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 differerences (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, $^3\bar{P}$, ^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

In a previous paper one of us[1] 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 Rydberg[2] in 1894 in the spectra of Ca and Sr, and Popow[3] discovered similar groups in the spectra of Ba and Al in 1915. In 1921, Götze[4] 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 Saunders[5], 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

*Communicated by the Authors.
[1] M. N. Saha, Phil. Mag., June 1927.
[2] Rydberg, Wied. Ann. lii. p. 119 (1891).
[3] Popow, Ann. der Physik, Bd. xlv. p. 147 (1914).
[4] Götze, Ann. der Physik, Bd. lxvi. p. 285 (1921).

[5] Russell and Saunders, Astrophysical Journal, lxi. p. 38 (1925).
[6] Wentzel, Phys. Zeits. xxiv. p. 106 (1923); xxv. p. 182 (1924).

terms arise when the stationary electron of Ca is in the metastable M_3-level.

In this investigation it will be shown that the conclusion of these authors regarding the origin of $\bar{p}$-terms is correct in the case of Ca, Sr, and Ba; but from this it is not safe to draw any general conclusion regarding the nature of the dashed terms. As was pointed out in the note on the spectrum of Neon[7] by the senior author, whenever from any particular distribution of electrons in potential orbits F, D, P terms simultaneously arise, they must then have the same combinatory powers, so that if F and P are treated like ordinary terms, D must be dashed. But we can also dash F and P and treat D as an undashed term. It is purely a matter of convention, in which we have to be guided by our previous knowledge of the history of the spectrum of the element.

Origin of PP̄-*Terms in the Spectrum of* Mg, Zn, Cd, *etc.*

As Bowen[8] and Millikan have pointed out, PP̄-terms are known in the spectra of Mg, Zn, and Cd, for which the metastable level of the ionized element is not ^2D, but ^2P. Bowen and Millikan, by their hot-spark method, were able, to discover PP̄ groups in the spectra of Be, B+, C++, N+++, O++++, and in Al+, Si++, P+++, S++++, Cl+++++, which have got a structure similar to that of Mg. They discovered the most interesting laws regarding the values of these PP̄-groups, and showed theoretically as well as experimentally that the values of these PP̄-groups were approximately the same as the value of the fundamental line ($^1S-^1P$) of these elements. Sawyer and Bees, in a note to 'Nature' of Dec. 26, 1925, however, find that in the case of Zn and Cd the values of PP̄-groups are the mean between the values of ($^1S-^1P$) of the normal element and $^2S-^2P$ of the ionized element. We shall not dwell upon Bowen and Millikan's explanation of the origin of these terms at this place, as this will come out later on in the course of discussion.

All these facts, and the other details discovered by Russell and Saunders in the spectra of Ca, Sr, and Ba, receive a unitary explanation on the lines suggested in the former paper of the senior author[9] and in the note on the spectrum of Neon. We shall begin by writing down the structure diagram for Mg and Ca.

Structure Diagram for Mg (12)

```
K₁
2
    L₁   L₂
    2    6
         M₁   M₂   M₃
         2
              N₁   N₂   N₃   N₄
                   O₁   O₂   O₃
```

Structure Diagram for Ca (20)

```
K₁
2
    L₁   L₂
    2    6
         M₁   M₂   M₃
         2    6
              N₁   N₂   N₃   N₄
              2
```

The normal state of Mg is obtained by keeping both the electrons in M_1; in the case of Ca, both in N_1. For transitions to higher levels, one electron has to be kept at M_1 for Mg, and at N_1 for Ca : the other electron has to be successively shifted to all positions on the right. Terms arising from levels on the same vertical column will have approximately the same scale of values, while they will decrease progressively as we pass to further columns on the right. It is emphasized at this point that we assign the total quantum number 1 to those terms which have their origin in the undisturbed outermost level. Thus the term arising from the combination $M_1 M_1$, viz. $^1S_0$, has the total quantum number 1. As the electron is shifted to successive levels on the right, the total quantum number increases by one at each step. This method of fixing up the total quantum number for optical terms is evidently more appropriate for expressing actual facts than Bohr's representation of terms by 3S (for Mg, M_{11}), 4S (for Ca, same as N_{11}), etc., though the latter method of representation has the merit of giving a unitary representation to the X-ray levels as well as optical levels.

