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AN EXPERIMENTAL STUDY OF THE RELATIVE INTENSITIES OF X-RAY LINES IN THE L-SPECTRUM OF THORIUM

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Abstract

The relative intensities of the thorium L-series lines have been measured at 31.8 kilovolts using an ionization chamber spectrometer. In addition to the lines previously reported by other investigators, the lines Th$L\eta$, Th$L\beta_7$, Th$L\gamma_2$ were found. No indications of Th$L\gamma_5$ or Th$L\gamma_4$ could be found. The relative intensities have been corrected for absorption in the mica windows and air in the path from x-ray tube to ionization chamber, and for the fraction of the radiation absorbed in the methyl iodide in the ionization chamber. It was found that in the voltage range between the critical excitation voltage V_0 and 31.8 kilovolts, the intensity of Th$L\alpha_1$ or Th$L\beta_{1,5}$ at any voltage V could be expressed by $I=k(V-V_0)^2$ within the limits of experimental error. Using this expression the relative intensities at 31.8 kilovolts were extrapolated to the relative intensities at high voltage, to which it was assumed the theoretical predictions apply. The intensity rules for doublets hold for lines involving the levels L_{21} and L_{22}. The predictions of Wentzel based on Schrödinger's new quantum mechanics for the relative intensities of "sharp" and "diffuse" series doublets are confirmed, but the experimental intensities of the "principal" series doublets are too low by a factor of 7. They are also too low in the measurements of Jönsson on tungsten. The results obtained are as follows:

Line	l	α_2	α_1	η	β_6	β_2	β_7	β_1	β_3	γ_5	γ_1	γ_2	$\gamma_3+\gamma_6$	γ_4
Rel. Int. (32 kv.)	3.6	12	100	1.1	1.4	26	.45	38	1.8	0	8.5	.81	3.1	0
Rel. Int. (high voltage)	3.6	12	100	1.8	1.4	26	.45	62	3.3	0	14	1.5	5.3	0

Introduction

The first estimates of the relative intensities of x-ray lines in the L-series were made by the visual observation of photographic plates. The observations of Coster[1] are particularly interesting. More precise measurements were made by Duane and Patterson,[2] and Allison and Armstrong[3] using an improved form of the Bragg ionization chamber method.

A fundamental problem in attempting to measure relative intensities of x-ray lines by the ionization currents produced in a gas is the question of the relative efficiency of different wave-lengths in producing gaseous ions. In an attempt to avoid this difficulty, Jönsson[4] has replaced the ionization chamber by a Geiger point-counter. It does not seem, however, that this

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[1] Coster, Phil. Mag. **43,** 1070 (1922) see especially page 1087.

[2] Duane and Patterson, Proc. Nat. Acad. Sci. **6,** 518 (1920); *ibid.* **8,** 85 (1922).

[3] Allison and Armstrong, Phys. Rev. **26,** 714 (1925).

[4] Jönsson, Zeits. f. Physik. **36,** 426 (1926); Zeits. f. Physik. **41,** 221 (1927). Since the subject matter of this paper is directly concerned with the first of the above papers by Jönsson, future reference in this article to the work of Jönsson will, unless expressly stated otherwise, refer to the first of these paper.

procedure has really avoided the main difficulty. For it is certainly true (speaking in the language of the corpuscular theory of x-rays) that not every quantum which enters the chamber of the point-counter produces a discharge, and it remains to be proved that the fraction of those entering to which the discharges are due is not a function of the wave-length. Nevertheless the fact that the measurements of Jönsson are in good agreement with those of Duane and Patterson, and Allison and Armstrong, seems to support the claims of both methods to give real measurements of relative *intensities* of x-ray lines. This question will be discussed again in a later section of this paper.

The measurements of Duane and Patterson and of Allison and Armstrong covered the relative intensities of lines in the γ, β, and α groups of the tungsten L-spectrum, but did not attempt to compare intensities of lines in different groups. This was first accomplished by Jönsson in tungsten and platinum. In as far as the measurements of Allison and Armstrong and those of Jönsson on tungsten can be compared, the agreement is fairly good. In one instance, the difference between the values reported seems to be outside the experimental error, namely the relative intensities of $L\gamma_3$ and $L\gamma_2$. Allison and Armstrong found 100:63, Jönsson 100:74. The reason for this is not yet clear. The difference between the reported values of $L\beta_3$ to $L\beta_4$ seems to be due to high absorption in the experiments of Allison and Armstrong, as suggested by Jönsson.

