ON THE X—RAY SPECTRA OF TUNGSTEN. '

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SYNOPSIS.

Critical Absorption and Emission Wave-lengths in ^K and ^L Series.—This paper describes accurate measurements of the critical absorption wave-lengths associated with the K and the L series, and also of the wave-lengths of most of the emission lines in the L series. The measurements were made by means of a new ionization spectrometer, similar to the one described in the PHYSICAL REVIEW for Dec., I9I7, at page 624. A high tension storage battery supplied the current through the X-ray tube, the voltage and current being kept constant by the procedure indicated in the reference. To eliminate errors due to the penetration of the rays into the crystal and to lack of exact adjustment between the axis of rotation of the crystal and the effective reflecting plane, etc., the authors employed the third method mentioned in the article referred to, above. In this method two slits between the X-ray tube and the spectrometer define the width of the beam of X-rays that strikes the crystal, and the slit in front of the ionization chamber has sufhcient breadth to allow the entire reflected beam to enter the chamber. With this arrangement of slits the angle through which the crystal turns (not the angle made by the *reflected* beam of rays with the zero of the instrument) measures the glancing angle that is used in the formula to calculate the wave-length.

Mean Values of the Wave-lengths Measured in Spectra of the 1st, 2d and 3d Orders.-The following table contains the weighted mean values of the wave-lengths obtained from measuremen'ts in spectra of the Ist, 2d and 3d orders, together with an estimate of the precision of the measurements. To estimate the absolute accuracy of the data we must take into account the errors in the value of the grating constant of the calcite crystal used. These add up to about o.o7 per cent. In the text the values of the emission wave-lengths obtained by this ionization method are compared with those measurements of the same lines by photographic methods in which special procedures have been employed to minimize the effects of the above mentioned errors.

Z-Ray Spectra of Tungsten. Grating Constant for Calcite 2a = $(6.056 \pm .004) \times 10^{-8}$ cm. Critical Absorption Wave-Lengths, $\lambda \times 10^8$ cm.

| Ka $.17806 + 7$ | La ₁ 1.2136 ± 1 | La ₂ 1.0726 ± 5 | La ₃ $1.024 + 3$ | |
|---|--|--|--|----------------------------|
| | | Emission Wave-Lengths, $\lambda \times 10^8$ cm. | | |
| $K\alpha_2$ $.21341 \pm 3$ \mathbb{R} Ll 1.6756 ± 10 $L\beta_4$ $1.2985 + 4$ L_{γ_1} $1.09608 + 7$ | $K\alpha_1$ $.20860 + 4$ $L\alpha_2$ 1.4839 ± 3 $L\beta_1$ $1.27892 + 9$ $L\gamma_2$ $1.0655 + 4$ | $_{\rm K8}$ $.18420 \pm 3$ $L\alpha_1$ 1.47306 ± 11 $L\beta_3$ $1.2601 + 3$ L_{γ_3} $1.0596 + 3$ | $K\gamma$ $.17901 + 6$ Ln $1.4176 + 7$ $L\beta_2$ 1.24193 ± 12 $L\gamma_4$ $1.0261 + 6$ | $L\beta_5$ $1.2040 + 7$ |

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The K emission wave-lengths have been taken from a paper by Dr. Stenström and one of the authors.

The Relative Intensity of the Lines.—The ionization spectrometer furnishes the best method of estimating the relative intensity, the relative breadth, etc., of emission and absorption lines, provided that they are so near together that the effect of absorption by the tube, etc., may be neglected or corrected for. The numerous curves in the text give a good idea of the relative intensity, etc., of the lines.

