8. *X-ray Energy Level Diagrams; the Selection Rules and Exceptions to Them*

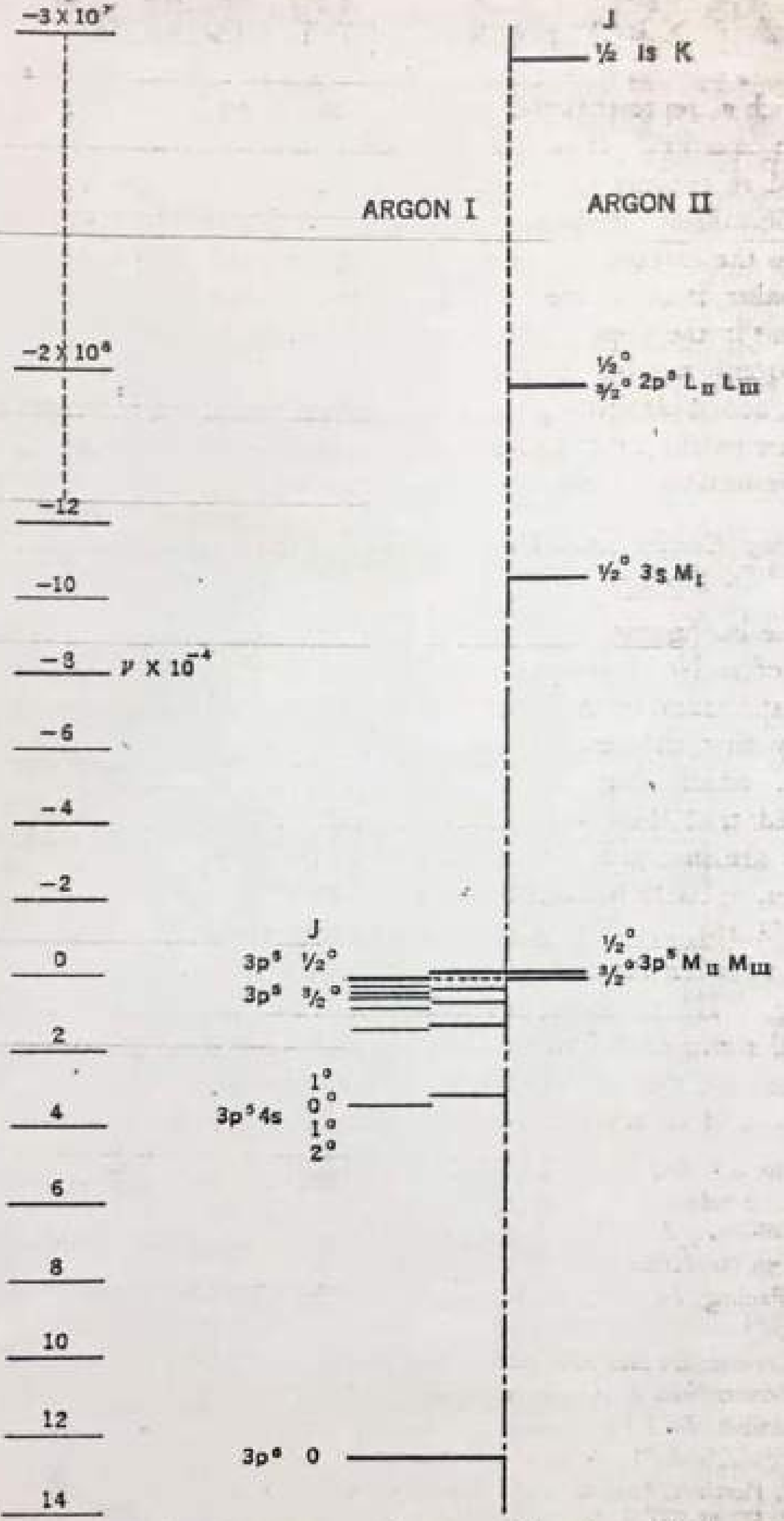
The configuration p^5 is the only unclosed group in the normal state of 10 Ne II and 18 A II. After the remarkable analysis of the Ne I spectrum by Paschen,[32] Meissner[33] made the important discovery that the series found by Paschen converge to two different limits, which thus are the normal levels of Ne II. Grotrian[34] realized that these two limits are really the $L_{II}L_{III}$ terms of neon, which are inverted, and showed that the wave-number separation, 780 cm.$^{-1}$, could be satisfactorily explained by Sommerfeld's formula (eqs. (8.18), (8.19)). This was probably the first direct connection found between the optical and x-ray terms of a given element.

