EXPERIMENTS ON THE RELATIVE INTENSITIES OF SOME X-RAY LINES IN THE L SPECTRUM OF TUNGSTEN AND THE K SPECTRUM OF COPPER

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Abstract

Tungsten L series lines.—The experiments of Duane and Patterson on the strong lines in the L series of tungsten were repeated with improved apparatus, and also some of the weaker lines were studied. The value 10 obtained by Duane and Patterson for the relative intensity of $L\alpha_1$ to $L\alpha_2$ was confirmed. The theoretical ratio is 9. For the β group the *relative intensities* were found to be, $\beta_1 : \beta_2 : \beta_3 : \beta_4 : \beta_5 : \beta_6 : \beta_7 : \beta_9 : \beta_{10} = 100 : 49.3 : 15.0 : 7.7 : .47 : 2.0 : .4 : .68 : .60$. The relative intensities of the weak lines among themselves are not very reliable on account of the faintness of the lines and the critical absorption of the target, yet it is clear that the forbidden lines β_9, β_{10} are of the same order of intensity as β_5, β_7. For the γ group the relative intensities were found to be, $\gamma_1 : \gamma_2 : \gamma_3 : \gamma_4 : \gamma_5 : \gamma_6 : \gamma_8 = 100 : 14.0 : 22.3 : 7.0 : 3.0 : 2.3 : 1(?)$. γ_8 could not always be obtained. The determination of the intensity ratios for α_1, β_1 and β_2, γ_1 was complicated by absorption in the target. The agreement of the observed value of the intensity ratio for β_3/β_4 with the theoretical value 2, tends to confirm Stoner's suggestion that there are twice as many electrons in the M_{22} orbit as in the M_{21}. The deviation of the observed intensity ratio for γ_3/γ_2 from 2 may be due to the influence of intervening levels.

Copper K series lines.—The average of two determinations of the *relative intensity* of β to γ gave 100/2.4. No reliable evidence of the non-diagram lines $K\alpha_3\alpha_4$ was obtained at 30,700 volts.

THE experiments of Duane and Stenström[2] on the K series of tungsten and of Duane and Patterson[3] on the L series of tungsten and the K series of molybdenum furnish the first precision measurements of relative intensities of x-ray lines by the ionisation method, although the relative intensities of the K series lines of rhodium are shown in curves published still earlier by Duane and Hu[4] in their study of absorption and emission frequencies.

This problem of the relative intensities of x-ray lines has received a fresh impetus from the work of Ornstein, Burger, and Dorgelo on the relative intensities in the optical region.[5] These investigators have

[1] National Research Fellow.
[2] Duane and Stenström, Proc. Nat. Acad. Sci. **6,** 477 (1920).
[3] Duane and Patterson, Proc. Nat. Acad. Sci. **6,** 518 (1920); ibid **8,** 85 (1922).
[4] Duane and Hu, Phys. Rev. **14,** 369 (1919).
[5] Burger and Dorgelo, Zeits. f. Physik **23,** 258 (1924); etc.;
Ornstein and Burger, Zeits. f. Physik **24,** 41 (1924); etc.

found that the relative intensities of lines in multiplets are expressible in terms of whole numbers and are related to the inner quantum numbers of the states involved by the so-called "sum rules."

A. Sommerfeld[6] and also Coster and Goudsmit,[7] using the well-known optical analogy of the x-ray levels as a guide, have extended the results of Burger and Dorgelo to the region of x-ray spectra. Some of the theoretical relative intensities in the K and L series obtained by this method are shown in Table I.

TABLE I

Theoretical relative intensities resulting from the extension of the rules of Burger and Dorgelo to x-ray spectra.†

