

AN INVESTIGATION OF THE TUNGSTEN X-RAY
EMISSION AND ABSORPTION SPECTRUM
WITH A VACUUM SPECTROMETER

BY R. V. ZUMSTEIN

ABSTRACT

M series lines of tungsten.—Using a cast bronze x-ray tube and a vacuum spectrometer, the M series of tungsten has been studied both in emission and absorption. A new type of window for the x-ray tube was made by grinding lampblack with collodion. In the *emission spectrum* between 7A and 5A, two faint lines have been observed: $\eta_1 = 6.857$ and $\eta_2 = 6.789\text{A}$. Two components of the α and β lines have been measured $\alpha' = 6.948$, $\beta' = 6.720\text{A}$, confirming the work of Hjalmar. In the *absorption spectrum* five lines $M_1 - M_5$ have been observed at 6.708, 6.475, 5.416, 4.800, 4.365A. The wave-length of the first two are less than their predicted values by an amount (about 2 percent) which is greater than the probable limits of error ($\pm .006\text{A}$). M_3 has a component $M_3' = 5.380\text{A}$. M_5 is very weak.

THE following article is a report on a portion of the study undertaken in this laboratory of the x-ray spectrum of one element. Tungsten was chosen as it seemed possible to study the K, L and M series both in emission and absorption. This work on the M series is reported in this article.

EXPERIMENTAL METHODS

A vacuum spectrometer and x-ray tube were constructed similar to that described by Siegbahn.¹ The x-ray tube was a bronze casting. The interior of the tube was coated with a layer of solder. A tray of phosphorus pentoxide absorbed water vapor. The spectrometer was evacuated with an oil pump and the tube with a mercury vapor pump. The voltage on the tube, which was between two and four thousand volts, was supplied by a transformer. A rectifying device was not necessary as at these low voltages the tube rectified the current itself. A three thousand volt d.c. generator set was also tried. It was necessary to use compound wound generators since the sudden appearance of small traces of gas in the tube caused a surge through the tube. With shunt wound generators this might reverse their polarity or puncture the field coils. If 3000 volts were required on the tube it would be of advantage to have 5000 volts at the generator. This would permit the insertion of a large inductance and a resistance in the circuit which would tend to minimize the disastrous effects of these surges.

¹ Siegbahn, Ann. der Phys. **59**, 56 (1919)

The filament was a 25 mil (.62 mm) tungsten wire placed about 3 mm from the target. No space charge effects were observed. This is probably due to the presence of mercury vapor from the pump. Due to this mercury vapor the filaments sputtered and had to be renewed in about 20 hours. Some of the tungsten from these sputtered filaments was deposited on the copper target where it was useful in giving the tungsten emission lines and as a strong continuous radiator for observing absorption spectra.

A window was placed over the slit between the x-ray tube and the spectrometer. The purpose of this window was to separate the low from the high vacuum and also to keep the light from the tungsten filament from fogging the photographic plate in the spectrometer. The windows were made by grinding lampblack with collodion in a mortar and then pouring the solution on a glass plate. These windows do not transmit any light and being made of light atoms they should be transparent to x-rays. However in the region of 7A these windows absorbed a large proportion of the x-rays, perhaps 75 percent. In absorption spectra, a second window was used in which tungsten trioxide was ground up with collodion.

The power supplied to the tube was about 1 kva. The width of slit used was .2 mm. The distance from the slit to the crystal and from the crystal to the plate were each approximately 12.9 cm. The crystal was of optical gypsum with a surface of about 3×7 cm. Using only a carbon window an exposure of 12 hours would give the continuous spectrum when the crystal was rotated through one degree. When the additional tungsten absorbing screen was used the exposures were between 75 and 125 hours for the spectrum at 7A.