The normal terms of Mg are therefore due to combinations :

(a) $M_1 M_1$ (both the electrons in M_1) giving $^1S_0$ only as first pointed out by Pauli[10].

$M_1 N_1$, $M_1 O_1$, $M_1 P_1$, ... will give higher Rydberg sequences of $^1S_0$-term, and a sequence of $^3S_1$-terms beginning with 2^3S_1 (form $M_1 N_1$ in the case of Mg).

(b) $M_1 M_2$ (one electron is in M_1, the running electron is in M_2).

Terms obtained : ^1P, ^3P.

M_1N_1, M_1O_2, M_1P_2, ... give higher Rydberg sequence terms to this set of singlet and triplet P's. The P-sequence begins with the total quantum number 2.

(c) M_1M_3 (the running electron is M_3).

Terms obtained : ^1D, ^3D.

$M_1 N_3$, $M_1 O_3$, $M_1 P_3$, ... give the Rydberg sequence. The D-sequence will begin with the total quantum number 3.

In the case of Ca,

(a) $N_1 N_1$...give us $^1S_0$, and

$N_1 O_1$, $N_1 P_1$, ...give us the ^1S and ^3S series.

(b) $N_1 N_2$ give us the first ^1P and ^3P terms and

$N_1 O_2$, $N_1 P_2$, the higher ^1P and ^3P Rydberg terms.

[7] M. Saha, Phil. Mag.
[8] Millikan and Bowen, Phys. Rev. xxv. p. 150 (1925).
[9] M. N. Saha, Phil. Mag., June 1927 and "Note on the Spectrum of Neon" (Phil. Mag., July 1927, p. 223).

[10] W. Pauli, Jun., *Zs. für Physik*, Bd. xxxi. p. 765 (1925).

In the (c) combination the first combination is $N_1 M_3$, and not $N_1 N_3$. As the M_3-level has at least the same order of value as N_2, $N_1 M_3$ will give us ^1D and ^3D terms of the same order of value as the first ^1P and ^3P terms. This explains the occurrence of large D-terms in the spectrum of Ca, and *mutatis mutandis* in Sr and Ba. Thus in Ca, Sr, and Ba the D-sequence will begin with 2, and not with 3 as in Mg.
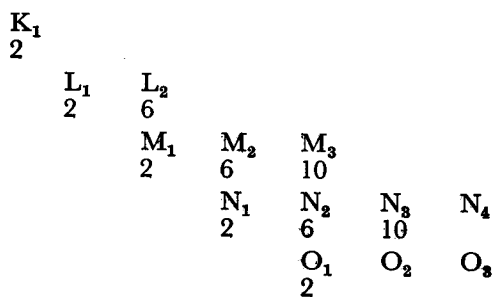
If we write out the structure diagrams for Zn and Cd, we see that the normal spectrum will be exactly like that of Mg. No D-terms comparable in value to the first P-terms will occur, and the sequence will begin with the total quantum number $n=3$.

Structure Diagram for Zn (30)

$$K_1 \quad 2$$
$$L_1 \quad L_2$$
$$2 \qquad 6$$
$$M_1 \quad M_2 \quad M_3$$
$$2 \qquad 6 \qquad 10$$
$$N_1 \quad N_2 \quad N_3 \quad N_4$$
$$2$$
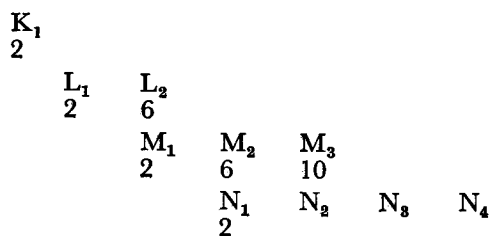
(Both electrons are in N_1. The next transition is horizontally from N_1 to N_2. M_3 is completely filled). A number of anomalous terms is possible from the combination $9M_3$, $2N_1N_3$, giving ^3F, $^3\overline{D}$, ^3P, ^1F, ^1D, ^1P, but it is not yet known whether they exist.