	Lines	Optical analogy	Relative intensity
K series	$\alpha_1 : \alpha_2$	$1s-2p_2, 2p_1$	2 : 1
	$\beta_1 : \beta_3$	$1s-3p_2, 3p_1$	2 : 1
	γ-doublet	$1s-4p_2, 4p_1$	2 : 1
L series	$\beta_3 : \beta_4$	$2s-3p_2, 3p_1$	2 : 1
	$\gamma_3 : \gamma_2$	$2s-4p_2, 4p_1$	2 : 1
	γ_4-doublet	$2s-5p_2, 5p_1$	2 : 1
	$l : \eta$	$2p_2, 2p_1-3s$	2 : 1
	$\beta_6 : \gamma_5$	$2p_2, 2p_1-4s$	2 : 1
	$\beta_7 : \gamma_8$	$2p_2, 2p_1-5s$	2 : 1
	$\alpha_1 : \alpha_2 : \beta_1$	$2p_2, 2p_1-3d_3, 3d_2$	9 : 1 : 5
	$\beta_2 : \beta_{15} : \gamma_1$*	$2p_2, 2p_1-4d_3, 4d_2$	9 : 1 : 5
	$\beta_5 : \beta_{16} : \gamma_6$*	$2p_2, 2p_1-5d_3, 5d_2$	9 : 1 : 5

† The notation is that recommended by Sommerfeld in the **4th** edition of "Atombau und Spektrallinien."

* The wave-lengths of β_{15} ($N_{32}\rightarrow L_{22}$) and β_{16} ($O_{32}\rightarrow L_{22}$) were measured and the lines named by Crofutt (Phys. Rev. **24**, 9, 1924).

In the K series it is well known that the relative intensity of $K\alpha_1/K\alpha_2$ is 2/1, as predicted in Table I. This ratio has been verified for a wide range of elements by the researches of Siegbahn and Žáček[8] and those of Duane and Stenström and Duane and Patterson referred to above. We have recently found[9] that the relative intensity of the components of the $K\beta$ doublet is also 2/1, as predicted. Since the $K\gamma$ doublet has not yet been separated, we cannot experimentally test the theoretical predictions in this case.

Unfortunately, only a few of the relative intensities predicted in the L series are suitable for experimental verification. With the exception of the combinations $\beta_3\beta_4$, $\gamma_3\gamma_2$, $\alpha_1\alpha_2$, and possibly $\beta_2\beta_{15}$, the lines in

[6] A. Sommerfeld, Ann. der Physik **76**, 284 (1925).

[7] Coster and Goudsmit, Naturwissenschaften **1**, 11 (1925).

[8] Siegbahn and Žáček, Ann. der Physik **71**, 187 (1923).

[9] Allison and Armstrong, Phys. Rev. **25**, 882 (1925); also preceding paper in this issue.

question are too far separated in wave-length or too weak to be measured at present.

The only previous measurements of relative intensities of lines in the L series, other than the qualitative visual estimation of photographic negatives, are those of Duane and Patterson[3] on the L series of tungsten. The results obtained by them are given in Table II. Sommerfeld[6] and Coster and Goudsmit[7] have pointed out that the intensity results of Duane and Patterson are in fair agreement with the predicted values of Table I, except perhaps in the case of $L\gamma_2$ $L\gamma_3$.

TABLE II

Results of Duane and Patterson on the relative intensities of L-series lines of tungsten.

Lines	Relative intensities
$\alpha_1 : \alpha_2$	10 : 1
$\beta_1 : \beta_2 : \beta_3 : \beta_4$	100 : 55 : 16 : 9
$\gamma_1 : \gamma_2 : \gamma_3 : \gamma_4$	100 : 14 : 18 : 6

We have recently repeated the experiments of Duane and Patterson with improved apparatus. The x-ray tube with which we worked had a water-cooled copper anode containing a button of tungsten on which the cathode rays from a Coolidge cathode fell. The radiation used in the spectrometer left the tube through a mica window .002 cm thick. This tube was constructed of glass and was pumped continuously while in operation on account of unavoidable leakage around the mica window. The tube was run at 20 m-amp. and a constant voltage of about 30.7 kv obtained from a high capacity 50 kv storage battery. This battery and the general arrangement of the apparatus have been described elsewhere.[10] The beam incident upon the calcite crystal was limited by two slits 37 cm apart. After reflection from the crystal the beam entered the ionisation chamber through a mica window .002 cm thick. The ionisation chamber was filled with the vapor of methyl iodide. It was constructed of Pyrex glass after the design developed in this laboratory[11] except that, as in the experiments of Duane and Patterson, an open end with a ground flange was substituted for the usual blown glass window. On this flange a steel plate in which a slit had been cut was fastened with DeKhotinsky cement and the mica was then cemented on to the plate over the slit. The resulting ionisation chamber was air tight and gave satisfactory results.