APPARATUS

(1) *Generating set.* 500-cycle alternating current was produced by a 2 kilowatt motor generator run on the laboratory storage battery circuit. The field current of the generator was supplied by the laboratory storage battery and regulated by appropriate resistances. The 500-cycle current went through the primary of an x-ray transformer, and the high potential 500-cycle current from the secondary was rectified by two kenotrons and stored up in a condenser which discharged through the x-ray tube.[5] The capacity (0.011 m.f.) was such that at the operating conditions (7.5 m.a. and 32 kv) the calculated voltage fluctuations were about 2.1 percent.

(2) *Voltage measurements.* The primary voltage on the high-potential transformer was read on a voltmeter with 0–240 volt scale. A rough indication of the voltage used on the x-ray tube was obtained from a General Electric attracted disc electrostatic voltmeter. Whenever in the course of the work it was essential to know the working voltage accurately (as in the measurement of the intensities of the lines as a function of voltage) the voltage was determined from the limit of the spectrum by the Duane-Hunt law (at the tube current and primary voltage used) and then the desired experiments were immediately performed. The measurement of high voltages by the Duane-Hunt law is probably as accurate a method as we now have for such work. The fluctuations in the root-mean-square voltage on the primary of the transformer were less than 0.5 percent.

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[5] A. W. Hull, Gen. Elect. Review, **19**, 173–81 (1916).

(3) *The x-ray tube.* The design of the x-ray tube is shown in Fig. 1. The tube was constructed of Pyrex glass. The cement used in attaching the removable metal parts was a high-vacuum cement with a chicle base, supplied by the Research Laboratories of the Westinghouse Electric Company. It proved to be very satisfactory. The metallic thorium used was obtained from the Westinghouse Lamp Works through the courtesy of Dr. C. T. Ulrey. It was in the form of a disk about 1 mm thick and 5 mm in radius. By working rapidly it was found that this could be spot welded to the face of the water-cooled copper target. The welds thus obtained were not highly perfect but nevertheless proved satisfactory. After welding, the face of the metallic thorium was filed down to a smooth surface. The portion of the radiation used in the spectrometer left the target at a glancing angle of 45° and went through a mica window 0.001 cm thick.

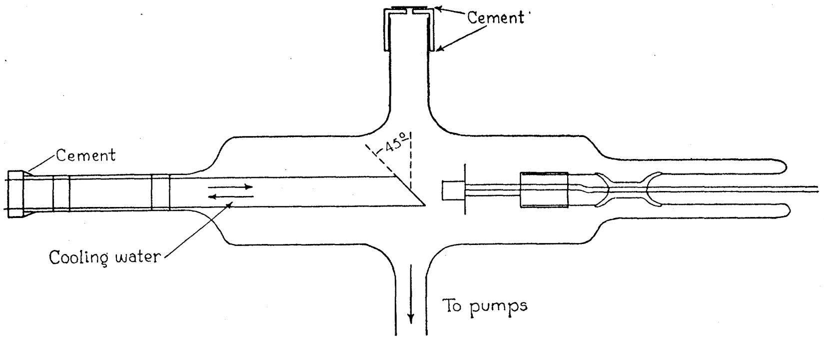

Fig. 1. X-ray tube with water-cooled copper target and mica window used in relative intensity measurements.

(4) *The spectrometer.* The spectrometer was a converted optical instrument. Settings of the calcite crystal could be made to 30'' of arc. The slits of the spectrometer were 42 cm apart and the width of each slit was 0.18 mm, making the angular breadth of the beam a little less than 3' of arc. The ionization chamber resembled closely those used by Duane[6] except that the window through which the radiation entered was of mica 0.001 cm thick, and the insulated electrode entered the chamber through an amberoid plug. The chamber was 32 cm long. The gas used in the chamber was methyl iodide. The ionization currents were measured with a Dolezalek electrometer and a lamp and scale arrangement giving a sensitivity of about 2.5 meters per volt.

MEASUREMENTS OF NEW WAVE-LENGTHS IN THE THORIUM L-SPECTRUM

In the course of the work several lines were found in the spectrum whose presence is called for by the energy level diagram and the selection principles but which have not been reported by previous investigators. These lines are all weak. A rough prediction of their wave-lengths was obtained from

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[6] J. C. Hudson, J. Opt. Soc. Am. and Rev. Sci. Inst. 9, 259 (1924).