Fig. VIII–16 shows an analogous case, the convergence of the optical terms of A I to two limits which arise from the configuration $3p^5$, and are the $M_{II}M_{III}$ levels of argon.[35] In this figure the zero of energy and of wave-number is chosen for the configuration $3p^5$ in

[31] The following papers deal with various aspects of the problem of calculation of x-ray term values:

G. Wentzel, Zs. f. Physik **6**, 84 (1921); Zs. f. Physik **16**, 46 (1923); Ann. der Physik **76**, 803 (1925).

L. Pauling, Zs. f. Physik **40**, 344 (1926); Proc. Roy. Soc. London. A **114**, 181 (1927).



VIII–16. Optical and x-ray terms of argon. Only a few of the known optical levels are shown, namely, those arising from $3p^4ms$.

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such an orientation that it gives rise to a term whose $J = 3/2$. Only a few of the known optical terms are shown, those included belonging to the configurations $3p^5ms$; $m = 4, 5, 6 \ldots$. The J values of these terms are given, and a superscript o added to indicate odd terms, the significance of which will be explained presently. Terms on the left hand of the center vertical line belong to Argon I; the x-ray terms on the right belong to Argon II.[36] The energy values of the optical levels are negative, with the exception of $3p^5$, $J = \frac{1}{2}^o$, and by eq. (8.15) the corresponding optical terms have positive wave-numbers. According to this convention, the x-ray terms have positive energies and negative wave-numbers.

Fig. VIII–17 shows the complete x-ray energy level diagram for a heavy element, indicating the transitions giving rise to lines in the K, L, M groups. In this figure no attempt is made to plot the energy values to scale. On the extreme right only the J values of the terms are given, since we have shown that the properties of the levels can be explained without assuming any coupling type. The strict interpretation of the symbol $2^2P_{1/2, 3/2}$ applied to the L_{III} level would mean that the l vectors of the five p-electrons were coupled to form a resultant $L = 1$, as indicated for two electrons in Fig. VIII–11*a*. More probably the coupling for these x-ray levels is intermediate between the type illustrated in Figs. VIII–11*a* and VIII–11*b*, and the L has little or no significance.

It is seen that in Fig. VIII–17 not all combinations of the x-ray terms appear as spectrum lines, which is an example of the working of the selection principles. In every spectrum, the terms may be divided into two great classes, called even and odd. In spectra in which the configuration underlying the level is unknown, this assignment can nevertheless usually be made from the experimental data. If the configuration is known, the term is even if the sum of the l values of the electrons is even, and odd if this sum is odd. Thus the L_{II} and L_{III} levels are odd, with $\Sigma l = 5$; the $M_{IV}M_{V}$ levels are even, with $\Sigma l = 18$. The selection rules for x-ray spectra may be stated as follows:

(*a*) Only transitions between odd and even terms occur, no two even or odd terms combine.[37]

(*b*) Permitted transitions involve $\Delta J = 1, 0$, or -1.

[36] The inclusion of the x-ray terms in the first spark spectrum was clearly indicated by R. T. Birge, Phys. Rev. **29**, 922 (1927).

[37] This method of stating the x-ray selection rules is not new, having been invented by Coster, who classified the terms with the letters *a* or *b*, such that only the *ab* combinations occur. If the coupling is Russell-Saunders, a rule equivalent to this is that $\Delta L = \pm 1$.

