

# On the Origin of the X-Ray Non-Diagram Lines in the $K$ Series

By

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(Received November 21, 1931)

## Abstract

To establish a scheme for the X-ray non-diagram lines (frequently called "spark lines" or "satellites"), the author assumed two-electron jumps in a doubly-ionized atom, obeying the Heisenberg selection rule for the quantum number  $L$ . The  $\frac{\nu}{R}$ -values were computed by this hypothesis and compared with the experimental data.

The results arrived at, which seem to account for the origin of these lines, are:

ORIGIN		NON-DIAGRAM LINE	ORIGIN		NON-DIAGRAM LINE
Initial state	Final state		Initial state	Final state	
$KL_I$	$L_I M_{II,III}$	$K\beta'''$	$KM_I$	$M_I M_{II,III}$	$K\beta''$
$KL_{II,III}$	$L_{II,III} M_{II,III}$	$K\beta'''$	$KL_{II,III}$	$L_I M_{IV,V}$	$K\beta'$ (or $K\beta_2$ )
$KM_{II,III}$	$M_I M_{IV,V}$	$K\beta''$	$KL_{II,III}$	$L_I M_I$	$K\beta\eta$ (or $K\beta_4$ )

The intensity of these lines, except that of  $K\beta''$ , was estimated from the experimental values of the lines of the  $L$  series, and found in close agreement qualitatively.

The term multiplicities, and the effect of chemical combination are also discussed. It is of interest to notice that the scheme of the non-diagram lines  $K\alpha'$ ,  $\alpha_2$ ,  $\alpha_4$ ,  $\alpha_5$ ,  $\alpha_6$ , etc. can be included in  $KL_I - L_I L_{II,III}$  and  $KL_{II,III} - L_{II,III}^2$ , by the experimental rules of the transition probability obtained in this paper, although the author cannot calculate the  $\frac{\nu}{R}$ -values in the case of the  $\{LS\}$  coupling. Hence the result of Langer concerning the origin of the non-diagram line of the  $K\alpha$  group was included in the present scheme.

## Introduction

In the X-ray emission spectra of an atom, there are a number of faint lines which do not belong to the so-called "*diagram lines*".

It is obvious that the "diagram lines" are produced by transitions between ionized states in which one electron is missing from one of the  $K, L, M, \dots$  levels, and follows the Moseley law.

We call an X-ray emission line, whose frequency cannot be *directly* derived from the well-known system of X-ray absorption levels, a "non-diagram line".

The non-diagram lines are frequently called "satellites", since apparently they accompany an intense diagram line, although this is not always the case; or "spark lines", since Wentzel<sup>1</sup> suggested that the non-diagram lines might originate from a multiply-ionized atom in the inner electron shells.

The characteristic features of these lines are broad and diffuse, and it has been verified that these lines consist of unresolved components by many authors.

In the  $K$  series there are  $\alpha', \alpha_3, \alpha_4, \alpha_5, \alpha_6$ , as the  $K\alpha$ -satellites, and  $\beta', \beta'', \beta'''$ , as the  $K\beta$ -satellites<sup>2</sup>.

Recently H. Beuthe<sup>3</sup> has obtained the new non-diagram lines  $\beta\gamma$  and  $\beta\eta$ , according to his terminology, in many elements between Y (39) and V(23). The line  $\beta\gamma$  of Beuthe is the same as the line  $\beta'''$ , or seems to be the continuation of it. This point has been discussed by S. Kawata<sup>4</sup> and G. B. Deodhar<sup>5</sup>.

The present writer<sup>6</sup> also obtained similar lines to  $\beta\eta$  in some other elements.

In this paper the origin of the non-diagram lines of the  $K\beta$  series will be treated in detail.