Structure Diagram for Cd (48)

$$K_1 \quad 2$$
$$L_1 \quad L_2$$
$$2 \qquad 6$$
$$M_1 \quad M_2 \quad M_3$$
$$2 \qquad 6 \qquad 10$$
$$N_1 \quad N_2 \quad N_3 \quad N_4$$
$$2 \qquad 6 \qquad 10$$
$$O_1 \quad O_2 \quad O_3$$
$$2$$

(In normal case other electrons are in O_1. Transition is horizontally from O_1 to O_2, giving O_1O_2 as the next state. N_3 is completely filled up. Here also the $9N_3.2O_1O_2$ combination is possible).

In order to account for the anomalous terms, let us put one electron permanently in the next higher level and move the second electron through the next successive levels. In the case of Mg, Zn, and Cd there is no metastable level diagonally across the fundamental level. Thus, taking the case of Mg, the level M_1 will be kept entirely empty: one electron will be kept permanently at M_2, the second electron will be moved successively through the M_2, M_3, N_1, N_2, N_3, ... levels. In Ca, however, the level next to the fundamental is M_3, so that the fixed electron will be always at M_3, and the running electron will move through the other possible levels, viz. N_1, M_3, N_3, ... *For this reason the large D-terms*

which *arise from the combination* $M_3 N_1$ *may be considered as the first of the anomalous terms in* Ca.

Anomalous Terms in Mg, Zn, Cd.

Let us now find out, by applying the combination rules of Pauli, Heisenberg, and Hund, the probable anomalous terms in the spectra of Mg, Zn, and Cd.

(a) $M_2 M_2$ give $^3P_{0,1,2}$, $^1D_2$, $^1S_0$.

The P's will be dashed, because $M_1 M_2$ give us $^3P_{0,1,2}$, and transition is possible between $(M_1 M_2)$ and $(M_2 M_2)$.

Value of $^3\overline{P}_{0,1,2}$.

Let us consider the relative values of the following sequences for Mg:—

M_1M_2	M_1N_2	M_1O_2	M_1P_2	M_1Q_2
$1\,^3P$	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$

M_2M_2	M_2N_2	M_2O_2	M_2P_2	M_2Q_2
$1\,^3\overline{P}$	$2\,^3\overline{P}$	$3\,^3\overline{P}$	$4\,^3\overline{P}$	$5\,^3\overline{P}$

Taking corresponding pairs of higher Rydberg terms, say $5\,^3P$ and $5\,^3\overline{P}$, we find that the second electron is in both cases far out. The atomic residue will therefore exert, on the inner of the two valence electrons, approximately the same force in both cases. In other words, we can write symbolically

$$(5\,^3P \rightarrow 5\,^3\overline{P}) = (M_1 Q_2) \rightarrow (M_2 Q_2)$$
$$= (M_1 \rightarrow M_2) \, Q_2$$

The symbol in the last step denotes that the energy of the electron in the Q_2 position has the same value in both cases because it is far out, hence $5\,^3P - 5\,^3\overline{P} = (M_1 \rightarrow M_2)$ of the atomic residue. This atomic residue is, however, the Mg^+ electron, M_1 corresponds to the fundamental ^2S of Mg^+, and M_2 corresponds to the ^2P of Mg^+. We therefore arrive at the rule that for the higher terms

$$(^3P - ^3\overline{P}) \text{ of } Mg = (^2S - ^2P) \text{ of } Mg^+.$$

When we pass on, however, to the lower terms like $2\,^3P - 2\,^3\overline{P}$, the influence of the atomic residue on the running electron can no longer be regarded as the same in both cases. Hence the above rule will not hold so well. Taking

$$1\,^3P - 1\,^3\overline{P} = (M_1 M_2 - M_2 M_2),$$

we find that the transition is obtained by moving one electron from M_1 to M_2, the other electron always remaining at M_2, *i.e.*,

M_1	M_2	
1	1	... ^3P.
$\rightarrow$	1,1	... $^3\overline{P}$.

