# AN EXPERIMENTAL STUDY OF THE RELATIVE INTENSITIES OF X-RAY LINES IN THE TANTALUM $L$-SPECTRUM

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Abstract

The relative intensities of 17 lines in the $L$ spectrum of tantalum have been investigated by the ionization spectrometer. The following precautions were taken: (1) the rays were taken at a glancing angle of 45° from a polished tantalum surface; (2) a tantalum filament was used; (3) the slits were enclosed in an arm of the tube reducing the air path of the rays to 7.35 cm; (4) the coefficient of reflection of the crystal used was measured for the various wave-lengths by means of the double-spectrometer; (5) the absorption coefficients of the mica windows used were directly measured; (6) the rays were completely absorbed in methyl iodide vapor of known pressure; and (7) the slits were sufficiently wide to eliminate effects arising from the different natural widths of the lines. Measurements were taken at 30.6 kv and 20.7 kv and corrected to high voltage. The results for lines of small wave-length separation agree well with previous measurements of Allison and Armstrong and Jönsson on tungsten. For lines of larger wave-length separation ($L\alpha_1$, $L\beta_1$) the results of Jönsson are not confirmed, but the previous qualitative estimates of Allison and Armstrong are substantiated. The assumption that the ionization currents produced are proportional to the relative intensities is supported by recent work of A. H. Compton. If the $\nu^4$ correction is made to the intensities at high voltage, the sum rules are approximately valid except for lines having initial state $L_{\text{I}}$. The intensity results are:

| | $l$ | $\alpha_2$ | $\alpha_1$ | $\eta$ | $\beta_4$ | $\beta_1$ | $\beta_3$ | $\beta_2$ | $\beta_7$ |
|---|---|---|---|---|---|---|---|---|---|
| Rel. Int. at 30.6 kv | 1.5 | 10 | 100 | 1.3 | 9.3 | 93 | 13 | 40 | 0.8 |
| Rel. Int. at high V. | 1.5 | 10 | 100 | 1.4 | 11. | 103 | 16 | 40 | 0.8 |
| | $\beta_5+\beta_{10}$ | $\beta_9$ | $\gamma_5$ | $\gamma_1$ | $\gamma_6$ | $\gamma_2$ | $\gamma_3$ | $\gamma_4$ | |
| Rel. Int. at 30. 6 kv | 1.1 | 0.8 | 1.2 | 29 | 0.6 | 5.0 | 7.2 | 2.2 | |
| Rel. Int. at high V. | | | 1.4 | 32 | 0.7 | 5.9 | 8.5 | 2.6 | |

## Introduction

THE relative intensities of the lines in the tantalum $L$ spectrum have been investigated with an ionization spectrometer, the method used being similar to that previously employed by Duane and Patterson,[1] Allison and Armstrong,[2] and Allison.[3] Considerable work has previously been done on the relative intensities in the tungsten $L$ spectrum (atomic number 74). Duane and Patterson investigated the relative intensities of lines in the $\alpha$, $\beta$, and $\gamma$ groups, the members of which do not differ greatly in wave-length. They did not attempt to compare intensities of lines in different groups. Allison and Armstrong repeated and extended this work, and in addition made some qualitative estimates of the relative intensities of the more intense

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

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

[3] S. K. Allison, Phys. Rev. **30**, 245 (1927), **32**, 1 (1928).

lines in the various groups, thus linking them together. Jönsson[4] investigated the relative intensities in the $L$ series of tungsten, using a Geiger counter, and gave results for all the lines in the $L$ spectrum. Within the $\alpha$, $\beta$, and $\gamma$ groups, where wave-length differences are small, the results of Allison and Armstrong and Jönsson were in fair agreement, but for lines of wider wave-length separation (i.e. those separated by the $L_{II}L_{III}$ frequency difference) there were large discrepancies. For instance, Allison and Armstrong reported that $L\beta_1(M_{IV}L_{II})$ was slightly more intense than $L\alpha_1(M_VL_{III})$ whereas Jönsson found the intensity ratio of $\alpha_1/\beta_1$ to be 100/51.8. He ascribed this lack of agreement to the fact that there was more absorption in the target in the experiments of Allison and Armstrong than in his; this explanation seemed quite reasonable, because they had obtained evidence of the $L$ critical absorption discontinuities of the target in their general radiation spectrum.

The present experiments on tantalum (atomic number 73) were undertaken in order to add to our knowledge of the $L$-series intensities in general, and to investigate the cause of the discrepancies mentioned above in particular. They show that Jönsson's explanation of the differences cannot be correct.