In Table I are collected the  $\frac{\nu}{R}$ -value of the non-diagram lines measured by many investigators<sup>7</sup>. Many of them are computed from

1. G. Wentzel, Ann. d. Phys. **66**, 437 (1921).
2. Handb. d. Experimentalphysik **24**, 2, 236 (1930).
3. H. Beuthe, ZS. f. Phys. **60**, 603 (1930).
4. S. Kawata, Mem. Coll. Sci. Kyoto Imp. Univ. (A) **13**, 383 (1930).
5. G. B. Deodhar, Roy. Soc. Proc. (A) **131**, 633 (1931).
6. M. Sawada, a paper in course of publication.
7. E. Hjalmar, ZS. f. Phys. **1**, 439 (1920); **7**, 341 (1921); Phil. Mag. **41**, 675 (1921).  
 V. Dolejšek, C. R. **174**, 411 (1922).  
 V. Dolejšek and M. Siegbahn, ZS. f. Phys. **10**, 159 (1922).  
 T. Wetterblad, ZS. f. Phys. **42**, 611 (1927); **49**, 670 (1928).  
 M. J. Druyvesteyn, ZS. f. Phys. **43**, 707 (1927); Dissertation, Groningen (1928).  
 S. Eriksson, ZS. f. Phys. **48**, 360 (1928).  
 S. v. Friesen, ZS. f. Phys. **58**, 781 (1929).  
 H. Beuthe, ZS. f. Phys. **60**, 603 (1930).  
 S. Kawata, *loc. cit.*

their wave-lengths by the present writer, use being made of the relation :

$$\log \frac{\nu}{R} = 5.9596469 - \log \lambda.$$

Table I

The  $\frac{\nu}{R}$ -values of the non-diagram lines in the  $K\beta$  group measured by Hjalmar (H.), Dolejšek (D.), Dolejšek and Siegbahn (D.-S.), Wetterblad (W.), Druyvesteyn (Dr.), Eriksson (E.), Friesen (F.), Beuthe (B.) and Kawata (K.)

Element	$\beta'''$ ( $\beta\gamma$ )	$\beta''$	$\beta'$	$\beta_2$	$\beta\eta$
11 Na	—	—	—	77.873 W.	—
12 Mg	—	—	—	94.46 H.W.	—
13 Al	116.55 116.99 Dr.	—	—	113.55 H. 113.31 W.	—
14 Si	137.28 137.95 Dr.	—	—	134.14 H.	—
15 P	159.87 160.46 Dr.	—	—	156.57 D.H.	—
16 S	184.45 Dr.	—	—	180.64 D. 180.56 H.	—
17 Cl	210.63 Dr.	—	—	206.82 D.	—
19 K	267.97 Dr. 267.67 W. 268.31	264.67 Dr. 264.71 H.	—	—	—
20 Ca	299.33 Dr. 299.01 W. 299.75	295.90 Dr. 295.95 H.	294.80 D.-S.	—	—
21 Sc	332.17 Dr.	329.28 Dr.	325.54 D.-S.	—	—
22 Ti	366.91 Dr. 366.94 F.	364.41 Dr.F. 364.32 F.	362.32 H. 361.95 F.	—	—
23 V	403.62 Dr. 403.63 F. 403.80 B. 403.34 403.95(V <sub>2</sub> O <sub>5</sub> ) B.	400.98 D. 400.84 F.	398.75 H. 398.32 F.	—	394.0 B.
24 Cr	441.99 Fr. 442.13 B. 441.82 442.13(Cr <sub>2</sub> O <sub>3</sub> ) B.	439.59 W. (Cr <sub>2</sub> O <sub>3</sub> )	436.91 D.-S.	—	431.5 B.
25 Mn	482.46 Dr. 482.06 483.23 B. 483.25(MnO) B. 482.97(MnS) B.	—	476.97 E.	—	FeK $\alpha$ B.

Table I *Continued*

26 Fe	524.59 524.41 524.45	Dr. B. K.	522.32 K.	518.81 E.	—	512.0 B.
27 Co	568.34 568.58	B. K.	565.97 K.	562.47 E.	—	555.0 B.
28 Ni	614.41	K.	611.56 K.	607.88 D.-S. E.	—	599.8 B.
29 Cu	—		659.32 K.	—	—	647.5 B.
30 Zn	710.87	B.	709.27 K.	—	—	696.3 B.
31 Ga	762.18	B.	—	—	—	746.3 B.
32 Ge	815.54	B.	—	—	—	803.8 B.
33 As	870.70	B.	—	—	—	—
34 Se	927.70	B.	—	—	—	—
35 Br	986.66	B.	—	—	—	—
37 Rb	1110.8	B.	—	—	—	—
38 Sr	1175.4	B.	—	—	—	—
39 Y	1242.9	B.	—	—	—	—

### Historical

To account for the origin of the non-diagram lines of the  $K$  group, the following explanations have been proposed by various investigators.