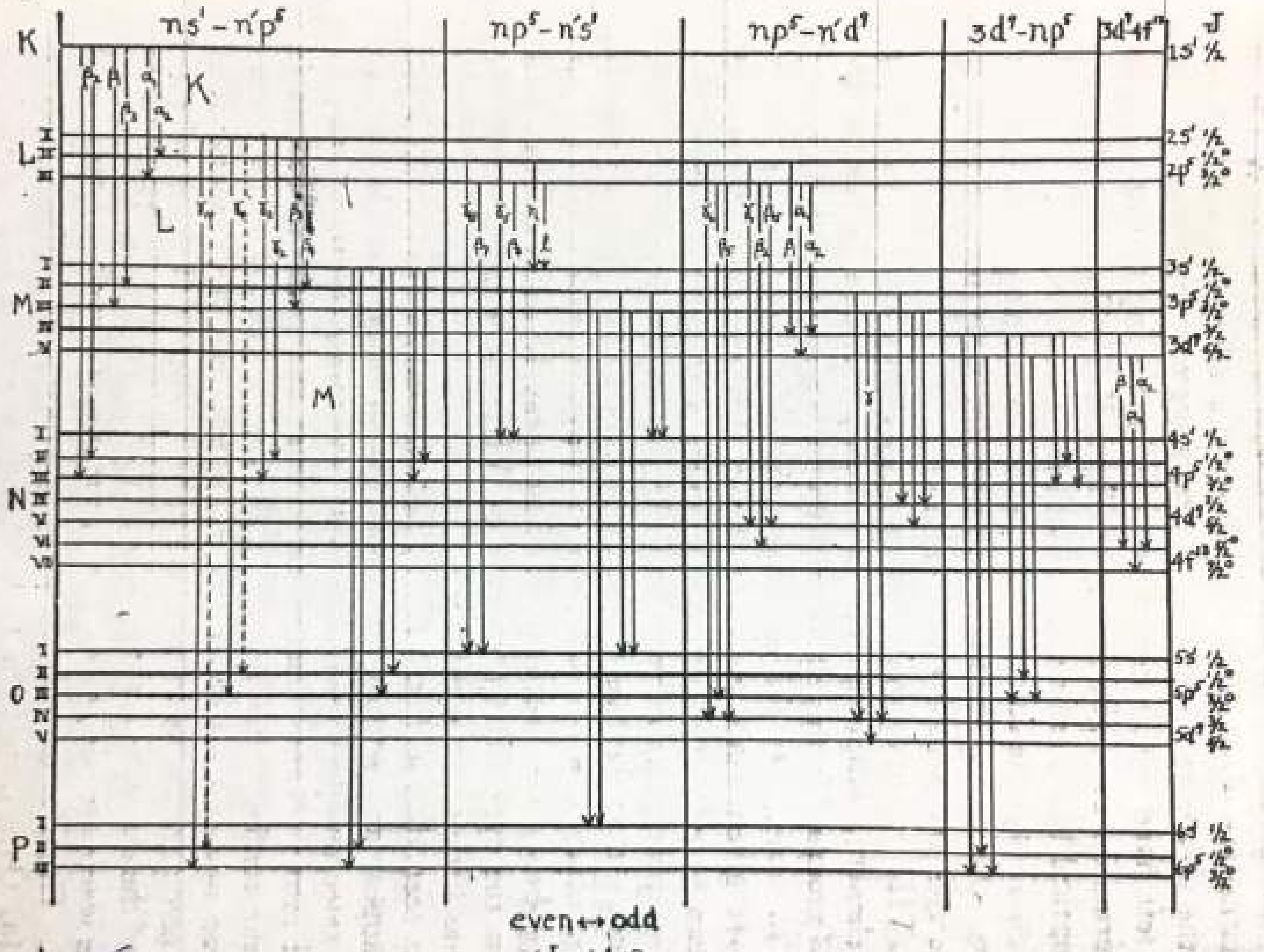

Fig. VIII-17. Qualitative term diagram for x-ray levels, showing lines in the *K*, *L*, and *M* series. No attempt has been made to plot the energy levels to scale.