[10] Armstrong and Stifler, J. Opt. Soc. Amer. and Rev. Sci. Inst. **11**, 509 (1925).

[11] Blake and Duane, Phys. Rev. **10**, 624 (1917); cf also for description, J. C. Hudson, J. Opt. Soc. Amer. and Rev. Sci. Inst. **9**, 259 (1924).

The table which carried the crystal could be turned with precision through an angle of a few seconds and its position read by means of a traveling microscope sighted upon a Genevoise scale. The reflected beam was followed by turning the ionisation chamber through twice the angle traversed by the crystal after the well-known method of the Braggs.

The previous experiments of Duane and Patterson were made with the tube voltage slightly under 25 kv and with a tube which did not have a water-cooled target. By running our tube at 30,700 volts and 20 m-amp. we have been able to measure the relative intensities of the lines previously reported by Duane and Patterson with greater accuracy, and we have also been able to study some faint lines which they were not able to detect with certainty. The results which we have obtained agree well with the previous measurements.

The $L\alpha$ Lines

Duane and Patterson give for the relative intensity of $L\alpha_1/L\alpha_2$ the value 10. The predicted value (Table I) is 9.

We have made three measurements of the relative intensity of these lines. The resolution which we obtained was about the same as that shown in Fig. 3 of the previous report.[3] In this figure it is evident that the lines are not *completely* resolved, though doubtless they would appear so on a photographic negative. The base-line between α_1 and α_2 is not down to the level of the base-line on either side of the two lines. Elsewhere[12] we have described a method of estimating the relative intensities of such incompletely resolved lines based on the assumptions (1) that each line is single and of the same intrinsic wave-length breadth; (2) that the curve representing each line is symmetrical about the center of the line; (3) that the resolution is great enough so that the radiation due to a line is neligible at a wave-length $\lambda \pm 2\Delta\lambda$ (where $\Delta\lambda$ is the separation of the two lines). On the basis of these assumptions it is logical to take as a base-line for α_1 the total radiation intensity at an angle corresponding to the wave-length $\lambda(\alpha_2) - \Delta\lambda$ and for α_2 the total radiation intensity at $\lambda(\alpha_1) - \Delta\lambda$. By assumption (1) the ordinate from the highest point on the line to the appropriate base-line for the line is proportional to its intensity. In this way we have been able to correct for incomplete resolution, though the correction is almost negligible in the case of $L\alpha_2$ $L\alpha_1$.

Our three measurements of the ratio of the intensities of $L\alpha_1$ and $L\alpha_2$ gave the results: 10.3, 10.7 and 9.1. The average is 10.0, the same value as that obtained by Duane and Patterson.

[12] Allison and Armstrong, preceding paper in this issue.

THE Lβ GROUP

Besides the strong lines β_1, β_2, β_3, β_4 it is known from many researches[13] that a number of very faint lines lie in this region of the spectrum. In our present experiments we have been able to find evidence of β_5, β_6, β_7, β_9, β_{10}, though not of the line β_8 nor of the lines β_{15} and β_{16} of Crofutt.[13] This result should not be interpreted as questioning the reality of the