(1) N. Seljakow and A. Krasnikow<sup>1</sup> suggested that the  $K\beta'$  line is a diagram line and that the combination of the lines  $K\beta_1$  and  $K\beta'$  is a "relativity doublet". But its  $\Delta\lambda$  does not coincide with the value calculated from the frequency difference of the  $M_{II}$  and  $M_{III}$  levels.

(2) G. Coster and J. M. Druyvesteyn<sup>2</sup> ascribed the origin of the  $K\beta'$  line to the influence of the incomplete  $M_{IV,V}$  shells on the  $M_{II,III}$  levels, so this line is a component of  $K\beta_1$ . This view is opposed by G. Ortner<sup>3</sup>.

(3) G. Ortner<sup>3</sup> assumed new  $M'$  levels in the iron group and

1. N. Seljakow and A. Krasnikow, *ZS. f. Phys.* **33**, 601 (1925).

2. G. Coster and J. M. Druyvesteyn, *ZS. f. Phys.* **40**, 765 (1927).

3. G. Ortner, *Wien. Sitzungsber. (IIa)*, **135**, 71 (1925); **136**, 369 (1927).

explained that the  $\beta'$  lines are the transitions from the  $M'$  level to the  $K$  level.

(4) M. J. Druyvesteyn<sup>1</sup> has numerically confirmed that the lines  $K\beta''$  and  $K\beta'''$  are due to the electron transition from the  $M$  shell to the  $K$  shell of the atom singly-ionized at an  $M$  or  $L$  shell respectively.

(5) H. Beuthe<sup>2</sup> proposed that when (say)  $K$ - and  $L_{III}$  shells are ionized simultaneously by a swiftly moving cathode-ray electron, the  $M_V$  electron jumps to the ionized  $L_{III}$  shells and further jumps to the ionized  $K$  shell, and as a result the lines  $K\beta\gamma$  and  $K\beta\eta$  are emitted.

Thus he calculated their wave-lengths as follows :

$$\nu\beta\gamma(Z) = \begin{cases} \nu K\alpha_1(Z) + \nu L\alpha_1(Z) \\ \nu K\alpha_1(Z) + \nu L\alpha_2(Z) \\ \nu K\alpha_2(Z) + \nu L\beta_1(Z) \end{cases} \quad \nu\beta\eta(Z) = \begin{cases} \nu K\alpha_1(Z) + \nu LK(Z) \\ \nu K\alpha_2(Z) + \nu L\eta(Z) \end{cases}$$

But if this idea is adopted, there are rather large discrepancies between the observed and the experimental values especially in the case of the line  $K\beta\eta$ .

(6) G. B. Deodhar<sup>3</sup> suggested that the  $K\beta'$  line probably arises from the double jump  $M_I \rightarrow L_{III}$  and  $L_{III} \rightarrow K$ , and calculated their wave-lengths, but the discrepancies seem to be rather large.

### Theoretical

To establish a scheme for the non-diagram lines, the present author assumed two-electron jumps in a doubly-ionized atom obeying the Heisenberg selection rule<sup>4</sup> and arrived at a result which seems to account for the origin of the emission of these lines.

#### (I) Doubly-ionized atom

The possible modes of generation of a doubly-ionized atom are these : ionization by (i) a high-speed electron, (ii) X-rays, and (iii) *Auger* effect. In the elements here concerned the *Auger* effect is remarkably efficient in producing a multiply-ionized atom.

