ respectively.

The investigation also shows that differences are expected between the spectra of Ca and Ba . These points are being investigated. It is also apparent that for the calculation of the higher Rydberg terms Pauli's rule is not necessary, and we no longer need the complex calculation involving the magnetic quantum numbers.

In conclusion, the author wishes to express his thanks to Mr. K. Mazumder, who has drawn the charts and tables for him.

39. ON THE EXPLANATION OF SPECTRA OF METALS OF GROUP II*

(PART II)

P. K. KICHLU AND M. N. SAHA

(*Phil. Mag., Sr. VII, 4, 193, 1927*)

In a previous paper one of us¹ has discussed the origin of the higher Rydberg sequence terms in the normal spectra of elements of group II. It is well known that besides these normal terms all these elements give a number of anomalous terms. They were noticed by Rydberg² in 1894 in the spectra of Ca and Sr , and Popow³ discovered similar groups in the spectra of Ba and Al in 1915. In 1921, Götze⁴ interpreted these groups as a transition between the normal p -group and another group which he called p' (sometimes also called \bar{p} , which notation we shall follow. That the \bar{p} -group was essentially of the same nature as the ordinary p was made clear from investigation of the Zeeman effect of these groups.

Since this time numerous groups of dashed (or barred) terms have been discovered in the spectra of elements of higher groups; but the first indication of the origin of these terms was given by Russell and Saunders⁵, and independently by Wentzel.⁶ Russell and Saunders discovered other groups of $p\bar{p}$ and $d\bar{d}$ combinations in spectra of Ca , Sr , and Ba . These \bar{p} and \bar{d} terms are sometimes negative, and the abovementioned authors noted that if a certain number was added to these terms they formed approximately a Rydberg sequence. This number was approximately 13700 in the case of Ca , which is about the same as the difference between the values of the fundamental 2S -term of Ca^+ and the next term in order of value, *viz.* 2D . From this fact the above-mentioned authors concluded that the anomalous

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¹M. N. Saha, *Phil. Mag.*, June 1927.

²Rydberg, *Wied. Ann.* lii. p. 119 (1891).

³Popow, *Ann. der Physik*, Bd. xlv. p. 147 (1914).

⁴Götze, *Ann. der Physik*, Bd. lxxvi. p. 285 (1921).

⁵Russell and Saunders, *Astrophysical Journal*, lxi. p. 38 (1925).

⁶Wentzel, *Phys. Zeits.* xxiv. p. 106 (1923); xxv. p. 182 (1924).