## Apparatus

(1) *Power supply.* The high voltage direct current generating apparatus was that used by S. K. Allison for his measurements on the $L$-series of uranium.[3] The potential difference applied to the x-ray tube was measured with an electrostatic voltmeter, consisting of a dumbbell hung on a bifilar suspension between two parallel plates, the whole being enclosed in a grounded metal case. A lens system formed an image of an incandescent lamp filament on a ground glass scale at a distance of 3.8 meters from a mirror mounted on the vertical axis of the dumbbell. The voltmeter was calibrated in the following manner: the crystal table angle corresponding to the $K$ absorption limit of molybdenum was first carefully determined by observing the reflected intensities while moving the crystal through small angular steps with a thin molybdenum sheet in the path of the beam. The crystal was then set at the proper position to reflect the wave-length corresponding to this absorption limit, and the sheet of molybdenum removed. The limiting voltage to excite this wave-length was then determined by lowering the voltage in steps until no reflected intensities were observed. Three other points were taken on the calibration curve by the use of thin sheets of silver, tin, and cadmium.

The experiments were performed largely at 30.6 kv, although some measurements were taken at 20.7 kv. With two condensers in series in the high potential circuits, each of 0.050 mf capacity, the calculated fluctuation in the high voltage at 30.6 kv was 0.4 percent when a tube current of 3 ma was used. It was found convenient to operate the tube with the cathode grounded through the milliammeter.

(2) *X-ray tube.* The x-ray tube, the glass parts of which were constructed of Pyrex, is shown in Fig. 1. The most important features of this tube were:

[4] A. Jönsson Zeits. f. Physik **36,** 426 (1926).

(1) The slits were built into the tube as an integral part, thus cutting down the path of the rays in air; (2) the orientation of the cathode stream with respect to the axis of the tube could be changed while the tube was evacuated, thus permitting the focal spot to be brought opposite the slits. The slits were of iron, mounted on a tube of iron enclosed in a glass arm of the x-ray tube. The width of the slits was 0.18 mm, the height 1.6 cm, and the distance between the slits was 40.0 cm. This limited the horizontal angular width of the beam to approximately 3 minutes of arc. The x-ray beam left the tube through a mica window in a brass cap on the arm carrying the slits. As the slit system was fixed with reference to the anode, it was necessary to adjust

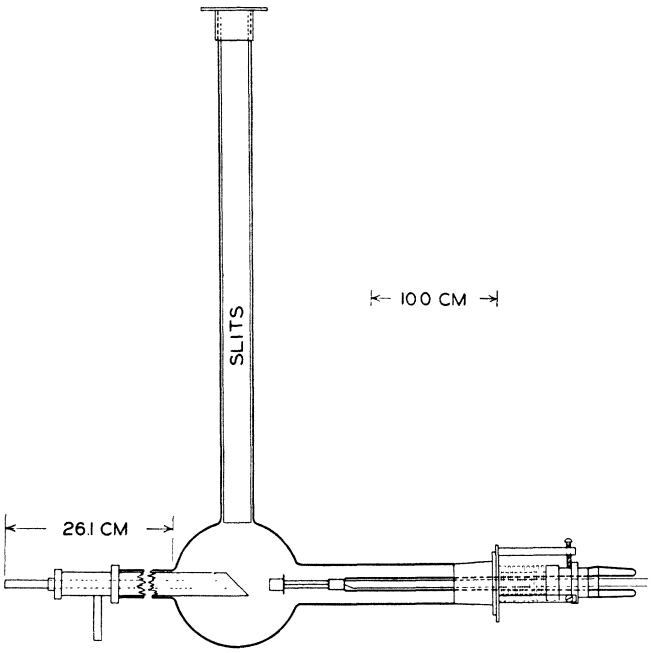


Fig. 1. Diagram of x-ray tube.

the position of the focal spot on the anode. This was accomplished by having a section of the arm of the tube carrying the cathode made of flexible silphon copper tubing. The orientation of the cathode beam with respect to the axis of the tube could then be changed by set screws, two of which are indicated in Fig. 1.

The anode was made of copper. A piece of sheet tantalum and a spool of tantalum wire 0.025 cm in diameter for filaments were given us by the Fansteel Products Co. The tantalum was 99% pure. The tantalum was spot-welded to a piece of nickel, and then the nickel soldered to the anode. With the tantalum spot-welded in about twenty points, no local heating was experienced at the low tube currents used, and the target was not pitted at the close of the experiments.

The anode was cooled by pumping kerosene through it. This prevented any electrical conduction to ground which might have taken place if water were used for cooling.