#### (II) Two-electron jumps

By two-electron jumps, the doubly-ionized atom changes into another doubly-ionized state. The difference of energy will be emitted as a

1. M. J. Druyvesteyn, ZS. f. Phys. **43**, 707 (1927).

2. H. Beuthe, *loc. cit.*

3. G. B. Deodhar, Roy. Soc., Proc. (A) **131**, 476 (1931).

4. M. Sawada, Mem. Coll. Sci. Kyoto Imp. Univ. (A) **14**, 248 (1931).

single quantum. Or more clearly to picture the process, it may be considered that, for example, by the transition of an electron of an outer orbit, the transition of an inner electron is *induced* and as the result of this process the atom emits a single quantum. Here it is assumed that this gives rise to a non-diagram line.

The non-diagram lines are known from element Y(39) to Na(11) for the  $K\beta$  group. The energy levels there concerned are the electrons from the  $K$ ,  $L$ ,....., and  $N_{I,III}$  shells, although some of them disappear as we pass to light elements. Hence many doubly-ionized states can be imagined, and if we pick out two of them at random, a very great number of combinations may result. Here we need a selection rule.

(III) *Selection rules for two-electron transitions*

In optical spectroscopy it is known that in the arc spectrum of a calcium-like atom new series are found which H. N. Russell and F. A. Saunders<sup>1</sup> attribute to the simultaneous jumping of two electrons. In this case it has been proved theoretically by Heisenberg<sup>2</sup> that  $l_i$  for one of them must change by  $\pm 1$ , and for the other by 0 or  $\pm 2$ . This leads to the more general Russell-Laporte rule, and the quantum mechanical proof of it has been given by E. Wigner<sup>3</sup> and H. Weyl.<sup>4</sup> But the observed combinations are almost without exception included under the Heisenberg rule. Recently S. Goudsmit and I. Gropper<sup>5</sup> proved that when two electrons jump, one can change only its  $n$ , and the other changes its  $l$  by  $+1$  or  $-1$ , and its  $n$  by an arbitrary amount, taking the first term of the series expansion for  $1/r_{12}$  (where  $r_{12}$  is the distance between two electrons) in the electrostatic interaction. From their paper<sup>5</sup>, it can be understood, after a little consideration, that this last rule is true irrespective of the type of  $\{LS\}$  or  $\{jj\}$  coupling. At any rate, it is assumed here that these rules are valid in the region of X-rays of light elements.

(IV) *The computation of the wave-lengths or  $\frac{\nu}{R}$ -values of the lines to be emitted by two-electron transitions*

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1. H. N. Russell and F. A. Saunders, *Astrophys. Journ.* **61**, 38 (1925).
  2. W. Heisenberg, *ZS. f. Phys.* **32**, 841 (1925).
  3. E. Wigner, *ZS. f. Phys.* **43**, 624 (1927); **45**, 601 (1927).
  4. H. Weyl, „Gruppentheorie und Quantenmechanik“ 181 (1928).
  5. S. Goudsmit and I. Gropper, *Phys. Rev.* **38**, 225 (1931).

For example take the combination of  $(LN)$  and  $(KM)$ , then the outer electron of an atom of the atomic number  $Z$  moves the field of an atom of the next higher element,  $Z+1$ . So the emitted frequency during the reorganization of the atom is given by  $\{M(Z+1) - N(Z+1)\}$ . At the moment when the jumping of the inner electron occurs, an outer electron is absent, so the frequency emitted is not precisely given by  $\{K(Z) - L(Z)\}$  although the correction will be of fairly small value. So here, as the  $\frac{\nu}{R}$ -values of the emitted frequency of a single quantum,

$$\{M(Z+1) - N(Z+1)\} + \{K(Z) - L(Z)\} \dots\dots\dots(1)$$

was chosen. This value of course must be equal to the energy change of the atom as a whole, namely,

$$\begin{aligned} KM(Z) - LN(Z) &= \{K(Z) + M(Z+1)\} - \{L(Z) + N(Z+1)\} \\ &= \{M(Z+1) - N(Z+1)\} + \{K(Z) - L(Z)\} \\ &\dots\dots\dots(2) \end{aligned}$$

The term values are taken from various authors' experimental and calculated values.

The various combination obeying the above selection rules were examined and finally the following combinations were found in best agreement with the experimental values and are collected in Table II.