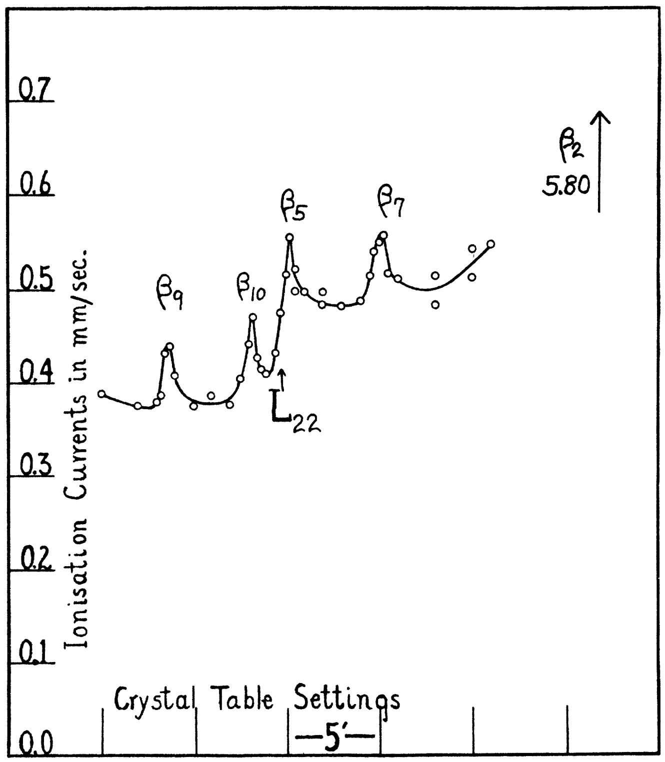

Fig. 1. Weak lines in the Lβ group.

lines, since they would undoubtedly appear with narrower slits than those we used. An attempt is now being made to separate β_2 and β_{15} in the third order.

Some of the β lines are shown in Fig. 1. On account of the wide range in intensity of these lines it is not practical to plot all of them on the

[13] E. Dershem, Phys. Rev. **11,** 461 (1918):
O. B. Overn, Phys. Rev. **14,** 137 (1919);
M. Siegbahn, Phil. Mag. **38,** 639 (1919);
D. Coster, Phil. Mag. **44,** 546 (1922), etc;
C. B. Crofutt, Phys. Rev. **24,** 9 (1924).

same scale. The results of the measurements are given in Table III. The critical absorption of the target (L_{22}) shows on the curve, and since β_9 and β_{10} are on the short wave-length side, the values for these two lines given in Table III can be considered only as minimum ones. The

TABLE III

Relative intensities of tungsten $L\beta$ *Lines.*

Date	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_9	β_{10}
May 19	(100)	51	16	8	....	2			
May 26	(100)	49	15	8	....	2			
June 13	(100)	48	14	7	....	2			
May 28	....	(49.3)	....	....	.5		....	.6	.3
May 29	....	(49.3)	....	....	.6	....	.6	.6	.6
June 11	....	(49.3)	....	....	.3	....	.2	.9	.9
June 11	....	(49.3)	....	....	....	....	....	.6	....
Averages	100	49.3*	15.0	7.7	0.47	2.0	0.4	0.68	0.60

* This value includes the small satellite β_{15} found by Crofutt.

values for the very faint lines β_5, β_7, β_9, β_{10} were difficult to reproduce in experiments carried out at different times. The slightest variation in the base-line due to general radiation and natural leak of the instrument was sufficient to change their apparent intensities greatly. The selection of a proper base-line for β_5 is complicated by the presence of the L_{22} absorption on its short wave-length side. Consequently the relative intensities of these small lines among themselves are not highly reliable, though their order of magnitude with respect to the more intense lines is of interest. The lines β_9 and β_{10} appear to be of about equal intensity.

The line β_6, which is not shown in the figure, appeared as a slight shelf on the long wave-length side of β_1.

Unfortunately, theoretical interpretations of most of the relative intensities which we have measured have not been advanced. The lines β_3, β_4, however, have according to our measurements an intensity ratio which is not appreciably different from the value 2 predicted in Table I. The lines β_9, β_{10} are generally supposed to represent transitions in violation of the selection principle, but at 30,700 volts, at least, they are of the same order of intensity as some of the permitted lines.

THE $L\gamma$ GROUP

In the γ group we have been able to obtain evidence of the lines γ_1, γ_2, γ_3, γ_4, γ_5, γ_6. In some of the curves we obtained slight evidence of γ_8, but the height of the peak above the general radiation was very variable. At times there seemed to be indications of the lines γ_{11} and γ_{12} of Crofutt,[13] but these were very uncertain. These lines must be very feeble. Fig. 2 is a composite of some of the curves obtained in this region. We have included readings which showed the presence of γ_8, although this