The x-ray tube was exhausted continuously while being operated. The tube and the glass part of the vacuum system were mounted on a stand which permitted translation, rotation, and leveling of the tube.

(3) *Spectrometer.* The spectrometer was of the Bragg type. Angular settings of the crystal were read with microscopes on an accurately divided circle 25.4 cm in diameter; settings could be made to 15 seconds of arc with ease, more precise settings were not necessary in this work. The axis of the spectrometer was 48 cm from the focal spot of the x-ray tube.

(4) *Ionization chamber.* The ionization chamber was of the type described by Williams and Allison.[5] It was made of a Pyrex glass tube 4.7 cm in internal diameter and 33 cm long. To one end were attached the tubing and valves for introducing the gas and a ground glass joint for an iron guard ring. An amber plug supporting a nickel rod fitted tightly into the guard ring. The nickel rod was connected to the electrometer by very carefully shielded wires. Just inside the inner wall a cylinder of nickel gauze was placed as the charged electrode. The length of the gauze was 28 cm, and the nickel rod was 1.4 cm from the nearest point of the gauze. The end of the chamber towards the crystal was closed with a brass cap having a slit 0.3 cm wide by 2.9 cm high, over which a piece of mica was sealed with deKhotinsky cement. The effective angular width of this slit at the axis of the spectrometer was about 4°, so that it was not necessary to move the ionization chamber frequently when taking readings. A potential of 170 volts supplied to the nickel gauze by means of a dry battery was sufficient to insure saturation currents through the gas in the chamber, since frequent trials during the measurements showed that the rate of deflection of the electrometer was proportional to the electron current in the x-ray tube. Methyl iodide was used as the absorbing gas. A clear colorless liquid was obtained by stirring the methyl iodide with granulated zinc to remove any traces of free iodine. The liquid was then filtered into a small bulb, frozen by immersion in liquid air and the bulb sealed to the ionization chamber through a stopcock. The ionization chamber was then evacuated, keeping the methyl iodide immersed in liquid air, and the methyl iodide vapor introduced into the chamber through phosphorus pentoxide by allowing the liquid to warm up to room temperature gradually. Air was finally introduced over phosphorus pentoxide to bring the vapor in the chamber to atmospheric pressure.

(5) *Electrometer.* The electrometer was a Compton type used heterostatically. The currents were measured by observing the time rate of charging of the insulated pair of quadrants. A sensitivity of about 1800 scale divisions per volt with a mirror to scale distance of 1.75 meters was sufficient for the majority of the measurements.

[5] Williams and Allison, J. Opt. Soc. Am. and Rev. Sci. Inst. **18,** 473 (1929).

## Method of Measuring Intensities

A fundamental assumption in this method of measuring relative intensities is that the observed ionization currents are proportional to the intensities of the x-ray beams entering the ionization chamber, even when these beams differ in wave-length. This assumption will be discussed later. At present the method of obtaining what may with strict accuracy be called the relative ionization currents from the observed electrometer readings will be described. These were taken as proportional to the height of the tip of the peak representing the line above the base-line of scattered and general radiation. This method is justified if the following conditions hold true: (1) the curve representing each line must be symmetrical about the center of the line; (2) the resolution must be great enough so that the radiation due to a line is negligible at a distance from the center of the line equal to twice the wave-length separation from the nearest line; (3) the resolution must not be so great that the natural breadths of the lines play any part in the curve representing the line. Allison[6] has found that in the iridium $L$ spectrum the line $L\beta_2$ has an angular width at half-maximum corresponding to a range of reflection of about 45 seconds of arc from a single crystal of calcite in the first order. The angular width of the beam was 3 minutes of arc, and all the lines measured had the same full width at half-maximum, namely 2′30″, so it is seen that assumption (3) was fulfilled. The angular width of the beam was not so great, however, as to violate the second assumption. For instance, the base-line for $L\alpha_1$, according to this method, is taken at an angle corresponding to $\lambda_{\alpha_2}+\Delta\lambda$, where $\Delta\lambda$ is the wave-length separation of $\alpha_1$ and $\alpha_2$. By the symmetry of the lines, the radiation at this point is the fraction of $\alpha_2$ appearing under $\alpha_1$ plus baseline currents. The intensity at this point, however, was found to be very little different from that of the base-line farther away in agreement with condition (2).