In Fig. 1 the difference between the  $\frac{\nu}{R}$ -values of the  $K\beta$  non-diagram lines and the diagram line  $K\beta_1$ , and the calculated values, is plotted against the atomic number.

The coincidence is rather good if we take into consideration the fairly rough values of the  $L_I$  and  $M_I$  levels which are computed with the irregular doublet law. So as to the transitions  $KL_{II,III} - L_I M_I$  and  $KM_{II,III} - M_I M_{IV,V}$ , several computations were tried, various data given by different authors being used. These values are also plotted in Fig. 1. The estimation of the line  $\beta\eta$  is especially difficult owing to the lack of knowledge of the exact values of the  $L_I$  and  $M_I$  levels.

The  $K\beta'$  lines have not yet been observed beyond the element copper, so that the discrepancies between the values of  $KL_{II,III} - L_I M_{IV,V}$  and  $K\beta_1$ , may be due to the uncertainty as to the values of the  $L_{II,III}$  levels.

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1. R. Thoraeus, Phil. Mag. 1, 312 (1926); 2, 1007 (1926).  
 G. Kellström, ZS. f. Phys. 58, 511 (1929).  
 C. E. Howe, Phys. Rev. 35, 717 (1930).  
 B. C. Mukerjee and B. B. Ray, ZS. f. Phys. 57, 345 (1929).





Table II

The calculated  $\frac{\nu}{R}$ -values of the lines expected from two-electron transitions.

Element	$KL_I - L_I M_{II,III}$	$KL_{II,III} - L_{II,III} M_{II,III}$	$KM_{II,III} - M_I M_{IV,V}$	$KM_I - M_I M_{II,III}$	$KL_{II,III} - L_I M_I$	$KL_{II,III} - L_I M_{IV,V}$
11 Na	80.515	79.914	78.838	78.647	77.437	77.998
12 Mg	98.188	97.570	95.829	96.665	93.401	95.117
13 Al	117.072	116.560	114.084	114.929	111.604	113.649
14 Si	137.665	137.220	134.545	135.326	131.636	133.649
15 P	160.616	159.960	156.609	157.399	153.942	156.252
16 S	184.509	184.240	180.890	181.627	177.419	180.076
17 Cl	210.873	210.321	206.712	207.420	203.171	205.977
18 A.	240.711	240.140	236.294	236.972	232.377	235.335
19 K	268.292	267.810	264.452	264.812	259.114	263.114
20 Ca	299.662	299.220	295.490	295.664	289.888	294.38
21 Sc	332.970	332.450	328.850	328.804	322.482	327.58
22 Ti	367.890	367.300	363.672	363.336	356.656	362.32
23 V	404.384	404.060	400.176	399.839	392.707	398.610
24 Cr	443.062	442.550	438.527	438.090	430.773	436.976
25 Mn	483.187	482.760	478.657	478.226	470.305	476.834
26 Fe	525.207	524.790	520.631	519.959	511.779	518.807
27 Co	569.139	568.530	564.532	563.600	554.912	562.680
28 Ni	614.681	614.140	610.628	608.849	599.780	608.561
29 Cu	662.085	661.610	658.219	656.259	646.360	656.020
30 Zn	711.598	711.067	707.683	705.549	694.783	705.735
31 Ga	762.847	762.340	758.858	755.962	745.580	757.184
32 Ge	816.159	815.680	812.436	809.157	798.026	810.787
33 As	871.218	870.580	867.629	863.845	852.212	865.948
34 Se	928.261	927.720	924.334	920.619	908.335	922.760

