THE

PHYSICAL REVIEW

AN EXPERIMENTAL STUDY OF THE RELATIVE INTEN-SITIES OF X-RAY LINES IN THE L-SPECTRUM OF URANIUM

BY SAMUEL K. ALLISON

ABSTRACT

The relative intensities of 17 lines in the L spectrum of uranium have been measured as a continuation of the work previously reported on thorium (Allison, Phys. Rev. 30, 245 (1927)). Changes in the apparatus are described which reduce the magnitude of the corrections to be applied. The variation of the intensity of U L_{α_1} with voltage has been studied and may be closely represented by $I = C(V - V_0)^{1.8}$, and with less accuracy by a function $I = C((V-V_0)/V_0 - \log(V/V_0))$ developed by Rosseland. The observed results at 52.8 kv have been extrapolated to the relative intensities at voltages very much greater than the critical voltages. Important results are: (1) The lines $\gamma_3\gamma_2$ and $\beta_3\beta_4$, known in other elements to deviate from the sum rule predictions have equal intensities in uranium although a ratio 2:1 is predicted. (2) The lines $\gamma_6\beta_5$ are 17 times more intense in uranium than in tungsten due presumably to the filling of the 5₃ orbits in the intervening elements. (3) The lines $\gamma_4\gamma_5$ which are present in the tungsten spectrum are absent in the uranium and thorium spectra. It is shown that if Rosseland's function (above) holds for electron collisions in which the velocity of the impinging electron is great compared to the velocities of the electrons in the atom, that the relative intensities of lines of a multiplet under these conditions are equal to the product of the transition probability by the statistical weight of the initial state with only a slight correction. The results are:

l α2 αι η βε βι βι βι βι βι βι χι γι γι γι γι
Rel.Int.at.52.8kv 2.4 11 100 0.83 1.6 28 3.2 0.4 6.4 40.5 3.3 0 9.7 1.1 1.1 1.8 0
Rel.Int.at.high V. 2.4 11 100 1.0 1.6 28 4.1 0.4 6.4 49.4 4.2 0 12 1.5 1.4 2.2 0

INTRODUCTION

 $'$ HE relative intensities of x-ray lines in the L series of uranium have been measured as a continuation of the work on thorium previously reported.¹ Since the atomic numbers of thorium and uranium are close together it was expected that the results on uranium would serve to confirm those previously reported on thorium, and, in certain cases, to extend them, because certain lines can be resolved in the uranium I. spectrum which cannot be separated in the thorium spectrum.

APPARATUS

A general description of the apparatus has appeared in the previous paper on thorium. In the present work, certain changes were made in an attempt to reduce the correction factors as much as possible.

¹ Allison, Phys. Rev. 30, 245 (1927).

 (1) *Voltage.* The experiments on thorium were performed at 31.8 kilovolts. In order to reduce the correction necessary to change the observed intensities to the intensities at voltages high above the critical voltages of the L series, the present work was done at 52.8 kilovolts. In order to attain this voltage it was necessary that both the anode and cathode of the x-ray tube be charged above gound potential. This made it essential that the water cooling system be insulated, which was realised by siphoning the water back and forth between two 80 liter bottles.

(2) Condenser. The capacity of the condenser used in smoothing out the fluctuations in the 550 cycle high voltage circuit was increased. The condenser was divided into two parts of equal capacity which were connected in the anode and cathode sides of the circuit respectively. The capacity of each of these condensers was 0.045 micro-farad, and since the current through the x-ray tube was 5.5 milliamperes the calculated fluctuation was 244 volts or 0.5 percent at 50 kilovolts.

(3) X -ray tube. The x-ray tube was unchanged from the design illustrated in the preceding paper. The uranium was obtained through the kindness of Dr. K. D. Coolidge of the Research Laboratories of the General Electric Company. Several unsuccessful attempts were made to solder or weld the uranium to the face of the copper target. Finally through the courtesy of the Engineering Department of the University a piece of uranium was pressed into a copper block with a hydraulic press. This apparently made good thermal contact and served admirably as a target.

(4) Ionisation chamber. The ionization chamber used in the experiments on thorium was 32 cm long and with a pressure of methyl iodide of 24 cm an appreciable fraction (25 percent) of the radiation of the harder lines in the L series passed through the chamber without being absorbed. In order to reduce this, a chamber 64 cm long was constructed and used. The fractional loss in the uranium $L\gamma$ lines was thus about 7 percent.