The above rules are well known in optical spectra. In addition to these rules, lines in which n does not change are very weak or absent. This apparent rule does not operate in optical spectra, the sodium D lines, $3^2S_{1/2}-3^2P_{1/2, 3/2}$ showing $\Delta n = 0$. If the transitions $L_I-L_{II}L_{III}$ exist in uranium, the lines should be found in the region of its M-series, and are not observed.[38] It has been suggested that the failure to observe these lines is connected with the ν^4 factor which appears in the intensity of radiation from a dipole (eq. (8.45)), and is taken over into the quantum mechanical theory of spectral intensities. Thus the frequency of the radiation resulting from the $L_I-L_{II}L_{III}$ transitions in question is so much smaller than that due to other possible transitions having L_I as initial state (i.e., $L\beta_3$, $L\beta_4$) that the intensity is negligible. In the very soft x-ray region, lines have been discovered which are attributed to the transitions $N_{IV}-N_{VI}$ and $N_V-N_{VI, VII}$.[39] Here the difference in the frequencies of possible transitions from the initial state is not so great as in the example previously cited.

Although the selection rules given account for the great majority of the observed x-ray lines, exceptions to them have been observed. These lines are always of low intensity compared to the more prominent diagram lines. In their investigation of the relative intensities in the tungsten L spectrum Allison and Armstrong[40] found that the ratio of the intensity of the forbidden lines $L\beta_9$ and $L\beta_{10}$ (L_I-M_V, L_I-M_{IV}) to the line $L\beta_3$ (L_I-M_{III}) is about 0.04 at 30.7 kv. in 74W. The line $L\beta_3$ is however one of the weaker L group lines, having at 30.7 kv. an intensity relative to $L\alpha_1$ ($L_{III}-M_V$) of only approximately 0.08. Ross[42b] has estimated that the intensity of the forbidden line $K\beta_5$ in 42 Mo and 45 Rh ($K-M_{IV, V}$) is of the order of 1/1000 of that of $K\alpha_1$ ($K-L_{III}$), although in 46 Pd the corresponding fraction seems to be nearer 1/250. Idei[41] has recently given a discussion of these lines, based upon his measurements in the K and L series, and most of the data in Table VIII–16 are taken from his report.

In the K series, a line is found in elements up to and including 29 Cu which was at first thought to be $K\beta_2$ ($K-N_{II}N_{III}$) because of its analogous position to that occupied by this line in heavier elements.

[38] D. Coster, Phil. Mag. 43, 1070; 44, 546 (1922).
[39] S. Idei, Nature 123, 643 (1929).
J. Thibaud, Compt. Rend. 188, 1394 (1929).
[40] S. K. Allison and A. Armstrong, Phys. Rev. 26, 714 (1925).
[41] S. Idei, Sci. Rep. Tohoku Imperial University I, 19, 559 (1930); 19, 641 (1930).

However, according to our ideas of the building of the periodic system, electrons do not enter the $N_{II}N_{III}$ shells below 31 Ga. Idei has shown that below 29 Cu the line in the position considered here corresponds closely to the transition K–$M_{IV}M_{V}$, a forbidden transition. He has therefore called this line $K\beta_5$. Beuthe[42] has measured a weak K series line up to 39 Y which is probably the extension of this line even after a regular K–$N_{II}N_{III}$ transition becomes possible. New

TABLE VIII–16

EXCEPTIONS TO THE SELECTION PRINCIPLES IN THE K AND L GROUPS

K group

Transition	Symbol	Type of Exception	Remarks
K–$M_{IV}M_{V}$	$K\beta_5$	Even-even	Found from 23 V to 51 Sb.
K–$N_{IV}N_{V}$	$K\beta_4$	Even-even	In 41 Cb, 42 Mo, 47 Ag, 51 Sb, called δ by Ross.

L group

Transition	Symbol	Type of Exception	Remarks
L_I–M_{IV}	$L\beta_{10}$	Even-even	From 73 Ta to 92 U
L_I–M_{V}	$L\beta_9$	Even-even	From 73 Ta to 92 U
L_I–$N_{IV,V}$	$L\gamma'_{2,3}$	Even-even	May be a spark line.
L_I–N_{V}	$L\gamma_{11}$	Even-even	In 74 W and 90 Th.
L_{II}–$N_{VI}N_{VII}$	Lv	Odd-odd	In 74 W, 77 Ir, 92 U.
L_{II}–M_{III}	$L\beta_{17}$	Odd-odd	β_{11} (Dauvillier)
L_{III}–$N_{VI}N_{VII}$	Lu	Odd-odd	73 Ta to 92 U
L_{III}–M_{II}	Lt	Odd-odd	73 Ta to 92 U.
L_{III}–M_{III}	Ls	Odd-odd	73 Ta to 92 U.