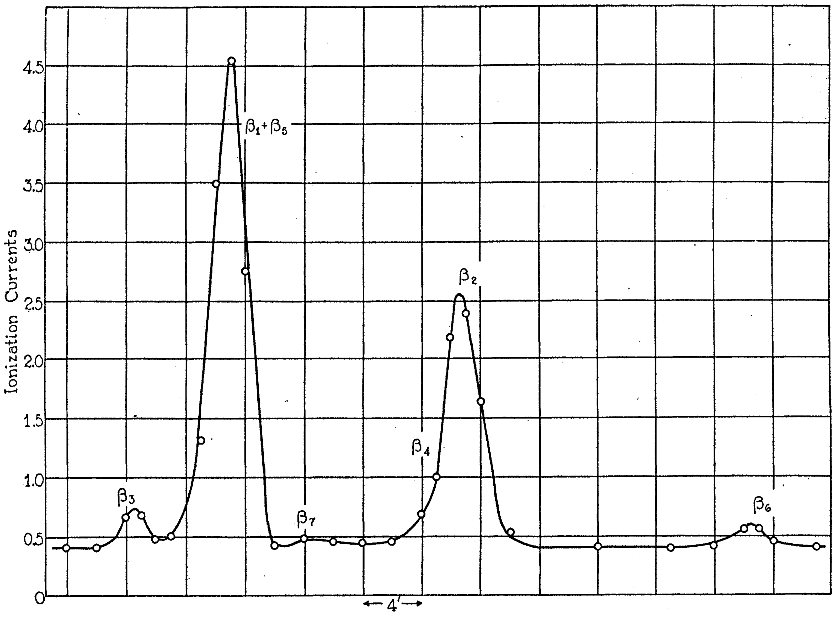

Fig. 2. Lines in the thorium $L\beta$ group. This curve is one taken merely for the purpose of locating the lines on the angular scale of the spectrometer, but gives a reliable indication of the relative intensities.

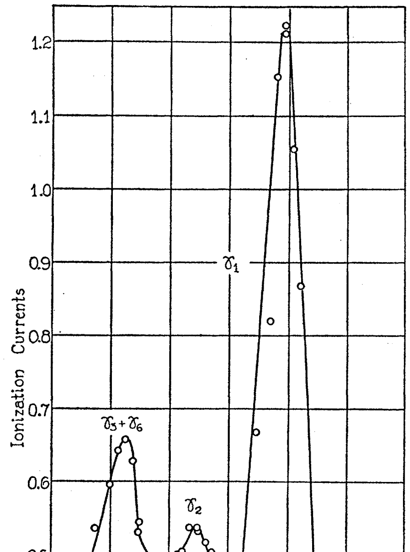

Fig. 3. Thorium $L\gamma$ group. In order to avoid a false impression of the intensity of these lines with respect to the general radiation it should be pointed out that the base-line of intensities is not that of zero intensity.

the energy level diagram for thorium given by Siegbahn in his "Spectroscopy of X-rays." The ν/R values of N_6, N_5, O_5, $O_{4,3}$ were estimated by interpolation. The following table gives the calculated and observed wave-lengths of the new lines. The spectrometer was not suited to wave-length measurements of high accuracy.

TABLE I

New wave-lengths in the thorium L-series.

Line	Calculated	Observed
η	852 (X. U.)	854 (X. U.)
β_7	772	772
γ_2	642	641

METHOD OF MEASUREMENT OF INTENSITIES

The intensity of a line was taken as proportional to the height of the tip of the peak above the base-line of the general radiation. In the case of the lines γ_3 and γ_6 which were not separated, the intensity of the combined lines relative to γ_1 was measured by comparing the products of the maximum ordinate by the half-breadth of the peak. This method has also been used by Jönsson in his second paper on intensities in the L series.

CORRECTIONS TO THE OBSERVED INTENSITIES

In order to obtain the relative intensities of the lines in the spectrum at some given voltage, the observed intensities must be corrected for relative absorption. The sources of this absorption may be listed as follows: (1) Absorption in the target itself due to generation of x-rays below the surface; (2) Absorption in the film of tungsten over the target due to the sputtering and vaporization of the tungsten filament; (3) Absorption in the mica windows and in the air path from the tube to the ionization chamber; (4) Absorption in the calcite crystal; (5) Correction for the fraction of the radiation absorbed in the ionization chamber.

(1) No correction was made for the absorption in the thorium target itself. It is believed[7] that for radiation leaving the target at 45° and voltages not above 2–3 times the critical voltage, this correction is very small for a smooth metallic target.