The Differences between the K and L Absorption Frequencies Equal the $K\alpha$ Emission Frequencies in Each Case to Within the Errors of Measurement.-The object of the research has been to obtain accurate values of both the absorption and the emission wave-lengths measured under the same experimental conditions. This becomes particularly important in testing theoretical laws and relations. According to the theory of the mechanism of radiation based on the Rutherford-Bohr atomic model the K critical absorption frequency should be complex, if, as Sommerfeld assumes, some atoms contain elliptic orbits and o'ther atoms of the same chemical element contain circular orbits. Further the difference between the *average* K critical absorption frequency and one of the L critical absorption frequencies should not exactly equal the frequency of one of the $K\alpha$ emission lines. As a matter of fact the authors have not observed a doubling of the K absorption frequency, and their new measurements verify the results obtained last year by Duane and Shimizu.¹ The difference between the K absorption frequency and one of the L absorption frequencies equals the frequency of one of the $K\alpha$ emission lines in each case to within the errors of measurement. Hence, if the effect due to diferent kinds of tungsten atoms exists at all, it is too small to be detected, at least for chemical elements of high atomic numbers.

Test of Sommerfeld's Formula for the Frequency Interval of the ^L Doublet.—^A Sommerfeld' has deduced from Bohr's theory an expression for the frequency interval of the L series doublet by making an interesting application of one of the equations in the quantum theory, which enables him to calculate the eccentricity of an elliptic orbit. The expression contains one undetermined constant, to which he gives the value 3.63. This value he obtains by using the published wavelengths of the lines in the L series of a great many chemical elements. Although there is some difficulty in giving a physical interpretation to the theory, yet, when one substitutes the constant in the formula, one obtains the frequency difference of the L series doublet in the tungsten spectrum to within less than one per cent. of the value we found by experiment.

Object.—The object of the research reported in this paper has been to measure both the critical absorption and the emission wave-lengths associated with the K and the L series of tungsten. Values of these absorption and emission wave-lengths- measured under the same experimental conditions are not available at present, and, evidently, for the purpose of testing certain relations deduced from theories of the structure of atoms and the mechanism of radiation, such a series of comparable wave-lengths should be obtained.

Apparatus and Method.—In order that the values of the wave-lengths might be as free as possible from errors due to the penetration of the X-rays into the reHecting crystal, and to lack of exact adjustment

[~] PHYsIcAL REvIEw, July, I9I9, p. 67.

[~] Atombau und Spektrallinien, Chapter 5.

SECOND SERIES.

between the axis of rotation of the crystal, the incident beam of rays, the *effective* reflecting plane in the crystal, etc., we have employed a new ionization spectrometer, similar to the one described in detail in the PHYSICAL REVIEW for December, 1917, at page 624. The new instrument does not differ essentially from the old one, but has circular scales that appear to be somewhat more exact. We were able to detect no difference between the readings of the two verniers attached to the crystal table that would give us a perceptible correction for excentricity in the parts of the scale used.

We have adopted the third method of arranging the spectrometer slits mentioned in the article referred to above. A narrow beam of X-rays, defined either by two slits in lead blocks between the X-ray tube and the spectrometer or by one slit and the focal spot on the target, falls on the reflecting crystal. The third slit, that in front of the ionization chamber, has sufficient breadth to allow the entire reflected beam to enter the chamber. The chief advantage of this arrangement lies in the fact that no correction is necessary for the penetration of the rays into the crystal and for the lack of exact adjustments in certain parts of the instrument. By taking readings corresponding to the same spectrum line on both sides of the zero, twice the glancing angle of incidence can be calculated by simply subtracting the angle through which the crystal has been turned from 180°. The angle through which the ionization table has been turned does not enter into the calculation. In those methods of using a spectrometer in which the glancing angle has to be calculated from positions of the reflected beam of rays {photographic methods, for instance) corrections for the above mentioned sources of error must be applied, or else special devices must be employed to eliminate them.

In making a series of measurements the crystal and ionization chamber are rotated through successive angular increments, the chamber always being moved twice as far as the crystal. In each position of the crystal the ionization current is measured. The graphs representing ionization currents as functions of the crystal table angles {see the figures) indicate peaks, corresponding to characteristic emission lines, and sharp drops, corresponding to characteristic absorption lines. To get the double glancing angle of incidence, 2θ , for substitution in the wave-length formula,

$\lambda = 2a \times 10^{-8} \sin \theta$ cm.,

we measure from the tips of the peaks or the centers of the drops, as the case may be.