## Corrections to be Applied to Observed Readings

Corrections to be applied to observed values arise from the following: (1) absorption of the rays in the target of the tube, (2) absorption in the mica windows in the tube and ionization chamber, (3) absorption by the air traversed by the beam, (4) incomplete reflection by the calcite crystal, (5) partial absorption in the ionization chamber. In computing the corrections for these factors ((4) excepted) the mass absorption coefficients of the materials were assumed to vary with the cube of the wave-length throughout the tantalum $L$ spectrum. If $\mu$ is the absorption coefficient of the material for the line $L\alpha_1$, $\mu'$ that for another line, and $t$ the thickness of the material, the correction to be applied to the intensity of the line relative to that of $\alpha_1$ is

$$e^{-(\mu-\mu')t}$$

(1) The radiation used in the experiments was taken at an angle of 45° from the target face so that the thickness of the target traversed was the same for the impinging electrons and the emerging x-rays. No evidence of the $L_{II}$ or $L_{III}$ absorption discontinuities in the general radiation spectrum

[6] S. K. Allison, Phys. Rev. **34**, 176 (1929).

was found, as in the previous work of Allison and Armstrong on tungsten. The extent of the correction to be applied for this effect is probably less than 5 percent and is rather uncertain,[7] so that no such correction has been applied here.

Further, since a tantalum filament was used throughout the experimental work, no foreign substance could have been deposited on the face of the target. This eliminates a doubtful correction which may enter when the target and filament are not of the same substance.

(2) The absorption coefficients of the mica used for windows were found by direct measurement to be 138 for Ta $L\alpha_1$, 93.5 for Ta $L\beta_1$ and 60.4 for Ta $L\gamma_1$. These values are approximately proportional to the cube of the wave-length, as expected. The total thickness of mica in the path of the beam was 0.0053 cm.

(3) Due to the fact that the slit system was a part of the x-ray tube, and therefore evacuated, the distance travelled by the x-rays in air was only 7.35 cm. From the values of $\mu/\rho$ for air listed in the International Critical Tables[8] a mean value of 8.65 was computed for the mass absorption coefficient of air for the wave-length corresponding to $L\alpha_1$ of tantalum. The values of $\mu/\rho$ for the other lines in the spectrum were obtained from this value by assuming a variation proportional to $\lambda^3$.

(4) The final measurments of the relative intensities of the lines $L\alpha_1$, $L\beta_1$ and $L\gamma_1$ which were used to link together the intensities in the $\alpha$, $\beta$, $\gamma$ groups were made with a crystal whose reflection coefficients for these wave-lengths were directly measured by the method of Davis and Terrill.[9] The double spectrometer constructed in this laboratory and described by Williams and Allison[5] was used, with a tungsten target tube. The voltage used was sufficiently low to prevent second order reflections at the angles concerned. The reflection coefficients per degree for the $L\alpha_1$, $L\beta_1$ and $L\gamma_1$ lines of tungsten were found to be 0.00208, 0.00222, and 0.00232 respectively. The corresponding wave-lengths in X.U. are 1473.5, 1279.2, 1095.5. The correction to be applied to the tantalum spectrum was computed from these values.

[7] The measurements of Backhurst (Phil. Mag. **7**, 353 (1929)) on the absorption coefficients of platinum and gold through the region of their $L$ absorption discontinuities has made it possible to calculate these corrections to the platinum $L$ spectrum, assuming that the penetration of the electrons in the target is roughly given by the Thompson-Whiddington law. The critical $L$ series ionization potentials of platinum average about 13kv. Using values of the constant in the Thompson-Whiddington law from the paper of Terrill (Phys. Rev. **22**, 101 (1923)) it is found that 34 kv electrons incident will penetrate $1.1\times10^{-4}$ cm before their velocity is reduced to 13 kv. The depth of penetration of a large majority of the electrons is considerably less than this, due to the curving paths, and furthermore the classical theory predicts that they are most efficient in ionizing when their energy is twice that of the level to be ionized, that is, 26 kv electrons are most efficient in excitation of the platinum atom to the $L$ state. If then we assume that the effective absorbing layer is half that above, and use Backhurst's absorption coefficients, we find that the largest correction to be applied in the $L$ spectrum is a 5 percent reduction in $L\beta_1$ with respect to $L\alpha_1$.

[8] International Critical Tables vol. VI, p. 16.

[9] Davis and Terrill, Phil. Mag. **44**, 463 (1923).

(5) The International Critical Tables[8] list four mass absorption coefficients for methyl iodide corresponding to wave-lengths in the tantalum $L$ spectrum. From these, a mean of 251 was computed for this coefficient for Ta $L\alpha_1$. The vapor pressure of the methyl iodide in the ionization chamber was 24 cm, the temperature, 20°C. This corresponds to a density of $2.17\times 10^{-3}$ gm/cm.[3] Neglecting the absorption of the air introduced into the chamber, these data indicate that 99.9 percent of the line of shortest wave-length, $\gamma_4$, was absorbed in the chamber. It is thus evident that no correction need be applied for the relative absorption in the ionization chamber.