The difference in energy may be assumed to be approximately the same as is required in the passage of the electron from $M_1 \rightarrow M_2$ from the $M_1 M_1$-stage:

M_1	M_2	
1,1		... $^1S_0$
$\rightarrow$	1	... ^3P, ^1P,

the difference being that in the first case the transition is

with the stationary electron at M_2, in the second case it is with the stationary electron at M_1. Hence

$$1^3P - 1^3P \text{ is } > {}^1S - {}^1P \text{ of the metal} \qquad \dots (A)$$
$$\text{and} \qquad < {}^2S - {}^2P \text{ of the ionized metal} \qquad \dots (B)$$

Rule (A) is given (with = instead of >) by Bowen and Millikan[11], whose arguments are almost the same as that given here: rule (B) is given by Sawyer and Beese, who make $^3P - {}^3P$ equal to the mean value of

$$({}^1S - {}^1P) \text{ of M and } ({}^2S - {}^2P) \text{ of } M^+$$

for Zn and Cd. The validity of the above rules will be apparent from the following table:—

TABLE I.

Element	Value of P — P.	$^1S - {}^1P$ of M.	$^2S - {}^2P$ of M^+
Mg	35982	35051	35669
Zn	47894	46745	48482
Cd	44088	43692	44135
Hg	?	54099	?
Al+	56690	59845	53918
Si++	76986	82878	71280
P+++	97037	105190	88649
S++++	116985	127144	105866
Cl+++++	136928	148949	123001

The figures in Table I, as well as theoretical arguments, show that Sawyer and Beese's rule represents facts more accurately than Millikan and Bowen's rule. The $^1D_2$, and $^1S_0$-terms expected from M_2M_2-combination has also been recently obtained by one of us in Mg.

Higher negative terms may be obtained by keeping the first electron at M_2, and allowing the other electron to run through the higher levels $M_3 \dots$ Though they are not yet known, one typical example may be given:—

Combination $M_2 M_3$ will give us

^3F	^3D	^3P
^1F	^1D	^1P

^3F will have the highest (i.e. lowest negative) value. They may be expected to have the value ^1D of Mg —35000, i.e. about —20000 for Mg. If they exist, they will combine with the ^1D, ^3D terms of Mg.

Origin of Anomalous Terms in Ca, Sr, and Ba.

Bowen and Millikan have pointed out that PP-multiplets of the above description have not yet been discovered in the spectra of Ca, Sr, and Ba. The fact receives a clear explanation when we look at the structure diagrams of these elements.

[11]Bowen and Millikan, Phys. Rev. vol. xxv. p. 150 (1925).

Structure Diagram for Sr (38)

2K
8L
18M

N_1	N_2	N_3	N_4
2	6		
	O_1	O_2	O_3
	2		

(Normal terms are obtained by keeping one electron permanently at O_1 and allowing the other to run through O_1, O_2, $N_3 \dots$; for anomalous terms, keep the electron at N_3 and let the other run through the levels O_1, N_2, O_3, etc.)

Structure Diagram for Ba (56)

2K
8L
18M

N_1	N_2	N_3	N_4
2	6	10	
	O_1	O_2	O_3
	2	6	
	P_1	P_2	
	2		

(To get the normal terms, one of the two electrons is placed at P_1 and the other moves through P_1, N_4, O_3, $P_2 \dots$ The N_1P_4 combination, which is expected to give a large ^1F and ^3F term, is not yet known with certainty.)

For Ca M_3 is the level next in value to N_1, and we keep the first electron in this level. The anomalous terms are then obtained by allowing the other electron to run through the other possible levels. We get the following combinations:

(a) M_3M_3

Since both electrons are in M_3-orbit (Pauli's rule will apply), we obtain:

$$^3F, \quad ^3P, \quad ^1G_4, \quad ^1D_2, \quad ^1S_0.$$

State (N_1 M_3) giving ^3D, ^1D will not combine with M_3 M_3, because $N_1 \to M_3$ is forbidden. Hence the D-terms arising from this combination will be of the same nature as the D-terms from M_3M_3, i.e. they are not dashed. This enables us to fix the nature of the other terms. M_3N_3, $M_3O_3 \dots$ will give us the higher members of the group:

	^3G	^3F	^3D	^3P	^3S	
	^1G	^1F	^1D	^1P	^1S	

(b) M_3N_2

This combination givess us

2^3F	2^3D	2^3P
2^1F	2^1D	2^1P

M_3O_2, $M_3P_2 \dots$ gives the higher members of the sequence.