RESULTS

Column 3 of Table I gives the observed, uncorrected, results on lines in the uranium L spectrum at 52.8 kilovolts. The measurements were made by comparing the heights of the tips of the peaks representing the lines above the level of the general radiation in the vicinity. In some instances the measurements were made in the second order. Here β_4 was easily separated from β_2 and also β_1 and β_5 were well resolved. An attempt to separate γ_6 and γ_3 more completely in the second order failed because of the weakness of the lines. The results given in column 3 are averages in each case of 3 or more trials.

CORRECTIONS TO BE APPLIED TO OBSERVED RESULTS

The corrections to be applied to the observed results may be grouped under two headings (1) corrections due to absorption; (2) corrections due to the fact that the voltage used is comparable with the differences between the critical voltages of the L series.

The corrections due to absorption have been discussed in the previous paper, and no innovations in the method of making these corrections have been introduced. The magnitude of the corrections is less however, due, in the case of correction for absorption outside the ionization chamber, to the fact that the wave-lengths of the uranium L series are shorter than those of thorium, and, in the case of absorption inside the chamber, to the fact that a longer ionization chamber was used. The magnitude of these corrections is given in columns 4 and ⁵ of Table I. The pressure of the methyl iodide was 26 cm and the calculations were carried out as in the previous paper.

The question of correction for absorption in the target has been taken up in some detail by Jonsson' for soft x-ray lines. He has attacked the problem by measuring the intensity of certain soft x-ray lines, notably Al $K\alpha$ and Ag $L\alpha$ as a function of voltage. The theoretical derivation of these voltageintensity curves involves three factors (1) the ionization function, or the number of ions produced per centimeter of path by an electron with a velocity of V kilovolts, (2) the law of decrease of velocity of an electron in traversing the target substance, and (3) the exponential law of absorption of the radiation produced in the target material itself. Jönsson has tested against his experimental observations the results of calculations involving two different ionization functions but otherwise the same. These ionization functions are those proposed by Bergen Davis³ and by Thomson⁴ and Rosseland.⁵ The formula of Bergen Davis may be written

$$
\eta = C(V - V_0)/V \tag{1}
$$

where η is the number of ions (strictly the number of pairs of ions) formed per centimeter of path, V is the velocity of the impinging electron in kilovolts, V_0 is the energy in kilovolts required to remove the electron which is struck from the atom, and C is a constant whose dimensions are L^{-1} .

The formula of Rosseland may be written, neglecting relativity corrections, as

$$
\eta = C\pi e^2 n N \left(\frac{1}{V_0} - \frac{1}{V}\right) / V \tag{2}
$$

where N is the number of atoms per unit volume, n is the number of electrons in the group whose ionization potential is V_0 kilovolts, and e is the charge on the electron in electrostatic units. C is here a numerical constant entering because V and V_0 are defined in kilovolts instead of electrostatic units. This formula results from the calculations of Maxwell on classical theory, and depends on certain assumptions, an important one being that the velocity of the impinging electron is great compared to the velocities of the electrons in the atoms. This is certainly true in the passage of high-speed β -particles from radioactive sources through air, but it is not obvious that

² Jönsson, Zeits. f. Physik 43, 845 (1927).

 B^3 Bergen Davis, Phys. Rev. 11, 433 (1918).

⁴ J.J. Thomson, Phil. Mag. 23, 449 (1912). '

⁵ Rosseland, Phil. Mag. 45, 65 (1923).

it is true in the target of an x-ray tube operated at moderate voltages where on the classical quantum theory the electrons in the groups under consideration are moving with velocities comparable to that of the incident particles. Nevertheless, Jönsson has found that function (2) in combination with the Thomson-Whiddington law and the exponential law of absorption of x-rays leads to a prediction of the intensity of soft x-ray lines as a function of voltage which agrees well with experiment, and is distinctly preferable to formula (1).