lines in the K group have been discovered by Duane,[42a] using a high resolving power photographic spectrometer; Ross,[42b] using a double spectrometer, and Carlsson,[42c] using a crystal of mica bent around the surface of a cylinder. Carlsson, working with molybdenum and silver targets, found evidence of the lines $K\beta_4$ and $K\beta_5$ listed in Table VIII–16, and found satisfactory agreement

[42] Beuthe, Zs. f. Physik **60**, 603 (1930).
[42a] W. Duane, Phys. Rev. **37**, 1017 (1931); Proc. Nat. Acad. Sci. **18**, 63 (1932).
[42b] P. A. Ross, Phys. Rev. **39**, 536 (1932); **39**, 748 (1932); **43**, 1036 (1933).
[42c] Carlsson, Zeits. f. Physik **80**, 604 (1933).

between calculated and observed frequencies on the postulated transitions. Ross worked in 42 Mo, 45 Rh, 46 Pd, 47 Ag, 41 Cb and 51 Sb. He found the lines δ and β_4, which are probably identical with β_4 and β_5 of Table VIII–16 respectively. In addition, he found a line called by him β_5, of wave-length only slightly shorter than β_1, which was not detected by Carlsson.

The lines $L\beta_9$ and $L\beta_{10}$ are probably the most intense lines violating the selection principles in the L group. The violations of the selection principles observed in x-rays are similar to those known in optical spectra, the observed combinations of ^2S and ^2D terms in the sodium and potassium arc spectra (even–even or $\Delta l = 2$) being one of the numerous possible examples.[43]

Siegbahn[44] has pointed out that in certain cases there is evidence that the x-ray critical absorption limits correspond to removal of an electron from an inner shell to an outer incomplete shell or optical level, rather than to infinity, and that in these cases we must apply the selection principles in absorption. Sandström[45] has shown that in the elements 73 Ta to and including 79 Au the frequency of the L_{III} absorption limit coincides with that of the line $L\beta_5$ (L_{III}–$O_{IV,V}$). The O shells of the final state are unfilled in this region of the periodic system. If the absorption act consists in the removal of the electron to infinity, we should, by Fig. VIII–17, have

$$(\nu/R)_{L_{II}} - (\nu/R)_{L\beta_1} = (\nu/R)_{M_{IV}}$$

and

$$(\nu/R)_{L_{III}} - (\nu/R)_{L\alpha_1} = (\nu/R)_{M_V}.$$

When the most precise measurements of these quantities[45a] are used in the attempt to verify these relationships, however, discrepancies larger than the experimental error are found. This is probably due

[43] References to articles dealing with lines arising from violations of the selection principles, other than those already given, are:

Coster, Phil. Mag. (6), **43**, 1070 (1922).

Rogers, Proc. Camb. Phil. Soc. **21**, 430 (1922–23).

Crofutt, Phys. Rev. **24**, 9 (1924).

Eddy and Turner, Proc. Roy. Soc. Lond. A **114**, 605 (1927).

Auger and Dauvillier, Compt. rend. 176, 1927 (1923).

[44] M. Siegbahn, Zs. f. Physik **67**, 567 (1931).

[45] A. Sandström, Zs. f. Physik **66**, 784 (1930).

[45a] L group lines. S. Idei, Sci. Rep. Tohoku Imperial University **19**, 559 (1930).
M absorption limits. E. Lindberg, Zs. f. Physik **54**, 632 (1929).
L absorption limits. A. Sandström, Zs. f. Physik **65**, 632 (1930).

to the fact that the L and M limits in question do not represent removal of the electron to infinity, and because of the selection rules the electron removed from the L limits in question must go to a different outer level than is possible for an electron ejected from the pertinent M levels. This leaves room for a so-called "combination defect," which would be the energy difference between the outer levels to which the L and M electrons are ejected. Siegbahn further shows that such a "defect" does not occur when the equation

$$(\nu/R)_{L_{III}} - (\nu/R)_{L\beta_2} + (\nu/R)_{M_{III}-N_{V}} = (\nu/R)_{M_{III}}$$

is tested, due to the fact that electrons ejected from L_{III} and M_{III} could go to the same outer level.