1	$KL_I - L_I M_{II,III}$	$K\beta'''$	11	$KM_I - M_I N_{II,III}$	} not yet detected	
2	$KL_{II,III} - L_I M_{IV,V}$	$K\beta'$	12	$KM_{II,III} - M_I N_I$		
3	$KL_{II,III} - L_I M_I$	$K\beta\eta$	13	$KM_{IV,V} - N_I^2$		
4	$KL_{II,III} - L_{II,III} M_{II,III}$	$K\beta'''$	14	$KM_{IV,V} - N_I N_{II,III}$		
5	$KM_{II,III} - M_I M_{IV,V}$	$K\beta''$	15	$KM_{II,III} - M_{II,III} N_{II,III}$		
6	$KM_I - M_I M_{II,III}$	$K\beta''$	16	$KM_{IV,V} - M_{II,III} N_I$		
7	$KM_{II,III} - M_{II,III}^2$	$K\beta''$	17	$KM_{IV,V} - M_{IV,V} N_{II,III}$		
8	$KL_I - L_I N_{II,III}$	} not yet detected		.....		
9	$KL_{II,III} - L_{II,III} N_{II,III}$					.....
10	$KN_{II,III} - N_{II,III}^2$					.....

(V) *Intensity or transition probability*

(a) By examining the results given above, we come to the following experimental rules as to the transition probability:—

(i) The interaction of the end orbit of the outer electron and the initial orbit of the inner electron is large, the transition probability is also large and the intensity of the emitted line is strong. For example, the combinations  $KM_{II,III} - L_I N_I$ ,  $KM_I - L_I M_{II,III}$  and  $KM_I - L_{II,III} N_I$  are very weak and cannot be observed experimentally, and  $KM_I - M_I M_{II,III}$  or  $KL_{II,III} - L_I M_{IV,V}$  is fairly strong and can be observed in the spectrogram.

(ii) It is expected that the combination in which one electron is excited and another emits the energy cannot be found.

(iii) The combination in which the end orbit of the outer electron is on a lower energy level than the initial orbit of the inner electron cannot be found.

(b) It is expected that combination (10)–(17) will appear, but it is estimated that they will appear at the short wave-length side of the  $K$  absorption edge with few exceptions, so there is present an experimental difficulty due to the absorption of the radiation by the anticathode itself, as is also the case with  $K\beta'''$ .

(c) Now it is of interest to test the transition probability quantitatively. The group of transitions involving  $K \rightarrow L_I$  is related to the emission lines of the  $L$  series and their intensity can be estimated, putting aside the question of coupling, as follows:

Non-diagram line	Origin	Related lines in the $L$ series	Relative <sup>1</sup> intensity
$K\beta'''$	$(M_{II,III} \rightarrow L_I) + (L_I \rightarrow K)$	$L\beta_3 + \beta_4$	0.08
<i>not yet detected</i>	$(N_{II,III} \rightarrow L_I) + (L_I \rightarrow K)$	$\gamma_3 + \gamma_2$	0.02
$K\beta'$	$(M_{IV,V} \rightarrow L_{II,III}) + (L_I \rightarrow K)$	$\alpha_1 + \alpha_2 + \beta_1$	1.00
$K\beta\eta$	$(M_I \rightarrow L_{II,III}) + (L_I \rightarrow K)$	$l + \eta$	0.03
<i>not yet detected</i>	$(N_I \rightarrow L_{II,III}) + (L_I \rightarrow K)$	$\gamma_5 + \gamma_6$	0.003

This order of intensity is correct if we consider the coupling strength of two electrons there related.

(VI) *Term multiplicities*

Assuming pure  $\{LS\}$  coupling, the following term multiplicities can be expected as the intense ones.

1. Allison & Armstrong, Phys. Rev. **26**, 714 (1925). These values are of W (74).

For example :

$$\begin{array}{lll}
 K\beta\eta & {}^1S - {}^1P, & {}^3S - {}^3P \\
 K\beta'(K\beta_3) & {}^3D - {}^3P, & {}^1D - {}^1P \\
 K\beta'''(K\beta_2) & \begin{cases} {}^1P - {}^1S \\ {}^3P - {}^3S \end{cases} & \begin{cases} {}^1P - {}^1P \\ {}^1S - {}^1P \\ {}^3D - {}^3P \\ {}^3P - {}^3P \\ {}^3S - {}^3P \end{cases} \\
 K\beta'' & \begin{cases} {}^3D - {}^3P \\ {}^1D - {}^1P \end{cases} & 
 \end{array}$$

In the case of satellites of  $K\alpha$  the multiplets can be separated but in the case of  $K\beta$  they cannot be separated but give only diffuse lines.