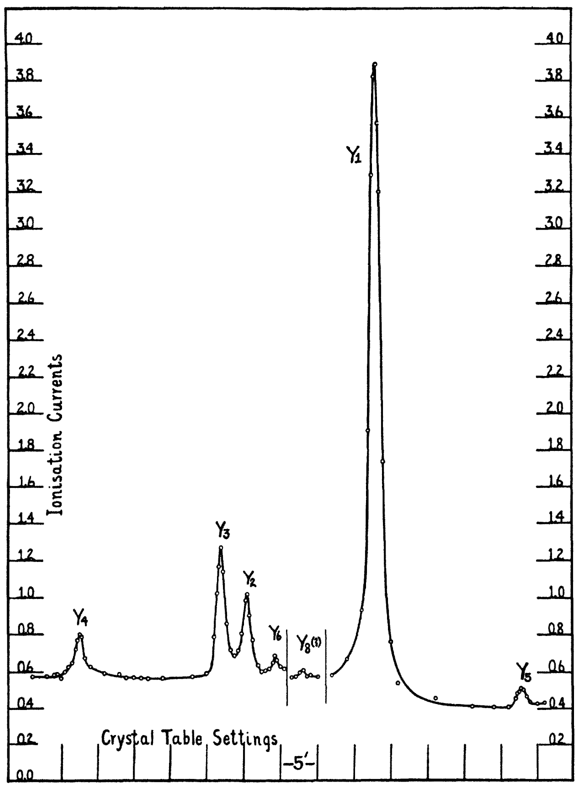

Fig. 2. The $L\gamma$ group of the tungsten spectrum.

peak could not always be reproduced with the same intensity. The intensity results are shown in Table IV. The estimation of the intensity of γ_6 is complicated by the absorption L_{21} which lies very near this line.

TABLE IV

Relative intensities of tungsten $L\gamma$ lines.

Date	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6	γ_8
May 21	(100)	14	24	....	....	3	1
May 22	(100)	14	22	....	3	1	1
May 25	(100)	14	21	7	....	3	
June 10	(100)	....	....	7	3	....	
Averages	(100)	14.0	22.3	7.0	3.0	2.3	1(?)

In the case of the lines γ_3, γ_2, for which the intensity ratio predicted by Table I is 2, we find 1.59. Duane and Patterson found 1.29. If their curves are corrected for incomplete resolution by the method in use in this work, a value may be obtained more nearly like that given here. In this case, then, we may state with some confidence that there is at least an apparent exception to the extension of the rules of Burger and Dorgelo. The lines in question are close together, so that corrections due to absorption by materials in the path of the beam do not enter. The deviation from the rule is not in the direction to be corrected for by absorption effects outside of the ionisation chamber. The electron transfers which produce these lines pass through the M groups between their initial and final states in the N and L levels, and it is possible that this passage through intervening electron orbits may change the intensity ratio from the simple predicted value.

Relative intensities of lines more widely separated in wave-length.

It is of course of great interest to measure the relative intensity ratios for such pairs of lines as α_1, β_1 and β_2, γ_1, for which the predicted values are 9/5. The difficulties accompanying such determinations, however, have not as yet been surmounted. From the results of Unnewehr[14] it is possible to correct for the absorption in the mica windows of the x-ray tube and ionisation chamber. The experiments of Davis and Stempel[15] indicate that the percentage of the monochromatic incident beam reflected by the crystal does not vary rapidly enough with wave-length to introduce large corrections. The point of uncertainty occurs in the absorption of the x-rays by the target itself. This is indicated in our curves by the presence of the L critical absorptions, notably L_{22}. A very small effective absorbing layer of the target substance would be sufficient to alter greatly the relative intensity of two such lines as α_1 and β_1. In our experiments β_1 was slightly more intense than α_1, while γ_1 was somewhat more than half as intense as β_2. It seems inadvisable to attempt to give values for use in testing theoretical predictions. Yet since the correction for absorption would change both ratios in the same direction, it could not bring them both to the value 9/5.

An interesting interpretation of the relative intensities in the $K\alpha$ doublet has been given by Stoner,[16] who points out that the observed ratio 2 may be taken as an indication that there are twice as many electrons in the L_{22} orbit as in the L_{21} orbit. He has extended this idea

[14] E. C. Unnewehr, Phys. Rev. **22,** 529 (1923).
[15] Davis and Stempel, Phys. Rev. **17,** 608 (1921).
[16] E. C. Stoner, Phil. Mag. **48,** 719 (1924).