## RESULTS

The principal results of the investigation are shown in Table I, which gives the results of measurements taken at 30.7 kv. In column 6 of this table a factor is given by which the intensities at high voltage can be calculated. The intensities calculated by this factor would not take account of absorption in the target which might become more pronounced at high voltage. In making this calculation it was assumed that the variation of intensity with voltage of a line can be represented by

$$I_v = C(V - V_0)^{1.8}. \tag{2}$$

The exponent 1.8 was chosen, not from any independent determination of the variation of the intensity of lines in the tantalum $L$ spectrum with voltage, but from the previous values of Jönsson[4] who found 1.7 for tungsten, and Allison[3] who found 1.8 for uranium. The voltage corrections to be applied to the tantalum $L$ spectrum at 30.6 kv are small and the difference between the corrections computed with exponents 1.8 or 1.7 would be negligible.

TABLE I. *Relative intensities of lines in the tantalum L spectrum from ionization measurements at 30.6 kv.*

| Line | Wave-length X.U. | Obs. Rel. intensity | Corr. factor for absorption | Rel. Int. 30.6 kv. | Factor to give rel. int. at high voltage | Rel. int. at high voltage. |
|---|---|---|---|---|---|---|
| $l$ | 1724 | 1.0 | 1.43 | 1.5 | 1.00 | 1.5 |
| $\alpha_2$ | 1530 | 10 | 1.02 | 10 | 1.00 | 10 |
| $\alpha_1$ | 1519 | 100 | 1.00 | 100 | 1.00 | 100 |
| $\eta$ | 1466 | 1.4 | .91 | 1.3 | 1.11 | 1.4 |
| $\beta_4$ | 1343 | 12 | .77 | 9.3 | 1.18 | 11 |
| $\beta_1$ | 1324 | 122 | .76 | 93 | 1.11 | 103 |
| $\beta_3$ | 1304 | 18 | .74 | 13 | 1.18 | 16 |
| $\beta_2$ | 1282 | 56 | .72 | 40 | 1.00 | 40 |
| $\beta_7$ | 1260 | 1.1 | .71 | 0.8 | 1.00 | 0.8 |
| $\beta_5+\beta_{10}$ | 1251 | 1.6 | .70 | 1.1 | | (1.1) |
| $\beta_9$ | 1243 | 1.2 | .69 | 0.8 | | (0.8) |
| $\gamma_5$ | 1170 | 1.9 | .64 | 1.2 | 1.11 | 1.4 |
| $\gamma_1$ | 1136 | 47 | .62 | 29 | 1.11 | 32 |
| $\gamma_6$ | 1110 | 1.1 | .60 | 0.6 | 1.11 | 0.7 |
| $\gamma_2$ | 1103 | 8.3 | .60 | 5.0 | 1.18 | 5.9 |
| $\gamma_3$ | 1097 | 12 | .60 | 7.2 | 1.18 | 8.5 |
| $\gamma_4$ | 1062 | 3.8 | .58 | 2.2 | 1.18 | 2.6 |

The observed relative intensity of $\alpha_1:\beta_1:\gamma_1$, listed as 100:122:47 in column 3 of Table I has already been corrected for the measured coefficient of reflection of the calcite crystal used. The values observed without this correction were 100:128:52. Each value given in column 3 of Table I is the result of at least four independent measurements, which were averaged.

In the $\beta$ group of lines, $\beta_1$ and $\beta_6$ could not be separated in the first order because of the wide slits used. Previous measurements with tungsten[2,4] indicate that $\beta_6$ is about 2 percent as strong as $\beta_1$; thus a large error in the measurement of $\beta_1$ could not be made by the inclusion of $\beta_6$ under part of the curve. $\beta_5$ and the non-diagram line $\beta_{10}$ have the same wave-lengths in tantalum; the sum of their intensities is given in the table, but not corrected to high voltage. No attempt was made to separate the very weak line $\beta_8$ from $\beta_2$.