The correction to be applied for absorption in the target depends on the value of b in the Thomson-Whiddington law

$$
V_x^2 = V^2 - bx \tag{3}
$$

where V_x is the velocity in kilovolts at the depth x below the surface, and V is the incident velocity in kilovolts. The value of b has been investigated by Terrill.⁶ The correction also depends on μ , the absorption coefficient of the target substance for the radiation produced. In the region of the L series, both b and μ^7 should have discontinuous jumps. Due to the great uncertainty of these values for uranium no correction has been made for absorption in the target.

The experimental results in column 6 of Table I are the relative intensities at 52.8 kilovolts. In order to be able to predict the relative intensites at other voltages the law of variation of intensity with voltage must

TARLE I. Results

* This value includes β_5

be known. As the exciting voltage is increased, the relative intensities of two lines belonging to different excitation groups approaches a limiting value,

³ Terrill, Phys. Rev. 22, 101 (1923).

[~] Kellstrom, Zeits. f. Physik 44, 269 (1927).

which may be calculated from the results at a single voltage if the law of variation with voltage is known.

The circles in the graph in Fig. ¹ give the experimentally observed values of the intensity of U $L\alpha_1$ at various values of $V-V_0$. The accuracy of these points is not all that can be desired, especially in the higher voltages. No electrostatic voltmeter was available which would read over the entire

Fig. 1. Variation of intensity of U $L\alpha_1$ with voltage. $V_0=17.11$ kv.

range, and the voltages had to be found in each case by measuring the short wave-length limit of the spectrum, which though very accurate, is very tedious.

Previous investigators, such as Webster and Clark,⁸ and Jönsson,⁹ have empirically expressed the law of variation as

$$
I = C(V - V_0)^m \tag{4}
$$

Webster and Clark found $m=1.5$ for platinum and rhodium; Jönsson found $m=1.7$ for tungsten, and in the preceding paper on thorium $m=2$ was found from three points on the curve. The solid curve in Fig. ¹ is a plot of (4) for $m = 1.8$ where C is chosen so that the solid curve fits the points at $V - V_0 = 20$. The dashed curve in Fig. 1 is a plot of the integrated ionization function (2). This integration is performed as follows. The total number

 8 Webster and Clark, Phys. Rev. 9, 571 (1917).

⁹ Jönsson, Zeits. f. Physik 36, 426 (1926).

of ions formed by an electron entering the target with a velocity of V kilovolts before it has been slowed down below a velocity of V_0 kilovolts will be given by

$$
\int_{V}^{V_0} \eta dx = C\pi e^2 n N \int_{V}^{V_0} (1/V_0 - 1/V) dx/V
$$

The voltage may be introduced as the only variable from (3) with the result

$$
N_i = C\pi e^2 n N \left(\frac{V - V_0}{V_0} - \log \frac{V}{V_0}\right) \tag{5}
$$

where N_i is the total number of atoms thrown into the *i*th state of ionization. Since the intensity of a line whose initial state is the state i should be proportional to N_i , the equation should give the variation of the intensity with voltage. The curve was plotted in the form

$$
N_i = C \left(\frac{V - V_0}{V_0} - \log \frac{V}{V_0} \right)
$$

by choosing C so that the ordinate for $V - V_0 = 34$ fell near a straight line connecting the last two experimental points. This was done because in the theoretical background of Eq. (5) the assumption is made that the velocity of the electrons in the atom is negligible in comparison with that of the impinging electron.

It is seen that the plot of Rosseland's function agrees fairly well with the slope of the last two measured points but gives values too high for the points at lower voltage. The empirical function fits the points in general better than the Rosseland function.

If R is the observed ratio of the intensity of a line whose critical voltage is V_0 to the intensity of $L\alpha$ whose critical voltage is V_0^{α} , then R_{∞} , or the ratio at high voltage may be easily shown to be, in terms of Eq. (4)

$$
R_{\infty} = R \left(\frac{V - V_0^{\alpha}}{V - V_0} \right)^{1.8}
$$
 (6)

and in terms of Eq. (5)

$$
R_{\infty} = R \frac{V - V_0^{\alpha} (1 + \log (V/V_0^{\alpha}))}{V - V_0 (1 + \log (V/V_0))}
$$
(7)

The corrections to be applied to lines having L_{21} and L_{11} as initial states are 1.²² and 1.28 respectively from Eq. (6), and 1.31 and 1.39 respectively from Eq. (7). In Table I the corrections are given from the empirical functions (4) and (6) since it is desired to keep the experimental results as free from theory as possible. If the corrections were made on the basis of Rosseland's equation the intensities of lines ending in L_{21} and L_{11} would be raised about 7 percent.