to such lines as $L\beta_3$, $L\beta_4$, in which the influence of intervening electron levels is presumably small. Thus the observed intensity ratio 2 for $L\beta_3$, $L\beta_4$ is taken to be evidence that there are twice as may electrons in the M_{22} orbit as in the M_{21}. If the perturbing effect of the L levels on the $K\beta$ transitions from M to K is small, our result of 2 for $K\beta_1/K\beta_3$ could be used as additional evidence of the relative numbers of electrons in M_{22} and M_{21}. In the case of $L\gamma_3/L\gamma_2$, as Stoner has anticipated, there is a deviation which may well be due to the influence of intervening levels. Sommerfeld[6] has pointed out that the relative intensities of the

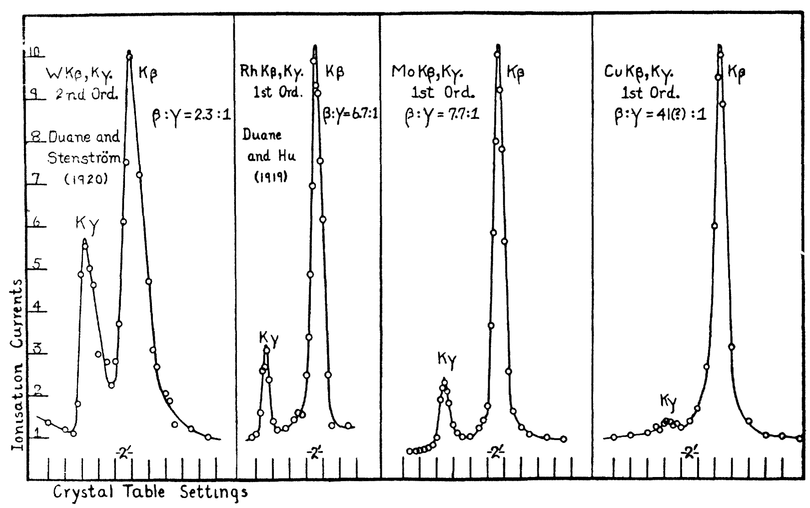

Fig. 3. Relative intensity of $K\beta$ to $K\gamma$ for W, Rh, Mo and Cu.

components of compound doublets are probably not related to the numbers of electrons in the orbits in the simple manner considered by Stoner.

INTENSITIES IN THE COPPER K SPECTRUM

The copper K spectrum was emitted strongly from the copper part of the anode. Siegbahn and Žáček[8] have measured the relative intensities of $\alpha_1 : \alpha_2 : \beta_1$ in the copper K spectrum and find 100 : 51.2 : 25.

We have made two measurements of the intensity ratio of β/γ. The γ line is extremely weak, and on account of the presence of the critical absorption in its immediate vicinity, estimates of its intensity are quite uncertain. For these two lines we have taken the difference between the highest point on the curve and the base-line as proportional to the intensity, since the uncertainty with regard to the γ line makes the more accurate method of area comparison superfluous. We obtained the values 100/2.7 and 100/2.2 for the intensity of β relative to γ.

It is known that the γ line becomes relatively weaker with decreasing atomic number, and we have drawn Fig. 3 to illustrate this fact. The values for tungsten are taken from the results of Duane and Stenström.[2] The curve for rhodium is obtained from one shown by Duane and Hu.[4] The numerical value of the intensity of Rh $K\beta$ relative to $K\gamma$ was determined by us by the method of areas. The curve for molybdenum is from the preceding paper.[12]

We have also examined the spectrum in the region of the non-diagram copper lines $K\alpha_3$, $K\alpha_4$, reported by Dolejsek and by Dolejsek and Siegbahn.[17] These lines have been interpreted as spark lines by Wentzel.[18] At 30,700 volts we could find no good evidence of this doublet, although the Cu $K\alpha_2$, $K\alpha_1$ lines were very strong. The relative intensity of $K\alpha_3$, α_4 to $K\alpha_1$ at this voltage must be less than 1/100. It is well known that in elements lighter than copper the intensity of these "spark" lines is greater relative to the lines due to the singly ionised atom.

We are greatly indebted to Professor William Duane for his valuable suggestions and kindly criticisms.

Cruft High Tension Electrical Laboratory,
Harvard University,
August 11, 1925

[17] Siegbahn, Spektroskopie der Röntgenstrahlen, p. 102.
[18] G. Wentzel, Ann. der Physik **66,** 437 (1921).