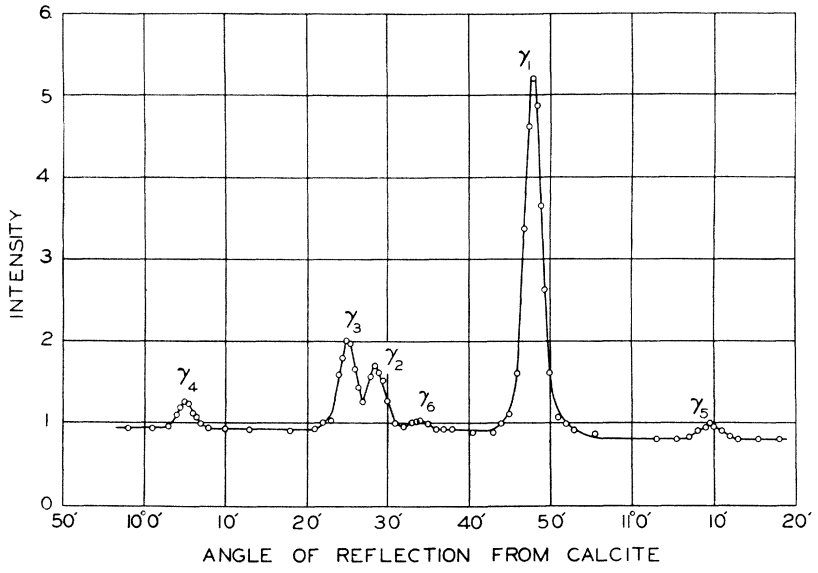


Fig. 2. Tantalum $L$ spectrum, $\gamma$ group.

In the $\gamma$ group intensity measurements were made on all the lines listed by Lindh[10] for tantalum. A typical ionization spectrum of the $L\gamma$ group is shown as Fig. 2.

## Discussion of the Experimental Method

Mention has previously been made in this paper of the grouping of the $L$-series lines (except the weak lines $l$ and $\eta$) in three regions of small wave-length range compared to that of the spectrum as a whole. This fact makes it convenient to divide the problem of determining the relative intensities of the lines into two problems: (1) finding the relative intensities of the lines in a single group; (2) comparing the intensities of lines in different groups. The first of these problems seems to be comparatively simple. All investiga-

[10] A. E. Lindh—Handb. der Experimentalphysik XXIV 2 Teil, p. 154 (1930).

tors have found the relative intensities of $\alpha_1/\alpha_2$ to be 100/10 or 100/11. Table II shows the results of three different investigations in the $\beta$ and $\gamma$ groups of the adjacent elements, tantalum and tungsten. The results of Allison and Armstrong quoted in Table II are the results originally in their paper multiplied by the appropriate high voltage factor to bring them to the same basis as the others.

TABLE II. *Relative intensities of lines in groups of small wave-length separation.*

| Line | $L\beta$ group. Ta (73) Hicks | W (74) Allison and Armstrong | W (74) Jönsson | Line | $L\gamma$ group Ta (73) Hicks | W (74) Allison and Armstrong | W (74) Jönsson |
|---|---|---|---|---|---|---|---|
| $\beta_1$ | (100) | (100) | (100) | $\gamma_1$ | (100) | (100) | (100) |
| $\beta_2$ | 39 | 43 | 39 | $\gamma_2$ | 18 | 15 | 16 |
| $\beta_3$ | 16 | 16 | 16 | $\gamma_3$ | 27 | 24 | 22 |
| $\beta_4$ | 11 | 8.2 | 10 | $\gamma_4$ | 8.1 | 7.5 | 6.5 |
| $\beta_5$ | | .41 | .39 | $\gamma_5$ | 4.4 | 3.0 | 4.5 |
| $\beta_6$ | | 1.8 | 1.9 | $\gamma_6$ | 2.2 | 2.3 | 3.3 |

In the measurement of the relative intensities of the lines $\alpha_1:\beta_1:\gamma_1$, representative of the $\alpha$, $\beta$, and $\gamma$ groups respectively, much larger differences between the measurements of Jönsson and the ionization chamber measurements are found. This is illustrated in Table III. It is evident that when larger wave-length separations are involved, much lower intensities for the

TABLE III.

| Line | Ta (73) Hicks | W (74) Allison and Armstrong | W (74) Jönsson |
|---|---|---|---|
| $\alpha_1$ | (100) | | (100) |
| $\beta_1$ | 103 | "slightly more intense than $\alpha_1$" | 51.8 |
| $\gamma_1$ | 32 | "more than $\frac{1}{2}$ as intense as $\beta_2$" | 9.1 |

shorter wave-length lines were obtained with the Geiger counter (Jönsson) than with the methyl iodide ionization chamber. The differences cannot be due to a sudden change in relative intensities between the elements tantalum and tungsten. In preliminary trials in these experiments a tungsten target was used and it was found that $\beta_1$ was somewhat more intense than $\alpha_1$, as previously reported by Allison and Armstrong, although quantitative measurements were not carried out on tungsten in the present research. In a later paper Jönsson has himself pointed out[11] that in the sensitive region near the point in the counter only a small fraction of the radiation is absorbed, and from the known absorption coefficients this fraction must vary with the wave-length of the line. Although Jönsson corrected his observations in the $L$ series of the elements of atomic numbers 42–47 for this partial absorption, he did not apply this correction to his results on tungsten and platinum.