(2) No correction was made for the absorption in the film of tungsten over the target face. If this film is 10^{-5} cm thick the correction for the lines γ_1 and α_1 is of the order of 5 percent, which is of the order of the experimental error. To avoid this difficulty, Jönsson has used oxide coated platinum filaments. It seems to be difficult to obtain steady operating conditions with coated

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[7] The order of magnitude of this correction is difficult to estimate. Webster and Hennings (Phys. Rev. **21,** 301 (1923)) found evidence that there was a mean depth of production of x-rays in a molybdenum target at 30 kv. of 1.4×10^{-4} cm. This depth would probably be less for Th, but very little is known about the absorption coefficient of Th for its own L-radiation. Very rough guesswork places the correction to the L-lines most widely separated in wave-length as 3 to 4 percent.

filaments. Fortunately there are no coincidences in wave-length in the tungsten and thorium L-spectra.

(3) The correction for absorption in the air path and mica windows was calculated from the absorption coefficients for air given in Siegbahn's "Spectroscopy of X-rays," and for mica by Unnewehr.[8] The length of path in air was 58 cm; in mica 0.002 cm. The extent of the correction applied is shown in the table at the end of this section.

(4) No correction was made for the absorption of the radiation in the reflecting crystal. Experiments on this point by Davis and Stempel[9] and by Wagner and Kulenkampff[10] have shown that for calcite the percent of the incident monochromatic radiation reflected is practically independent of the wave-length throughout this range.

(5) For the harder lines of the thorium L-series, an appreciable fraction of the radiation passed through the methyl iodide vapor without being absorbed. It was assumed that the intensity of the radiation was proportional to the ionization current caused by that fraction which is absorbed. This has been shown to be true for air by the experiments of Kulenkampff.[11] Glocker[12] has stated that this is true for all gases if the radiation has wave-lengths sufficiently far removed from the critical absorption wave-lengths of the gas.

In order to make this correction it was necessary to know the pressure of the methyl iodide vapor in the ionization chamber. The methyl iodide in liquid form contained in a Pyrex glass bulb was attached to the ionization chamber and then was frozen by immersion in liquid air. The air in the ionization chamber was then pumped out and as the methyl iodide was allowed to return to room temperature its pressure in the chamber could be measured on a manometer. It was found that best results could be obtained with a pressure of 24 cms. This corresponds to a density of 1.65×10^{-3} grams of iodine per cc. The mass absorption coefficient of iodine for wave-length 1A was assumed to be 104, and to vary with the cube of the wave-length throughout the thorium L-spectrum. The length of the ionization chamber was 32 cm. Since the absorption of the line Th$L\alpha_1$ was practically complete, the correction to be applied to any other line of wave-length λ could be obtained from the expression

$$1/(1-e^{-\mu_\lambda t})$$

where μ_λ is the absorption coefficient for the wave-length λ. The resultant corrections from this formula are shown in the table at the end of this section. The fraction of the radiation transmitted by the methyl iodide vapor was scattered and absorbed in the glass wall at the rear of the ionization chamber. No correction was made for this contribution to the ionization current.

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[8] Unnewehr, Phys. Rev. **22**, 529 (1923).

[9] Davis and Stempel, Phys. Rev. **17**, 608 (1921).

[10] Kulenkampff, Ann. d. Physik. **68**, 369 (1922).

[11] Kulenkampff, Ann. der Physik. **79**, 97 (1926).

[12] Glocker, Zeits. f. Physik. **40**, 479 (1927).

TABLE II

Absorption corrections.

Line	λ (X. U.)	μ for air (t = 58 cm)	μ mica (t = .002 cm)	Correction factor for absorption outside chamber	μ for iodine (t = 32 cm)	Correction factor for absorption inside chamber	Total correction for absorption
l	1112	5.3×10^{-3}	36	1.17	23×10^{-2}	1.00	1.17
α_2	965	3.7	20	1.02	16	1.00	1.02
α_1	953	3.6	19	1.00	15	1.00	1.00
η	852	2.8	15	.95	11	1.03	.98
β_6	826	2.5	14	.94	10	1.05	.98
β_2	791	2.3	13	.92	8.6	1.07	.98
β_7	772	2.1	12	.90	7.9	1.09	.98
$\beta_1+\beta_5$	763	2.1	12	.90	7.6	1.10	.99
β_3	752	2.0	11	.90	7.3	1.11	1.00
γ_5	(673)	1.5	8.5	.88	5.1	1.24	1.09
γ_1	651	1.4	7.8	.86	4.8	1.27	1.10
γ_2	640	1.4	7.5	.86	4.5	1.32	1.14
$\gamma_3+\gamma_6$	632	1.3	7.4	.86	4.3	1.34	1.16
γ_4	(608)	1.2	6.7	.86	3.9	1.42	1.22