To sum up, the above described arrangement of slits and general

procedure eliminates errors due to the following causes: (a) penetration of the rays into the crystal; (b) the axis of rotation of the crystal not lying exactly in the effective reflecting plane; (c) the center of the incident beam not passing exactly through the axis of rotation and (d) certain of the defects in crystal structure.

A further advantage of the ionization method lies in the fact that very good estimates of the relative intensity of spectral lines may be

Fig. 1.

obtained, provided that the lines lie so close together that we may neglect, or correct for errors due to changes in the coefficients of absorption and of reHection with wave-length.

For the tungsten emission spectrum we used an X-ray tube of the Coolidge type equipped with a tungsten target. The rays emerged from the tube through a thin glass window blown in a side arm attached to it. This materially reduced the absorption of the relatively soft L series lines. The rays emerging through this window left the target at almost grazing angles. This gave so narrow a source of rays that only one slit was needed to make the incident pencil of rays as narrow as desired.

As in earlier researches a high tension storage battery supplied the current through the X-ray tube, the voltage being kept constant during an experiment by gradually changing a resistance in series with the tube.

The usual method of control of the current through the tube enabled

us to maintain the apparatus in a steady state, and to keep the temperature of the target, etc., constant.

We used a lead ionization chamber filled with methyliodide or ethylbromide and provided with a very thin mica window to reduce the absorption of the reflected beam of X-rays as it entered the chamber. A quadrant electrometer measured the ionization currents.

Tungsten L emission Lines.—Thirteen lines in the L series of tungsten have been measured. Figs. 1, 2 and 3 show typical curves platted from actual measurements on the α , β and γ groups of lines respectively. The position of a peak can always be located as between two crystal

Fig. 2.

angle readings, 30" of arc apart. Moreover, a good estimate may be made as to how much nearer the actual peak lies to one of these readings than to the other. We believe that, by making several complete series of measurements, we have been able to determine the value of the double glancing angle, 2θ , to within less than $10''$ of arc in many cases. This means an error of not more than .or to .o2 of a per cent. in the value of the glancing angle, depending upon its magnitude. The grating space, d , of calcite is known to within about 0.07 of a per cent. No other grating space appears to have been determined as accurately as this. The best determinations of the grating space of calcite lie within a few hundredths of a per cent. of 3.028×10^{-8} cm. We have chosen this value, therefore, to use in calculating our wave-lengths. Hence, taking the grating space of calcite as fixed, we may assume that the relative

530

values of our wave-lengths are correct to within .01 or .02 of a per cent., according to their magnitudes, in our best experiments.

The lines *l*, α_1 , α_2 , η , β_1 , β_2 , γ_1 , and γ_3 have all been measured on both sides of the zero position of the crystal. The glancing angles for β_3 , β_4 ,

 β_5 , γ_2 and γ_4 , however, have been determined by comparison with the glancing angles for neighboring strong lines.

Measurements of the glancing angles for α_1 , β_1 and γ_1 have been

made in the first and second order spectra, and for β_1 also in the third order spectrum. Fig. 4 shows the curves obtained for β_1 in the second and third order spectra. There is a slight indication in the third order spectrum that this line has a close and weaker satellite on its short wavelength side.

Table I. contains the glancing angles and computed wave-lengths for α_1 , β_1 and γ_1 .

TABLE I.

L Series of X-Rays.

Tungsten.

Grating Constant for Calcite $2d = 6.056 \times 10^{-8}$ cm.

It is interesting to note that the wave-lengths computed from data in higher orders are slightly shorter than those computed from lower orders. Stenström¹ has found similar differences in the case of certain longer wave-lengths which he measured by means of the crystals sugar and gypsum. He has ascribed the differences to a small amount of refraction and dispersion of the X-rays by the crystals. The differences here noted, however, are of the order of magnitude of the experimental errors.