[11] Jönsson, Zeits f. Physik **46**, 383 (1928).

If this correction is applied to his results as given in column 4 Table III, values somewhat nearer those in column 2 are obtained. The remaining discrepancy may be due to the photo-electron range which in air is great enough to allow the ejected electrons to escape from the sensitive region near the point without producing their full quota of ions.

In the present research an experiment was performed to demonstrate the effect of this partial absorption in the detecting device. The methyl iodide vapor was pumped out of the ionization chamber and dry air admitted to a pressure of 15 cm. In a chamber 28 cm long this gives the same mass of air in the path of the x-ray beam as in Jönsson's experiments where a chamber 5.5 cm long was used at atmospheric pressure. Ionization measurements of $\alpha_1:\beta_1:\gamma_1$ were carried out in this air-filled chamber, and all corrections for absorption outside the chamber were made. The resulting "intensities" at high voltage were 100:43:5.7, which is of the order of Jönsson's results as quoted in column 4 of Table III. It must therefore be concluded that Jönsson's results in tungsten and platinum for lines of different groups are seriously in error due to neglect of this partial absorption factor.

Another difference between Jönsson's method of measuring and the one reported here is that his measurements were taken at 20 kv and extrapolated to high voltage, whereas the present measurements were taken at 30.6 kv and extrapolated. In order to find out if part of the differences between these results and his were due to this cause, a number of observations were made on the relative intensities of $\alpha_1:\beta_1:\gamma_1$ at 20.7 kv. These are listed in Table IV.

TABLE IV. *The ratios $\alpha_1:\beta_1:\gamma_1$ from measurements at 20.7 kv.*

| Line | Observed rel. int. | Corr. factor for absorp. | Rel. Int. 20.7 kv. | Voltage Corr. | Rel. Int. high voltage |
|---|---|---|---|---|---|
| $\alpha_1$ | (100) | 1.00 | (100) | 1.00 | (100) |
| $\beta_1$ | 112 | .76 | 85 | 1.24 | 105 |
| $\gamma_1$ | 46 | .62 | 28 | 1.24 | 35 |

The "observed relative intensities" given in column 2 of this table have already been corrected for the variation of the coefficient of reflection of the crystal with wave-length. From a comparison of Table IV and Table I it is apparent that measurements taken at 20.7 kv give approximately the same values as those taken at 30.6 kv when extrapolated to high voltage.

The method of measuring relative intensities used here has received considerable support from recent work by A. H. Compton.[12] Compton has shown that unless the saturation currents obtained in his ionization chamber (corrected for the fraction of the beam absorbed in the chamber, and the fraction of the fluorescent radiation produced in the chamber which escaped to the walls without production of photo-electrons in the gas) were proportional to intensities, the efficiency of production of fluorescent radiation for a given atom would be found to vary with the wave-length of the primary radiation. Compton states that his experiments support the conclusion that the ioniza-

[12] A. H. Compton, Phil. Mag. **8**, 961 (1929).

tion by $\beta$-rays per unit energy is independent of their energy. Such conclusions had already been reached by Kulenkampff,[13] Kircher and Schmitz[14] and Crowther and Bond,[15] but the experimental arrangement used by Compton was more like that used in these experiments in that he used an ordinary methyl bromide filled chamber rather than air. In the present experiments, the tantalum radiations entering the ionization chamber were never sufficiently hard to excite the $K$ series of the iodine; only the relatively soft $L$ series of wave-length around 2.8A could be emitted. From the dimensions of the chamber it may be calculated that only a negligible fraction of this iodine fluorescent radiation could reach the walls without expending itself in the production of photo-electrons. Furthermore, the range of the photo-electrons ejected by the tantalum $L$ series wave-lengths from the iodine atoms was not over 2.5 mm as can be calculated from the Thompson-Widdington law. Therefore no photo-electrons could have reached the walls of the chamber without producing their full quota of ions.