(c) M_3O_1

This combination gives us

$$3^3D, \quad 3^1D$$

These terms will form higher Rydberg sequence of displaced type with the large ^3D and ^1D. Evidence of their

existence has been obtained in the spectrum of Ba. For reasons stated before

$$1\,{}^3\bar{D}\text{ of }Ca = 1\,{}^3P\text{ of }Ca + ({}^1S - {}^3D)\text{ of }Ca \qquad \ldots(A)$$
$$\text{or} \qquad + ({}^1S - {}^1D)\text{ of }Ca \qquad \ldots(B)$$

Relation (A) will be approximately correct, but (B) indicates only an upper limit. The same argument will hold for Sr and Ba. The values of ${}^2S_1 - {}^2D_3$ for Ca+, Sr+ and Ba+, and ${}^1S_1 - {}^3D_2$ and ${}^1S_1 - {}^1D_2$ for Ca, Sr and Ba are shown below:—

TABLE II.

	M		M+.
	$({}^1S - {}^3D_2)$.	$({}^1S - {}^1D_2)$.	${}^2S_1 - {}^2D_2$.
Ca	20350	21850	13650
Sr	18219	20149	14557
Ba	9215	11395	4884

M=neutral element; M+=ionized atom of the element.

In Barium we have followed Paschen's[14] identification of the D-term. According to Fowler[15] ${}^2S - {}^2D$ for Ba+=11990.

A preliminary comparison with the new terms obtained by Russell and Saunders shows that the above conclusions are well verified. The detailed identification is shown in Table III.

Table III shows that Russell and Saunders' f'', p'', and d' terms can be identified with the ${}^3F$, ${}^3P$, and ${}^3D$ terms arising from the M_3N_2 combination. In fact they observe that f'' and p'' are in all respects like ordinary f and p terms. They also follow the usual rule which has been brought to light by Hund[16] and others, that when from the same combination F, D, and P terms arise, F is usually $> D > P$.

A number of singlet terms have been mentioned by Russell and Saunders, but their nature has not yet been clearly elucidated. We have therefore refrained from trying to identify them with singlet terms ${}^1F_3$, ${}^1D_2$, ${}^1P_1$. But in the case of Ca, we can hazard the identification mentioned in Table III. Of these, $Y = {}^1F_3$ seems to be pretty certain. X may be put $= {}^1D_2$, but it seems to be very difficult to fix up the nature of the "x". Back[17] finds from Zeeman-effect data that "x" is not a singlet term, but a triplet term, ${}^3F_2$. He has also given ${}^3F_3$, ${}^3F_4$. But he finds that the splitting

TABLE III

State	Present notation	Russell & Saunders' notation	Term values					
			Ca		Sr		Ba.	
(a) M_3M_3	${}^3\bar{F}_{4,3,2}$	..	....		....		19077·9 19510·1 19990·3	432·2 480·2
	${}^3P_{2,1,0}$	p'	10753·0 10839·8 10887·1	86·8 47·3	10250·7 10525·5 10731·8	247·8 206·3	18110·5 18549·3 18820·3	438·8 271·0
	${}^1S_0$ ${}^1D_2$ ${}^1G_4$	X	8584·9		8964·9		9929·0	
(b) M_3N_2	${}^3F_{4,3,2}$	f''	13407·6 13485·9 13573·9	78·3 88·0	12006·0 12335·7 12658·5	329·7 322·8	18372·6 19082·1 19964·8	709·5 882·7
	${}^3D_{3,2,1}$	d'	11045·3 11085·3 11112·0	40·0 26·7	9365·9 9543·4 9661·1	177·5 117·8	17049·8 17498·1 17837·6	448·3 339·5
	${}^3P_{2,1,0}$	p''	9964·3 9969·1 9971·0	4·8 1·9	8588·5 8622·2 8633·0	33·7 10·8	16073·1 16325·5 16387·5	252·4 62·0
	${}^1F_3$ ${}^1D_2$ ${}^1P_1$	Y	8767·0		9836·1		15213·4 13475·2[12]	
(c) M_3O_1	${}^3D_{3,2,1}$ ${}^1D_2$		....		....		4526[13]	