All measurements were made with reference to emission lines. The wave-lengths of the reference lines were taken from Siegbahn's article.² The wave-lengths were determined for each absorption line from two reference lines not farther apart than $1/2$ cm. The distances on the plate were measured with a very low power traveling microscope which was focused on the long wave-length edge of both the emission and absorption lines. A more accurate method of determining wave-lengths was not necessary because of the lack of sharpness of the new emission and absorption lines here measured.

EXPERIMENTAL RESULTS

The *emission spectrum* of tungsten was investigated from 7A to 5A. A pure tungsten disk was used as a target. Later on, films of sputtered tungsten were found to give the same results.

² Siegbahn, Jahrb. der Radioaktiv., April 1922

The emission lines α , β and γ which had been measured by Stenstrom³ and by Hjalmar⁴ were found to be very intense. The α and β lines appeared sharp on both edges and with a faint component on the short wave-length side as reported by Hjalmar. The γ line appeared broad and with both edges diffuse. Two new faint lines were observed on seven plates. Taking Stenstrom's values for α and β as standard, the following measurements were made: $\alpha' = 6.948\text{A}$,

$$\eta_1 = 6.857\text{A}, \quad \eta_2 = 6.789\text{A}, \quad \beta' = 6.720\text{A},$$

(error $\pm .006\text{A}$). The α' line appeared sharp on the short wave-length edge. The long wave-length edge was not separated from the α line. In this case the traveling microscope was focused on the short wave-length edges of α and α' . Exactly the same can be said of β and β' . One cannot say whether the lines η_1 and η_2 are sharp or diffuse as they were just visible on the plate.

The *absorption spectrum* of tungsten was investigated from 7A to 4A. Table I gives for each absorption line the reference lines used. The fifth column gives for each plate the value obtained for the wave-length of the absorption line. In Table II are given the wave-lengths assumed for the reference lines.

TABLE I
Absorption M spectrum

| Line | Plate | Reference lines | Wave-length | Mean |
|------------------|-------|---|-------------|--------|
| M ₁ | No. 1 | WM α , WM β , SiK α | 6.710A | 6.708A |
| | 2 | SiK α | 6.708 | |
| | 3 | WM α , WM α | 6.705 | |
| M ₂ | 1 | WM α , WM β | 6.483† | 6.475 |
| | 2 | WM α , WM β | 6.467† | |
| M ₂ | 1 | SK α , PbM α | 5.417 | 5.416 |
| | 2 | SK α , PbM α | 5.418 | |
| | 3 | SK α , PK β | 5.412† | |
| | 4 | SK α | 5.418 | |
| M ₂ ' | 1 | SK α , PbM α | 5.374 | 5.380 |
| | 2 | SK α , PbM α | 5.383 | |
| | 3 | SK α , PbM α WM β | 5.383 | |
| M ₄ | 1 | MoL γ , PbM β | 4.793 | 4.800 |
| | 2 | MoL γ , SKA | 4.793 | |
| | 3 | BiM β , PbM β | 4.808 | |
| | 4 | AgL α , MoL γ , SKA | 4.805 | |
| M ₆ | 1 | AgL α , MoL γ | 4.363 | 4.365 |
| | 2 | AgL α , AgL β | 4.366 | |
| | 3 | AgL α , ClK β | 4.373 | |
| | 4 | AgL α , ClK β | 4.360 | |

† plate under-exposed

³ Stenstrom, Ann. der Phys. 57, 347 (1918)

⁴ Hjalmar, Zeits. f. Physik 15, 65 (1923)

The M_1 absorption line was found to be very close to the β emission line. It could be observed only by using molybdenum filaments in the x-ray tube. With these filaments the current through the tube could not be greater than .2 ampere. The time of exposure was one week. The tungsten emission lines are either entirely absent or faintly present.