## Discussion of Results

If it is conceded that the ionization method, as employed here and by Allison and Armstrong in tungsten, and Allison in thorium and uranium gives the correct relative intensities of the lines, the present results give the problem of the intensities of x-ray lines in the $L$-series an entirely new aspect. It is necessary to assume that the agreement between the measurements of Jönsson on tungsten (74) and those of Allison on thorium (90) and uranium (92) was fortuitous, and that the relative intensities in the $L$ series undergo a large change in the region between atomic numbers 73 and 92. This is illustrated in Table V.

Table V. *Relative intensities at high voltage in the tantalum and uranium L-series*

| | $l$ | $\alpha_2$ | $\alpha_1$ | $\eta$ | $\beta_6$ | $\beta_2$ | $\beta_4$ | $\beta_5$ | $\beta_1$ | $\beta_3$ | $\gamma_5$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $\gamma_6$ | $\gamma_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ta(73) (Hicks) | 1.5 | 10 | 100 | 1.4 | | 40 | 11 | <1.1 | 103 | 16 | 1.4 | 32 | 5.9 | 8.5 | 0.7 | 2.6 |
| U(92) Allison | 2.4 | 11 | 100 | 1.0 | 1.6 | 28 | 4.1 | 6.4 | 49 | 4.2 | 0 | 12 | 1.5 | 1.4 | 2.2 | 0 |

The development of the new quantum mechanics has made it increasingly evident that there is a factor in the expression for the intensities of spectral lines which is the fourth power of their frequency.[16] This $\nu^4$ correction is to be applied to widely separated multiplets in optical spectra, and the intensities so corrected should be governed by the sum rules or their extension in case the Boltzmann factors are not appreciably different for the initial levels of the transition. In the $L$-series, instead of the Boltzmann factor, we have an ionization function, which gives the relative number of atoms in the target ionized in the $L_I$, $L_{II}$, $L_{III}$ levels by the impinging electrons.

[13] H. Kulenkampff, Ann. d. Physik **79**, 97 (1926).

[14] Kircher and Schmitz, Zeits. f. Physik **36**, 484 (1926).

[15] Crowther and Bond, Phil. Mag. **6**, 401 (1928).

[16] For instance Pauling and Goudsmit: The Structure of Line Spectra, McGraw Hill (1930) pp. 128–143.

Allison[17] has pointed out that if the classical ionization function is taken, the relative intensity at high voltage of two lines having different initial states is very nearly equal to the ratio of the product of the transition probability by the statistical weight of the initial state. Since the transition probabilities involve $\nu^3$ this suggests a $\nu^3$ correction for lines involving different $L$ sublevels. Table VI gives the observed and corrected intensities and comparison with sum rule values.

TABLE VI.

| Lines | | Experimental relative intensities. | Corrected for $\nu^4$. | Corrected for $\nu^3$ (for lines of different initial states) | Sum rules |
|---|---|---|---|---|---|
| $\alpha_1:\alpha_2:\beta_1$ | Ta(73) | 100:10:103 | 100:10:59 | 100:10:68 | 100·11:56 |
| | U (92) | 100:11:49 | 100:11:19 | 100:11:24 | |
| $l:\eta$ | Ta(73) | 100:93 | 100:49 | 100:57 | 100:50 |
| | U (92) | 100:46 | 100:15 | 100:20 | |
| $\beta_3:\beta_4$ | Ta(73) | 100:69 | 100:78 | | 100:50 |
| | U (92) | 100:98 | 100:120 | | |
| $\beta_2:\gamma_1$ | Ta(73) | 100:80 | 100:49 | 100:56 | 100:50 |
| | U (92) | 100:43 | 100:19 | 100:23 | |
| $\gamma_3:\gamma_2$ | Ta(73) | 100:69 | 100:71 | | 100:50 |
| | U (92) | 100:107 | 100:112 | | |

From Table VI it is seen that a $\nu^4$ correction brings the relative intensities of lines in tantalum multiplets containing the large $L_{II}L_{III}$ separation surprisingly near the sum rule values. In uranium, on the other hand, the experimental results, uncorrected for frequency, are near the sum rule values, and if frequency corrections are made, wide departures from the rules are found.

In x-ray spectra, in contrast to optical spectra, there always exists the possibility of an internal radiationless transition, or Auger effect. If the probability of such an event taking place varies with the atomic number of the element, and is different for different $L$-series lines, an explanation of Table VI could perhaps be presented on this basis. So very little is known about the Auger effect for $L$-series lines, however, that at present, speculation seems futile.

It is indeed a pleasure to thank Professor S. K. Allison for the suggestion of this problem and for valuable assistance during the investigation.

[17] S. K. Allison, Phys. Rev. 32, 1 (1928).