But it is reported that in the case of the line  $K\beta'$  the breadth is greater for the lower elements and that it has been found to be two unresolved doublet-lines<sup>1</sup>. They are probably the lines  ${}^3D-{}^3P$  and  ${}^1D-{}^1P$ , in pure  $\{LS\}$  coupling, or due to the difference between  $L_{II}$  and  $L_{III}$  in pure  $\{jj\}$  coupling. It is well known that the  $\beta'''$  line is also resolved in two components, especially in lower elements.

This is probably the transition of the type  $KL_I - L_I M_{II,III}$ ,  $KL_{II,III} - L_{II,III} M_{II,III}$  or some other included in the transitions (10)-(17) given in section (IV).

(VII) *The effect of chemical combination*

(i) *The  $K\beta'''$  line (The  $K\beta_y$  line) Mn(25) - Ti(22)*

H. Beuthe<sup>2</sup> examined the effect of chemical combination of some elements : Mn(25), Cr(24), and V(23). In every case one line appears or disappears and the other remains in sensibly the same place not influenced by the chemical valency. The line which appears or disappears is probably the line due to a valency electron cooperating in the two-electron transitions.

(ii) *The  $K\beta''$  line K(19), Ca(20)*

This line is very weak and difficult to obtain. In potassium this  $K\beta''$  line is probably due to the transitions  $KM_I - M_I M_{II,III}$ , so it will not be chemically influenced. This has been experimentally verified by O. Lundquist<sup>3</sup>.

The  $K\beta''$  line of calcium is probably of the same origin. In the elements beyond calcium, the line due to these transitions will be

1. V. Dolejšek & H. Fišláková, Nature, **123**, 412 (1929).  
 2. H. Beuthe, *loc. cit.*  
 3. O. Lundquist, ZS. f. Phys. **33**, 901 (1925).

superposed on the  $K\beta_1$  line, and not separated as shown in Fig. 1.

(iii) *The  $K\beta'$  Line Ni(28)—K(19)*

This line is greatly affected by chemical combination, as has been reported by many authors, especially G. Ortner<sup>1</sup>.

This fact is clearly explained by the cooperation of an  $M_{IV,V}$  electron in this transition. In an element where no electron exists in the  $M_{IV,V}$  level, the  $K\beta'$  line will be completely missing, and even if the  $\beta'$  line exists it will be very weak.

Actually, in potassium, this  $K\beta'$  line is completely missing, and in calcium, it is very faint and hardly measurable.

(iv) *The  $K\beta_3$  line Cl(17)—Na(11)*

The non-diagram line  $K\beta_3$  is to be looked upon as the continuation of  $K\beta'$  in the region Ni—Ca, as has been suggested by E. Hjalmar<sup>2</sup> and G. B. Deodhar<sup>3</sup>.

According to my view, this speculation seems to be supported by the following experimental facts.

(1) In the chemical compounds of P(15), the  $\beta_2$  line appears with the  $\beta_x$  line<sup>4</sup>.

(2) In the chemical compounds of S(16), the  $\beta_3$  line appears when  $\beta_x$  is stronger than  $\beta_1$ , the exception being some compounds where  $\beta_3$  is very weak. But these compounds are expected to be unstable at the anticathode under the cathodic bombardment, and consequently it is not strange that the  $\beta_1$  line is stronger than  $\beta_x$ .

On the whole the  $\beta_3$  line is strong in the sulphate compounds.

(3) The  $\beta_3$  line of pure sulphur listed by Hjalmar is suppressed by Deodhar<sup>5</sup>.

(4) In Al(13), Mg(12), Na(11), the  $\beta_3$  line was stronger in the case of the oxide than the pure metal.