VARIATION OF THE INTENSITIES OF THE LINES WITH VOLTAGE

Because of the existence of three critical excitation potentials in the L-series, the relative intensities of L-lines vary with the voltage. In order to give a more general interpretation to the results, the variation of the intensity with voltage was studied. As the voltage is raised, the relative intensity of lines belonging to different excitation potentials undoubtedly approaches a constant ratio, and the value of this ratio can be calculated from the results of measurement at any known voltage if the law of increase is known. It was assumed that in the range studied the intensity could be represented by

$$I = k(V - V_0)^n,$$

where I is the intensity of the line at the voltage V; V_o is the critical voltage of the line, and k is a constant characteristic of the line. The variation with voltage was first expressed in this form by Webster and Clark.[13] This is in agreement with the procedure of Jönsson, but not in agreement with the theoretical predictions of Bergen Davis[14] which have been confirmed by Wooten,[15] Kettman,[16] and Stumpen[17] at voltages considerably above the critical voltages.

The following table gives the values of n resulting from measurements on the relative intensities of $L\alpha_1$ and $L\beta_{1,5}$ at 31.8, 27.7, and 23.1 kilovolts, respectively. For convenience in tabulation, n is found analytically from pairs of observations on the same line by the formula

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[13] Webster and Clark, Phys. Rev. **9**, 571 (1917).

[14] Davis, Phys. Rev. **11**, 433 (1918).

[15] Wooten, Phys. Rev. **13**, 71 (1919).

[16] Kettman, Zeits. f. Physik. **18**, 359 (1923).

[17] Stumpen, Zeits. f. Physik. **36**, 1 (1926).

$$n=\frac{\log I_1-\log I_2}{\log(V_1-V_0)-\log(V_2-V_0)}$$

where I_1 and I_2 are the intensities at two different voltages V_1 and V_2. The critical voltages (in kilovolts) of the thorium L-series are as follows: L_{11}, 20.45; L_{21}, 19.66; L_{22}, 16.29. In view of these results the value of n was taken to be 2. There seems to be a slight trend in the values of n, in both $L\alpha_1$ and $L\beta_{1,5}$. The experiments were not pushed far enough to see if this is real or not. The value of n used by Jönsson for tungsten and platinum was 1.7. The correction to be applied to observations at any one voltage is

$$\left(\frac{V-V_0{}^{\alpha}}{V-V_0{}^{\lambda}}\right)^2$$

where $V_o{}^{\alpha}$ is the critical voltage for Th $L\alpha_1$ and $V_o{}^{\lambda}$ is the critical voltage for some other line λ.

TABLE III

Variation in intensity of $L\alpha_1$ and $L\beta_{1,5}$ with voltage.

Observation No.	Voltage (kv)	$\log(V-V_0)$	Intensity (corr.)	$\log I$	Observations used	n calc.
			Observations on $L\alpha_1$			
1	31.8	1.190	13.29	1.123	1, 2	1.96
2	27.7	1.057	7.30	0.863	1, 3	2.07
3	23.1	0.832	2.41	0.382	2, 3	2.14
			Observations on $L\beta_{1,5}$			
4	31.8	1.082	5.99	0.777	4, 5	1.95
5	27.7	0.903	2.68	0.428	4, 6	2.08
6	23.1	0.531	0.43	−0.367	5, 6	2.14

TABLES OF RESULTS

The results of the individual trials of relative intensities at 31.8 kv and 7.5 m.a. are given in Table IV, and some idea of the experimental errors

TABLE IV

Direct, uncorrected results for the relative intensities of the L-series lines of thorium.

η/l	α_2/α_1	$\beta_{1,5}/\alpha_1$	$\beta_{1,5}/\beta_3$	β_2/β_6	β_1/β_2	β_2/γ_1	γ_1/γ_2	$\gamma_1/\gamma_{3,6}$	β_1/β_7	β_2/η
0.40	0.133	0.380	0.040	0.056	0.695	0.292	0.110	0.344	0.013	0.049
.26	.128	.382	.049	.066	.663	.297	.080	.35	.010	.034
.42	.104	.382	.054		.695	.328	.100			
	.127	.364	.051			.279	.080			
	.106									
	.127									
	.119									
	.112									
0.36	0.12	0.38	0.048	0.061	0.681	0.30	0.092	0.35	0.012	0.042

involved may be gained there. The averaged and corrected results are given in Table V.