[12] Identified by Russell and Saunders, loc. cit.
[13] We have for Ba, ${}^3D_{3,2}-4526 = 12523\cdot18$ (1), $12972\cdot3$ ($8u$); $b\ {}^3F-4526 = 14556$ ($6r$).
[14] Paschen and Götze, 'Serienspektren,' Chap. on Barium.
[15] A. Fowler, 'Series in Line-Spectra', p. 137 (1922).

[16] F. Hund, Zs. für Physik, Bd. xxxiii. p. 841 (1925).
[17] Back, Zs. für Physik, Bd. xxxiii. p. 584.

factor g for Zeeman effect is different ($\frac{3}{4}$) in the case of $^3F_2$ from the value of g given by Landé's formula ($\frac{2}{3}$), and sees in this a justification of Landé's "Verzweigungs-prinzip." The nature of the large term W, or of Z also, cannot be fixed up from the present data. It may be added that Russell and Saunders have taken only those lines which are given by King from his furnace-spectra data. If the full list of arc lines is taken from Kayser and Konen's 'Handbuch der. Spektroskopie,' vol. vii., it is found that there are many lines yet to be classified.

Values of the Terms.

The identification is rendered more probable from the following theoretical considerations about their values :—

It will be seen that the Barium values of anomalous terms are much larger than Ca or Sr values. Further, the terms arising from M_3N_2 combination have the same order of value as those arising from M_3N_3 combination. Let us consider the sequence of terms arising from the following pairs of combinations :—

M_3N_2	M_3O_2	M_3P_2	M_3Q_2	M_3R_2
$^1\bar{D}, {}^3\bar{D}$	$2^1\bar{D}, 2^3\bar{D}$	$3^1\bar{D}, 3^3\bar{D}$	$4^1\bar{D}, 4^3\bar{D}$	$5^1\bar{D}, 5^3\bar{D}$
N_1N_2	N_1O_2	N_1P_2	N_1Q_2	N_1R_2
$^1P, {}^3P$	$2^1P, 2^3P$	$3^1P, 3^3P$	$4^1P, 4^3P$	$5^1P, 5^3P$

Of the set of terms arising from $M_3 X_2 \ldots \ldots$ we have taken only the D's. Compare the values of each corresponding pair in each vertical column.

Now,
$$M_3R_2 \rightarrow N_1R_2 = (M_3 \rightarrow N_1)R_2$$
$$= (M_3 - N_1) \text{ of Ca}^+ \text{ approximately}$$
$$= (^2S - {}^2D) \text{ of Ca}^+.$$
$$\therefore 5^3\bar{D} \text{ of Ca} = 5^3P \text{ of Ca} - (^2S - {}^2D) \text{ of Ca}^+ \ldots \ldots \ldots \ldots (A)$$

The value of $^3\bar{D}$ and other terms like $f''(b^3F)$ arising from this level will therefore lie between the limits :

	$^3p_2 - (^1S - {}^2D)$	$^3p_2 - (^2S - {}^2D)$	f''.	Actual values $^3\bar{D}$.
For Ca	12139	20338	13485	11085
Sr	10888	16480	12335	9543
Ba	17120	23631	19082	17498

1 $^3\bar{D}$ values are thus seen to be slightly lower than the lower limit, and b 1^3F values higher than the lower limit. Higher Rydberg terms to the above set have not yet been obtained in sufficient number to enable us to make a satisfactory comparison and to see whether a member like
$$5^3\bar{D} = 5^3P - (^2S - {}^2D) \text{ of M}^+$$
also follows the expected order.

Values of Terms arising from $M_3 M_3$-levels.