The fourth column in Table II. contains our weighted mean values for the wave-lengths, measured in a number of complete series of experiments. For comparison we have tabulated the wave-lengths recorded by Overn² and by Siegbahn³ in the second and sixth columns respectively. A slight correction, amounting to one thirtieth of one per cent., has been subtracted from the values they give in order to make their wave-lengths correspond to the grating constant for calcite that we use. Columns

^{&#}x27; Doctor's Dissertation, Lund, I9I9.

² PHYS. REV., Aug., 1919.

³ Phil. Mag., Nov., 1919.

three and five contain the respective differences. It appears that the wave-lengths measured by the ionization method agree in most cases with those measured by the. photographic method to within the limits of experimental errors. In each of the series of measurements by the photographic method great care was taken by the respective authors to

TABLE II.

L Series of X-Rays. $\lambda \times 10^8$ cm.

Tungsten.

Grating Constant for Calcite $2a = 6.056 \times 10^{-8}$ cm.

correct for or eliminate the sources of error mentioned above. In particular Siegbahn designed an interesting spectrometer for the express purpose of reducing the errors due to penetration of the X-rays into the crystal, etc., to a minimum.

Overn does not include the lines l and η in his table of wave-lengths. He suggests, however, that the marks on photographic plates corresponding to η may represent the α_1 line in the K series of molybdenum in the second order spectrum. As the lines l and η are of considerable theoretical importance we have tested this point by examining the spectrum in the neighborhood of K_{α_1} for molybdenum in the first order spectrum. We found evidence for both molybdenum Ka_1 and Ka_2 , but their intensities were less than that of the line we regard as $L\eta$ of tungsten. As the intensity of the second order spectrum is very much less than that of the first order spectrum it is impossible that the peak on our curve should represent molybdenum Ka_1 in the second order.

Critical Absorption Wave-Lengths.—In general the measurement of critical absorption wave-lengths is more difficult and slightly less accurate than that of emission lines. In order to make such a measurement we usually place a screen containing the chemical element to be investigated

in the path of the incident beam of rays between the X-ray tube and the spectrometer, take a series of readings in the neighborhood of the critical point and draw the corresponding ionization current crystal

critical point.

table angle graphs. Figs. 5, 6 and 7 contain such graphs. Owing to the fact

that the absorbing substance absorbs

X-rays of longer wave-length than the

critical wave-length to a less extent than

it does X-rays of shorter wave-length a

sharp drop in the curve occurs at the

to the target itself, which was so placed

that the beam of X-rays that struck

the crystal left the target almost grazing

its surface. Under these conditions the

target absorbs a large part of its own

radiation. Fig. 5 clearly shows the rela-

tive magnitudes of the emission and ab-

sorption spectra. The absorption drop

is the largest of the three critical ab-

sorptions that have so far been observed

in the L series of X-rays. The glancing

angle, θ_{a1} , in this case has been estimated

by taking the difference between it and

In Fig. 5 the absorption drop is due

Fig. 5.

the glancing angle, θ_{82} , of the neighboring emission line.

The other two absorption drops fall so close to emission peaks that good measurements of them can not be made without using an X-ray tube with a target of a different chemical element. Professor D. L. Webster kindly loaned us such a tube, with a molybdenum target. Using it we obtained the curves, represented in Figs. 6 and 7, on both sides of the zero. We estimated the grazing angles, θ_{a2} and θ_{a3} , by measuring from the centers of the corresponding drops.

Fig. 7 contains curves for the K critical absorption of tungsten, obtained in the first, second and third order spectra. We are indebted to Dr. Stenström for his assistance in making these K series measurements.

Table III. contains the glancing angles and computed wave-lengths for the K and L characteristic absorption lines of tungsten.