TABLE V

Relative intensity of thorium L-series lines.

Line	Observed uncorrected intensity (31.8 kv)	Intensity corrected for absor. (31.8 kv)	Voltage correction	Rel. int. at high voltage
l	3.1	3.6	1.00	3.6
α_2	12	12	1.00	12
α_1	100	100	1.00	100
η	1.1	1.1	1.64	1.8
β_6	1.6	1.4	1.00	1.4
β_2	26	26	1.00	26
β_7	.45	.45	1.00	.45
$\beta_1+\beta_5$	38	38	1.64	62
β_3	1.8	1.8	1.85	3.3
γ_5	0	0	1.64	0
γ_1	7.7	8.5	1.64	14
γ_2	.71	.81	1.85	1.5
$\gamma_3+\gamma_6$	2.7	3.1	1.7	5.3
γ_4	0	0	1.85	0

Two attempts each were made to find indications of the lines γ_4 and γ_5 but no trace of these lines could be found. They must be extremely weak at 31.8 kilovolts.

DISCUSSION OF RESULTS

In comparing these results with theoretical predictions it will be assumed that these theoretical predictions apply to the relative intensities at high voltages, that is, far above the critical excitation voltages. The following predictions of Sommerfeld[18] and of Coster and Goudsmit[19] as to the relative intensities of x-ray doublets and compound doublets can be tested from the observed data.

TABLE VI

Relative intensities of L-doublets.

Lines	Predicted	Observed
$\alpha_1 : \alpha_2 : \beta_1$	100 : 11 : 56	100 ; 12 : 62*
$(\beta_2+\beta_{15}) : \gamma_1$	100 : 50	100 : 53
$l : \eta$	100 : 50	100 : 50

*This value includes $L\beta_5$.

The unfortunate fact that γ_3 lies too near γ_6 to be separated and β_4 could not be separated from β_2 prevents determinations of the relative intensities of the very interesting doublets resulting from electron transitions ending in L_{11}. The results in Table VI show that for the lines representing electron transitions ending in L_{21} and L_{22} the predictions are experimentally

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[18] Sommerfeld, Ann. d. Physik. **76,** 284 (1925).

[19] Coster and Goudsmit, Naturwiss. **1,** 11 (1925).

realized. If a rough estimate of the intensity of β_5 is computed (assuming the rules to hold) from half the combined intensity of $\gamma_6+\gamma_3$, and then subtracted from the combined intensity of $\beta_1+\beta_5$ the theoretical ratio of $\alpha_1:\beta_1$ is more nearly approached.

The advent of the new quantum mechanics has made it possible to calculate the relative intensities of lines involving different azimuthal quantum number changes by a new method. Formerly only the correspondence principle was available.[20] This has been carried out by Wentzel,[21] and he has compared his results with those of Jönsson on tungsten. In Table VII this comparison is reproduced and the present results on thorium added.

TABLE VII

Comparison of experimental results on relative intensities of different series with theory. (Wentzel).

Lines	Transitions	Intensity Calc.	Obs. in W (Jönsson)	Obs. in Th
$\alpha_2+\alpha_1+\beta_1$	3_3-2_2	(1.00)	(1.00)	(1.00)
$l+\eta$	3_1-2_2	.02	.03	.03
$\beta_4+\beta_3$*	3_2-2_1	.21	.08	.03
$\beta_2+\gamma_1$	4_3-2_1	.43	.18	.23
$\beta_6+\gamma_5$	4_1-2_2	.01	.01	.008
$\gamma_2+\gamma_3$†	4_2-2_1	.12	.02	.02

* In the experimental work on Th, β_4 could not be separated from β_2. Since the intensity of β_3 was 3.3, by analogy with W, β_4 was taken to be 2.

† γ_3 could not be separated from γ_6 but it is estimated to be about 2 since γ_2 is 1.5.

An interesting fact brought out by Table VII is the weakness of β_4 and β_3 in thorium as compared with tungsten. This is at once apparent from the curve of the β-group (Fig. 2) if one keeps the corresponding curves for tungsten in mind.

Another marked difference between thorium and tungsten is the strength of γ_6 in thorium. Unfortunately the other member of the compound doublet, β_5, is coincident with β_1 so that it cannot be separately measured and compared with β_5 in tungsten.

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[20] F. C. Hoyt, Phil. Mag. **46,** 135 (1923).

[21] Wentzel, Naturwiss, **14,** 621 (1926).