In the last two columns of Table I are given the resultant intensities at high voltage obtained from obserations on uranium and thorium.

DISCUSSION OF RESULTS

Interest in the relative intensities of the L series lines may at present begrouped under three heads. (I) The variation of the relative intensities of corresponding lines in the spectrum as a function of the atomic number of the radiator. (2) The relative intensities of lines constituting a series, that is, of lines in a given element as a function of the change in azimuthal and total quantum numbers. (3) The relative intensities of members of multiplets.

Information on the variation with atomic number and with the change of azimuthal and total quantum number may be obtained from Table II. The variation of the intensities of $\beta_3 \beta_4$, $\beta_5 \gamma_6$ and γ_4 and γ_5 with atomic number are especially interesting. Table II, together with previous results of Jönsson¹⁰ on lighter elements shows that the intensities of these lines decrease

TABLE II. Variation of relative intensities of multiplets as a function of atomic number and as a function of the change in total and asimuthal quantum numbers.

Lines	Δn_k	Theory (Wentzel)	Obs. 74W Jönsson	Obs. 90Th	Obs. 92 U		
$\beta_1\alpha_1\alpha_2$ nl $\beta_3\beta_4$	$3_3 \rightarrow 2_2$ $3\rightarrow 2$ $3\rightarrow 2$	(1.00) .02 .21	(1.00) .03 .08	(1.00) .03 .03	(1.00) .02 .05†	Total $3 - 2$ (1.00)	$H\alpha$ Bongers (1.00)
$\gamma_1\beta_2$ $\gamma_5\beta_6$ $\gamma_3\gamma_2$	$4_3 \rightarrow 2_2$ $4_1 \rightarrow 2_2$ $42\rightarrow 2$.43 .01 .12	.18 .01 .02	.23 .01 .02	.25 .01 .02	Total $4 - 2$.26	$H\beta$. 13
$\gamma_6\beta_5$ $\gamma_8\beta_7$ γ_4	$5\rightarrow 2_2$ $5_2 \rightarrow 2_2$ $52\rightarrow 21$.003 .004	.003 $\mathbf{0}$.05 .003 $\mathbf{0}$	Total $5 - 2$ $.05*$	$H\gamma$.02

† This value is more accurate than the value .03 given for thorium because β_4 had to be guessed at in thorium.
* This value applies to the uranium spectrum

with respect to other lines in the L series with increasing atomic number. This behavior is not true of the lines $\gamma_3\gamma_2$ which have the same initial state (L_{11}) . No adequate explanation has as yet been advanced for this behavior.

The behavior of the lines $\beta_5\gamma_6$ can be explained to a certain extent by Bohr's theory of the periodic system. It is seen that the relative intensity of these lines is 17 times greater in uranium than in the tungsten L spectrum. The electron transitions which give rise to these lines come from the levels $O_{32}O_{33}$. In tungsten these levels are in the process of filling, while in uranium they are filled. The behavior of these lines is thus in accord with the observations of Allison and Armstrong¹¹ and Jönsson¹² on similar cases.

¹⁰ Jönsson, Zeits. f. Physik 46, 383 (1928).

SAMUEL K. ALLISON

The case of the lines γ_4 and γ_5 is interesting and apparently anomalous. These lines exist as moderately weak lines in the tungsten L spectrum but all attempts to find them in the thorium and uranium L spectra have failed. A curve taken in search of these lines is shown in Fig. 2. These lines have been reported in the spectrum of uranium at 42 kilovolts by Dauvillier¹³ but their presence could not be confirmed. No values of wave-lengths for these lines are given in Siegbahn's book "The Spectroscopy of X-Rays. "

Fig. 2. Uranium L spectrum, γ group.

In Table II the variation in intensity as a function of the change in total and azimuthal quantum numbers is given in a manner that shows the relation between the x-ray spectra and the alkali arc and hydrogen atom spectra. Thus in the L series lines involving transitions from M to L shells we have the components of the non-degenerate $H\alpha$ line. The theoretical values are those given by Wentzel¹⁴ on the basis of the Schrödinger mechanics. For comparison the observations of Bongers¹⁵ on the corresponding lines in the Balmer series are included.