We wish to call attention to the relative magnitudes of the critical absorption wave-lengths and the wave-lengths of the emission lines.

534

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No. 6.

TABLE III.

Tungsten Absorption Spectrum.

K and L Critical Absorption Wave-Lengths.

Grating Constant for Calcite $2d = 6.056 \times 10^{-8}$ cm.

The critical absorption wave-length L_{a1} is about $2\frac{1}{3}$ per cent. shorter than that of the β_2 emission line and about .8 of a per cent. longer than

that of the β_5 emission line. La₁ lies in the midst of a number of faint lines that have been observed on photographic plates by Dershem, Overn and Siegbahn. La₂ lies between γ_1 and γ_2 (about 0.7 per cent. from γ_2). La₃ lies within a fraction of one per cent. of γ_4 , and apparently on its short wave-length side.

Many of the general laws and theoretical equations relating to X-ray spectra are expressed in terms of the frequencies of vibration, the wavenumbers or the ratios of the frequencies to the fundamental Rydberg frequency for heavy atoms. The following table contains the values of ν/ν_{∞} calculated from our data. In making these calculations we have used Paschen's value for the wave-number, v_{∞} , namely $v_{\infty} = 109,737.11$ \pm 0.06, the accuracy of which far exceeds that of any X-ray measurement that can be made at the present time.

TABLE IV. Tungsten X-Ray Spectrum.

Values of ν/ν_{∞} for the K and L Critical Absorption and Emission Lines.

In the PHvstcxt, REvrEw for July, i9r9, Duane and Shimizu published an account of experiments which showed that each of the α emission frequencies in the K series equaled the difference between the K critical absorption frequency and one of the L critical absorption frequencies. Theoretically this should be true provided that all the atoms (of the same chemical element) are exactly alike, *i.e.*, have the same kinds of orbits: for, if W and W_1 represent the amounts of energy in an atom of

 $^{\text{\tiny{1}}}$ The values for the K series emission lines are taken from a paper by Duane and Stenströn presented to the Physical Society in February, 1920. See the PHYSICAL REVIEW, April, I920, P. 328.

tungsten when in its natural state and when one electron has been removed from the K orbit respectively, the K critical absorption frequency is given by the equation

$$
h\mathbf{K}a = W_1 - W.\tag{1}
$$

Similarly, if W_2 represents the energy of the system when one of the electrons has been removed from an L orbit, the corresponding L critical absorption frequency is given by the equation

$$
hLa = W_2 - W.\t\t(2)
$$

According to the theory a Ka characteristic X-ray is emitted when an electron falls from the La orbit to the Ka orbit, and during this transfer the energy of the atom changes from W_2 to W_1 . The difference between these amounts of energy is radiated at a frequency Ka given by the equation

$$
h\mathbf{K}\mathbf{a} = W_1 - W_2. \tag{3}
$$

From equations (1) , (2) and (3)

$$
Ka = Ka - La.
$$
 (4)

And this is the relation found by experiment to hold within the limits of error.

If, however, some atoms contain circular orbits and others elliptic orbits, both Ka and La will have different values for the different kinds of atoms. In fact all critical absorption, critical ionization and emission lines will have complex structures. We have not been able to observe such a structure in the absorption drops for chemical elements of high atomic weight. Further the data obtained this year corroborate the results arrived at last year to within the limits of experimental errors. These errors are smaller than those of last year's measurements, for (a) the wave-lengths are averages of a larger number of individual determinations, (b) some of them were measured in spectra of higher orders and (c) the thin glass window in the X-ray tube allowed a larger amount of X-ray energy to emerge from the tube.

The following values taken from Table III. show the precision with which the Ka emission frequencies equal the differences between the critical absorption frequencies.

Second
Series.

It is impossible to test directly the above law as applied to the L and the M series, for the M critical absorption wave-lengths have not been measured for tungsten.