Compare, as before, the set of values arising from the combinations:

M_3M_3	M_3N_3	M_3O_3	M_3P_3	M_3Q_3
$^1P, {}^3P$	$2^1P, 2^3P$	$3^1P, 3^3P$	$4^1P, 4^3P$	$5^1P, 5^3P$
N_1M_3	N_1N_3	N_1O_3	N_1P_3	N_1Q_3
$^1D, {}^3D$	$2^1D, 2^3D$	$3^1D, 3^3D$	$4^1D, 4^3D$	$5^1D, 5^3D$

By the same argument as before the values of the higher terms like $5 \ {}^3\bar{P}$ will approximately be equal to
$$5^3\bar{D} - (^2S - {}^2D) \text{ of M}^+,$$
while the value of $1 \ {}^3\bar{P}$ will be between $1,^3\bar{D} - (^1S - {}^1D)$ of M and $1 \ {}^3\bar{D} - (^2S - {}^2D)$ of M$^+$. The following table shows the expected values of $^4\bar{P}$ compared to the limits calculated as above:—

	Limits	$3\bar{P}$
Ca	7106-15666	10839
Sr	7567-13159	10525
Ba	21419-27930	18549

The value of $^3\bar{P}$ in the case of Ca and Sr is approximately the mean of the limits. But the Ba value of $^3\bar{P}$ is less than even the lower limit.

The above comparison explains a feature of the Barium spectrum. The anomalous terms are much larger than the corresponding terms in Ca and Sr. It is easily seen that it is due to the smaller value of the shift numbers $^1S - {}^1D$ and $^2S - {}^2D$ in the case of Ba. The value of the terms arising from $X_3 Y_2$ and $X_3 X_3$-levels are of the same order, since ^3P and ^3D terms have the same order of value. In Barium ^3D is much larger than ^3P, and we therefore find that the terms arising from $X_3 X_3$ are much larger than the terms arising from $X_2 Y_3$.

The Rydberg Sequence of Anomalous Terms.

Rydberg sequence has been established satisfactorily up to the fifth term only in the case of Ca $^3\bar{P}$ terms. The comparison of values is given below :—

	$1^3\bar{P}$	$2^3\bar{P}$	$3^3\bar{P}$	$4^3\bar{P}$	$5^3\bar{P}$
	10840	767	−4983	−8313	−10063
$^3D − (^2S − {}^2D)$	15306	−2097	−7090	−9359	−10649
$^3D − (^1S − {}^1D)$	7106				

Russell and Saunders find that if $13711 (^2S - {}^2D)$ be added to the sequence of ^3P terms, they form approximately a Rydberg sequence.

Existence of ^3F-terms.

The most important group of terms from the combination $M_3 M_3$ is ^3F, which is expected to be larger than ^3P, identified with certainty with Russell and Saunders' p'. But these terms have not yet been identified. The cause is to be traced to its combinatory properties. It can combine with
$$^3F \quad {}^1F \quad {}^3\bar{D} \quad {}^1D$$
arising from combination ($M_3 M_2$) and with the triplet F of the normal spectrum and also with the $N_1 N_2$ terms (Ca). But the terms $^3F, {}^1F, {}^3\bar{D}, {}^1D$ of combination $M_3 N_2$ have values very nearly equal to ^3F, i.e. the difference $^3F - {}^3F$ would be very small; the lines, if they exist, would be in the

far infra-red. Only in the case Ba can we expect ^3F to have a sufficiently large value. We have not yet been able to identify the ^3F terms without ambiguity, but the following identification may be provisionally given:—

	$\bar{F}_2(480\cdot2)$ 19990·3	$\bar{F}_3(432\cdot2)$ 19510·1	$\bar{F}_4$ 19077·9
$3^3F_2 = 7426\cdot8$	(1u) 12563·5		
$3^3F_3 = 7412\cdot8$	?	(2) 12097·3	(1r) 11665·4
$3^3F_4 = 7398\cdot6$		(1) 12112·0	(6u) 11679·3

The combination with ^3F of state $M_2 M_3$ ought to give us strong lines, but they would be hopelessly in the infra-red if these values of ^3F prove to be correct. But we can take the higher Rydberg sequence terms of this ^3F, for which Russell and Saunders give the values 4966·3, 4747·5, and 4558·6. We get the following multiplet:—

	$\bar{F}_2$ 19990·3	$\bar{F}_3$ 19510·1	$\bar{F}_4$ 19077·9
$2b^3F_2 = 4966\cdot3$	(1) 15024·1	(1) 14543·2	
$2b^3F_3 = 4747\cdot5$	?	(1) 14762·8	(1) 14330·5
$2b^3F_4 = 4558\cdot6$		?	?