1. G. Ortner, Wien. Sitzungsber. (IIa), **135**, 71 (1925); **136**, 369 (1927).

2. E. Hjalmar, *loc. cit.*

3. G. B. Deodhar, Roy. Soc. Proc. A **131**, 476 (1931).

4. *Note on the origin of the  $\beta_x$  line.* It is well known that the cathode-ray bombardment and the consequent heating effects may cause a transformation of the substance placed on the anticathode. Therefore, the lines  $\beta_1$  and  $\beta_x$  are the diagram lines due to the transition  $M_{II,III} \rightarrow K$  in the destroyed element and compounds. From many experimental facts found by various authors, it seems to be verified that in the elements from Cl(18) to P(15), the long wave-length one is due to free element and the short wave-length one is due to the chemical compound, and from Si(14) to Na(11) the reverse is the case. The cause of this peculiar fact is probably intimately related to the fact that the elements from Cl(17) to P(15) are electronegative, and those from Al(13) to Na(11) are electropositive.

5. G. B. Deodhar, *loc. cit.*

From the above-cited evidence, it can be accepted that the chemical compound gives the  $\beta_3$  line strongly.

In the present scheme, the origin of the  $\beta_3$  line is the transition  $KL_{II,III} - L_I M_{IV,V}$ .

The objection to this view is that the existence of the  $M_{IV,V}$  electron in the lower elements has been questioned. Dealing with this point, recently F. London<sup>1</sup> showed that in the homopolar compound the distributions of the electrons are as follows:—

Element	Homopolar valency	No. of electrons		
		$M_I$	$M_{II,III}$	$M_{IV,V}$
P (15)	1	2	3	
	3	2	3	
	5	1	3	1
S (16)	0	2	4	
	2	2	4	
	4	2	3	1
	6	1	3	2
Cl (17)	1	2	5	
	3	2	4	1
	5	2	3	2
	7	1	3	3

In heteropolar compounds like MgO and  $Al_2O_3$ , all of the valency electrons cannot be considered as they are completely transferred to the oxygen atom<sup>2</sup>. At least one electron will exist in the  $M_{IV,V}$  levels or the  $M_{II,III}$  levels of Mg or Al atoms.

So the line  $\beta_1$  ( $M_{II,III} \rightarrow K$ ) should not be taken as a semi-optical one.<sup>3</sup>

And also there is a chance that the  $\beta_3$  line will appear.

Thus it can be concluded that some elements—in chemical combination and in the solid state, the  $M_{IV,V}$  levels are occupied by the valency electrons—will give rise to strong  $\beta_3$  lines.

(v) *The  $K\beta_4$  lines.*

In very stable compounds on the anticathode, such as strontium

1. F. London, ZS. f. Phys. **46**, 455 (1928); R. Swinne, Chemiker-Kalender **50**, III, 63 (1929).

2. Wyckoff, The Structure of Crystals, 272 (1924).

3. In the case of the halide of Na, the ionization is complete and really the  $\beta_1$  line is very difficult to obtain compared with that of  $Na_2O$ .

sulphide, barium sulphide, cadmium sulphide, the  $\beta_4$  line was found. This  $\beta_4$  line together with the  $\beta_4$  line of P and Si is probably the continuation of the non-diagram line  $\beta\eta$  in the region Ge—V, detected by Beuthe<sup>1</sup> and in the case of Ti by the author<sup>2</sup>.

### Remarks

(1) The lines  $K\beta\eta$  of Ge and  $K\beta'$  of Sc deviate from the  $\frac{\nu}{R}$ -curves of  $K\beta\eta$  and  $K\beta'$ .

But these are fitted into the transition of the type  $KM_I - M_I^2$ , although this is forbidden by the present scheme.

(2) *The origin of non-diagram lines of the  $K\alpha$  group*

If the rules mentioned in (V) (a) (i), (ii) and (iii) are valid, the origin of the  $K\alpha$  satellites may be expected to be the transitions  $KL_I - L_I L_{II,III}$  and  $KL_{II,III} - L_{II,III}^2$ . This scheme agrees with the recently published result of R. M. Langer<sup>3</sup>.

In conclusion the author wishes to express his hearty thanks to Prof. M. Ishino for his kind guidance and the interest he has taken in this research, and also to Prof. M. Kimura, Dr. Y. Nishina and Mr. S. Kawata for much valuable advice during this work.

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1. Beuthe, *loc. cit.*

2. M. Sawada, *loc. cit.*

3. R. M. Langer, *Phys. Rev.* **37**, 457 (1931).