The fact that the relative intensities of members of multiplets which involve transitions whose initial state is L_{11} are exceptions to the Burger-Dorgelo rules has been known for some time by the work of Allison and Armstrong¹¹ and $\overline{\ }$ Jönsson.¹⁶ Further information on these interesting mul-

'4 Wentzel, Naturwissenschaften 14, 621 (1926). In a private communication, Wentzel has pointed out that the theoretical values in question were calculated on the basis of equal excitation of all the L levels, and that correction for this may explain the large discrepancy in the experimental and theoretical values of transitions ending in L_{11} .

¹¹ Allison and Armstrong, Phys. Rev. **26,** 714 (1925) see p. 722.

¹² Jönsson, Zeits. f. Physik 41, 221 (1927). It is interesting to note that the results of Jönsson in this paper indicate that the $N_{32}N_{33}$ levels are completely filled for the first time at the element Ag 47. Spectroscopic evidence (McClennan and Smith, Proc. Roy. Soc. A112, 110 (1926)), on the other hand, has shown that the $N_{32}N_{33}$ orbits are filled at Pd 46 whose lowest term is ${}^{1}S_{0}$. This discrepancy may very likely be accounted for by the fact that in the solid state the $N_{32}N_{33}$ orbits in Pd are greatly distorted by the van der Waals forces, while in Ag 47 most of the distortion is in the orbit O_{11} .
¹³ Dauvillier, Jour. d. Physique **3**, 221 (1922).

¹⁵ Reported by Ornstein, Physik. Zeits. 28, 688 (1927).

¹⁶ Jönsson, see ref. 9 and Zeits. f. Physik 41, 801 (1927).

tiplets could not be obtained from the thorium spectrum because of interference of other lines. In the case of uranium it was possible to obtain β_3 and β_4 , $(M_{21},_{22} \rightarrow L_{11})$ free from other lines, and the ratio of β_3 to β_4 is 100:98 instead of 100:50. These lines have been investigated in Mo, Rh, Pd, Ag, Sn, W, by Jönsson¹⁶ and found to have a ratio $100:63.3$. The results of this investigation show an increase in intensity of the weaker member with increasing atomic number. A curve showing $L\gamma_3$ and γ_2 is shown in Fig. 2. The intensity of γ_3 is uncertain because of the presence of γ_6 but appears to be about equal to that of γ_2 . Table III shows the relative intensities of some multiplets in thorium and uranium.

It has been stated that the intensities of multiplets involving the initial states L_{21} , L_{22} obey the sum rules, but the measurements here show exceptions to these rules, namely $\gamma_5\beta_6$ and $\gamma_6\beta_5$. From the results in Table III, it may be stated that while in these elements the relative intensities of

Lines	Transitions	Theory	Obs. Th	Obs. U
γ_3 : γ_2 β_3 : β_4 $\gamma_5:\beta_6\ni l$ γ_6 : β_5 γ_1 : β_2 $\beta_1:\alpha_1:\alpha_2$	$N_{21}N_{22}+L_{11}$ $M_{21}M_{22} \rightarrow L_{11}$ $N_{11} \rightarrow L_{21}$, L_{22} $M_{11} \rightarrow L_{21}$, L_{22} $O_{32}O_{33} \rightarrow L_{21}, L_{22}$ $N_{32}N_{33} \rightarrow L_{21}L_{22}$ $M_{32}M_{33} \rightarrow L_{21}L_{22}$	100:50 100:50 50:100 50:100 50:100 50:100 56:100:11	0:1.4 50:100 53:100 62 *:100:12	100:107 100:98 0:1.6 46:100 34:100 43:100 49:100:11

TABLE III. Comparison of observed intensities and sum rule predictions,

* This value includes β_{κ} .

 $\beta_1\alpha_1\alpha_2$, $\gamma_1\beta_2$ and ηl are given to a fair degree of approximation by the sum rules, the deviations of $\gamma_3\gamma_2$, $\beta_3\beta_4$, and the two doublets mentioned above are definitely greater than the experimental errors. It may be remarked that the anomalous cases are those in which one or both of the orbits involved are highly elliptic. Jonsson has noted that the lines $\beta_3\beta_4$ are broader than the more intense lines and has mentioned a possible connection between this and the ellipticity of the orbits involved.