Theoretically,¹ however, if two emission lines in the L series are produced by electrons falling from the same outer orbit to the $La₁$ and $La₂$ orbits respectively, the difference between their frequencies should equal that between the two critical absorption frequencies (except for the possible small correction due to the complex structure of the lines as explained above). The difference between the two critical absorption frequencies is

$$
La_2 - La_1 = 98.7 \pm .5.
$$

Turning to the emission lines we find that the following three pairs have frequency differences that equal the difference between the two critical absorption frequencies to within the limits of experimental error:

$$
L\eta - Ll = 99.0 \pm .6,
$$
 $L\beta_1 - L\alpha_2 = 98.4 \pm .2,$
 $L\gamma_2 - L\beta_5 = 98.4 \pm .7.$

This would seem to indicate that the electrons producing the two lines in a pair fall from the same outer orbit. For instance we may suppose that $\text{L}\alpha_2$ and $\text{L}\beta_1$ are due to electrons falling from one of the M orbits. Measurements of the absorption frequencies for thorium and uranium which the authors presented to the Physical Society in April agree very well with this hypothesis. Further we may assume that Ll and $L\eta$ are produced by electrons falling from an orbit between the L and the M orbits. This orbit, however, has not been identified by means of a critical absorption frequency in the case of any chemical element. On the other hand there appears to be some difhculty in the theoretical interpretation in the case of the third pair, for the frequencies of the emission lines $L\beta_5$ and $L\gamma_2$, are greater than those of the critical absorption frequencies La_1 and La_2 respectively.

The difference between the frequencies of a fourth pair of emission lines is almost, but not quite equal to that between the critical absorption frequencies, namely

$$
L\gamma_1 - L\beta_2 = 97.5 \pm .1.
$$

It would seem that in this case the electrons producing the lines did not come from exactly the same outer orbit.

Siegbahn² finds that the difference in frequency between the lines in these pairs decreases slightly as the frequency itself increases.

¹ Compare an interesting discussion of this subject by A. Sommerfeld in Atombau und Spektrallinien, Chapter 3.

538

² Phil. Mag., Nov., 1919.

Sommerfeld (Atombau und Spektrallinien, Chapter 5) has deduced a formula for this L series frequency difference from his theory of elliptic orbits. Making the relativity correction for the change of mass of an electron with its velocity he finds that the energy of an electron travelling in an elliptic orbit differs somewhat from that of the electron in the corresponding circular orbit. This means that those atoms which have elliptic L orbits produce spectra that differ in frequency from the spectra of atoms with circular L orbits. Sommerfeld's equation for this difference $\Delta \nu$ in frequency (divided by ν_{∞}) reduces to

$$
\frac{\Delta \nu}{\nu_{\infty}} = \frac{I}{\alpha^2} \left(\sqrt{2} \sqrt{I + \sqrt{I - b^2}} - \sqrt{4 - b^2} \right),
$$

for the L series. In this equation

$$
\alpha = \frac{2\pi e^2}{hc} = 7.295 \times 10^{-3}, \quad \text{and} \quad b = \alpha(N - n),
$$

where $e =$ the electron's charge, $h =$ Planck's constant and $c =$ the velocity of light.

The function representing the frequency difference, varies roughly as the fourth power of the atomic number, N , of the chemical element. It contains an arbitrary constant, n , the value of which he deduces from the wave-lengths in the X-ray spectra of a great many chemical elements. This value is $n = 3.63$. Putting it and $N = 74$ (for tungsten) in the formula we get 97.9 for the value of $\Delta \nu/\nu_{\infty}$, which agrees very well with our experimental results.

Sommerfeld recognizes the difficulty of giving a satisfactory physical interpretation to the above value of n (l. c.). Further it is worth noting that the formula does not take into account the changes in the energy of the other electrons in the atom when one of them is removed. These energy changes for the other electrons in the L orbit itself do not appear to be negligible, although, of course only the differences between their values for elliptic and circular orbits would enter into the equation.

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 ${\rm Fig.}$ 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.