Probably the last term, viz. 4558, has not been correctly identified, for we have failed to establish it from other sources. The reality of the ^3F for Ba here given is strengthened by the following further combinations:—

$$19990\cdot3 - q_1 = 13305\cdot2 \ (1u),$$
$$19510\cdot1 - 3^3F_3 = 13372\cdot0 \ (2), \ 19510\cdot1 - q_2 = 12270\cdot0 \ (2),$$
$$19510\cdot1 - q_3 = 12311\cdot2 \ (2),$$
$$19077\cdot9 - q_3 = 11880\cdot9 \ (1u).$$

Though the existence of the ^3F terms has not yet been established, except in the case of Ba, they form very prominent members in the spectra of Sc+, Y+, and La+. Here $^2S - ^2D$ of M+ (*i.e.* of Sc++, Y++, La++) is negative, *i.e.* the ^2D-term is larger than ^2S; hence terms which arise when the stationary electron is at M_3 are much larger than the terms arising out of the combination $N_1 X$: in other words, though the elements have a structure similar to that of the alkaline earths, the spectrum is just reversed, the anomalous terms become normal terms, and the normal terms become anomalous. Thus in Sc+,[18] for which the structure diagram is the same as that for Ca, we have the following terms (since the absolute value is not known, the largest term is given the value 0; the values of the other terms are obtained by subtracting the number placed against each number from the value of the biggest term :—

Sc+

State	Terms	Term values
N_1M_3	^3D	0, 67·6, 177·8
	^1D	?
M_2M_3	^3F	4802, 4883, 4987
	^3P	12073·8, 12101·3, 12154·1
M_2N_2	^3F	27440·9, 27602·7, 27841·4
	^3D	27918·1, 28021·6, 28161·5
	^3P	?

Thus here ^3F forms the second biggest set of terms. The same feature is observed in the spectra of Y+ and La+.[19] The barium spectrum is intermediate in nature between the two groups Ca and Sr on one hand, Sc+, Y+, L+ on the other hand.

[18] S. Goudsmit, J. van der Mark, and P. Zeeman, Proc. Amst. vol. xxviii. p. 127.
[19] Y+-spectrum: Meggers, Journ. Opt. Sci. Am. vol. xii. p. 418 (1926). La+: Goudsmit, *loc. cit.* Goudsmit has apparently taken the terms in the reverse order.

40. A NOTE ON THE SPECTRUM OF NEON*

Though the spectral lines of Neon have been completely grouped into series by Paschen, the nature of the series terms was not clearly understood, and a good deal of discussion has been devoted to it. Paschen[1] discovered

A set of four terms ($s_2 s_3 s_4 s_5$)
of value ranging between 38040—39887;
a set of ten terms ($p_1 \ldots \ldots \ldots p_{10}$)
of value ranging between 20958—25671·65;
a set of 12 terms ($d_1 d_1' \ldots \ldots \ldots d_6, s_1', s_1'' \ldots \ldots s''''$)
of value ranging from 11493—12419.

None of these terms, however, constitute the fundamental level of Neon, which must have a very large value corresponding to the observed ionization potential of 21 volts. This level was discovered by Hertz[2], by means of his vacuum spectrograph. It gives rise to two lines $\lambda = 735\cdot7$ and $\lambda = 743\cdot5$, separated by a frequency interval of 1428, which is just the difference between the values of Paschen's s_2 and s_4 terms.

From these data, and from a discussion of data on the Zeeman effect of Neon-lines, Goudsmit[3] has proposed the

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*Communicated by the Author.
[1] Paschen, *Ann. d. Physik*, vol. lx, and lxiii.

[2] Hertz, *Zs. für Physik*, vol. xxxii. p. 933.
[3] See Goudsmit, *Zs. f. Physik*, vol. xxxii. and Back, vol. xxxvii.