Recently Ornstein, Eymers, and Coelingh¹⁷ and Ornstein and Burger¹⁸ have shown that the sum rule is only an approximate rule holding for small frequency differences, and that in certain cases the observed values of intensities of widely separated multiplets divided by the fourth power of the frequency obey the sum rules. It is obvious that this cannot be the explanation of the deviations in Table III.

CALCULATION OF TRANSITION PROBABILITIES AND STATISTICAL WEIGHTS FROM INTENSITY DATA ON THE L-SERIES

The results given here for thorium and uranium are stated in terms of the relative intensities at voltages much greater than the critical voltages of the L series. It can be shown that if the classical mechanics is adequate to

¹⁷ Ornstein, Eymers and Coelingh, Zeits. f. Physik 44, 653 (1927),

¹⁸ Ornstein and Burger, Zeits. f. Physik 40, 403 (1926).

describe the impacts of fast electrons against electrons relatively at rest (J. J. Thomson's ionization function Eq. 2) that these relative intensities are related to the transition probabilities and statistical weights in the following way:

$$
E_1 S_1 / E_2 S_2 = I_1 V_{01} \nu_2 / I_2 V_{02} \nu_1 \tag{8}
$$

where E represents transition probability, S the statistical weight of the initial state, I the observed intensity at high voltage, V_0 the critical voltage of the line, and ν the frequency of the line.

Fig. 3. X-ray energy level diagram showing lines in the K , L , M series and their grouping into multiplets. The sum rule intensities of the multiplets are given in the divisions at the top of the diagram. At the right the analogous optical levels in the alkali arc spectrum are given.

On the quantum theory the intensity of a line is given by

$$
I = EN_i h\nu \tag{9}
$$

where N_i is the number of atoms in the initial state ready to radiate the line in question. Eq. (5) gives us information concerning relative values of N_i at high voltages, namely (taking the limit as V approaches infinity of the ratio of the N_i 's for two different levels as given by Eq. (5)),

$$
N_{i1}/N_{i2} = n_1 V_{02}/n_2 V_{01}
$$
 (10)

11

 n_1 and n_2 from Eqs. (2) and (5) are the numbers of electrons per atom in the groups in question. The classical theory does not predict equal excitation of two levels of the same electron content by high speed beta-particles, but excitation in the inverse ratio of the ionization potentials. If we think of the groups L_{21} and L_{22} respectively, the numbers n_1 and n_2 are 2 and 4. It is known that on the Hund theory of spectral terms it is unnecessary to consider sub-divisions of electrons having the same azimuthal and total quantum numbers. The analogous quantities to the numbers 2 and 4 are the statistical weights (2j+1) of the terms, and so we set $n_1/n_2 = S_1/S_2$. Making this substitution, Eqs. (10) and (9) give (8).

The correction to be applied to the relative intensities of members of the $L_{21}L_{22}$ multiplets in order to obtain relative values of ES is very small since the terms V_{01}/V_{02} and ν_2/ν_1 of Eq. (8) almost completly neutralize each other. We may therefore say that within the limits of experimental error the values of Table I represent the product of transition probability and statistical weight of the initial state for each member of a multiplet.

In a recent paper Jönsson¹⁰ has used an equation based on Eqs. (2) and (5) to correct the observed values of the intensities in the L series of Ag, Pd, Rh, Mo. His procedure corresponds to dividing the observed intensities by the corresponding value of the variable part of the right-hand member of Eq. (5). The corrected results given by him are then the relative intensities for equal excitation of all levels but the equation of Rosseland which he uses predicts that such equal excitation will never occur. In order to change the values given by him in Table 3 of his paper to the relative intensities at high voltage, they must be multiplied by the factor V_{01}/V_{02} of Eq. (8) where V_{01} is the critical voltage of the level L_{22} . For instance the values of α_1/β_1 and β_2/γ_1 for Ag are reported as 100/59 and 100/57 respectively. If the suggested correction is made, they become 100 /55 and 100/53 respectively, which brings them nearer to the sum rule values.

UNIVERSITY OF CALIFORNIA) BERKELEY. March 24, 1928.