TABLE II

| <i>Wave-lengths of reference lines</i> | | | | | | | |
|--|--------|--------------|--------|--------------|--------|--------------|--------|
| WM α | 6.973A | SK α | 5.361A | PK β | 5.786A | AgL α | 4.145A |
| WM β | 6.745 | SK A | 5.012 | MoL γ | 4.711 | AgL β | 3.926 |
| SiK α | 7.109 | PbM α | 5.273 | BiM β | 4.894 | ClK β | 4.395 |
| | | PbM β | 5.065 | | | | |

For the M_2 absorption line only two plates were obtained and they were both underexposed.

Four plates were obtained of M_3 . It is accompanied by another absorption line which is here called M_3' . M_4 was also obtained on several plates. The absorption at M_5 is very slight. Table III gives the wave-lengths of these absorption lines as found by experiment. The ν/R values are added for comparison with the theoretical values which had been obtained by Crofutt,⁵ Bohr and Coster⁶ and Sommerfeld.⁷ For all these absorption lines neither edge appeared sharp. This is probably due to the wide slit which was used, .2 mm. It was found impractical to work with a narrower slit.

TABLE III

Tungsten absorption spectrum, M Series

| Wave-length measured | ν/R values | | | |
|-------------------------|----------------|---------|-----------------|------------|
| | Observed | Crofutt | Bohr and Coster | Sommerfeld |
| M ₁ 6.708A | 135.9 | 133.6 | 133.2 | 132.43 |
| M ₂ 6.475 | 140.8 | 138.1 | 137.8 | 137.03 |
| M ₃ 5.416 | 168.2 | 168.8 | 167.4 | 166.7 |
| M ₃ ' 5.380 | 169.4 | | | |
| M ₄ 4.800 | 189.9 | 190.2 | 188.9 | 188.2 |
| M ₅ 4.365 | 208.8 | 207.8 | 207.6 | 206.86 |

THEORETICAL CONCLUSIONS

A recent article by Thoraues⁸ on the emission spectrum of tungsten in the M series, gives a list of seventeen lines expected by the selection principle, of which he has found thirteen. He has examined the spectrum

⁵ Crofutt, Phys. Rev. **24**, 9 (1924)

⁶ Bohr and Coster, Zeits. f. Physik **12**, 347 (1923)

⁷ Sommerfeld, Atomic Structure etc., p. 517

⁸ Thoraues, Zeits. f. Physik **26**, 398 (1924)

from 9A to 4.4A. Several of these lines were apparently very faint on his plates. It appears as if an element in a solid target does not easily radiate those frequencies which originate from stationary states near the surface of the atom. It seems possible that the vacuum sparks as used by Millikan⁹ in the extreme ultraviolet would be a much better source of the M series of tungsten since in this case the tungsten atoms are in the vapor state.

The emission lines α' , η_1 , η_2 , β' , which were observed on several plates, do not agree with the selection principle and were not observed by Thoriaeus; also the line measured by him as $M_{2O_{3,4}} = 6.750 \text{ \AA}$ was not observed in this work. These differences may be connected with the voltages used on the tube. I have used a voltage which would not excite the second order spectrum. It may also be that his windows were more transparent to x-rays of this wave-length.

In the absorption spectrum of tungsten in this series it is worth noting that the absorption at M_5 is very slight. An absorbing screen that would give M_4 satisfactorily must be made three times as thick to show M_5 . This appears to be connected with the fact that the only emission lines known to originate from M_5 are the l and η lines of the L series and they are both of low intensity.

The absorption at M_3' which is close to M_3 has not been predicted from theory. According to the table given by Bohr and Coster⁶ an absorption limit with ν/R value of 169.4 could have the following origin: zirconium L_2 , lutecium M_4 , gold M_2 , mercury M_1 . This absorption could not be due to the gypsum crystal used nor to the mercury vapor since it was not obtained when the region of each absorption line was photographed without an absorbing screen in the path. While we cannot be certain of its origin until the absorption at M_3 has been studied for other elements in the neighborhood of tungsten, the present evidence is that it is in the screen.

It is to be noted also that M_1 and M_2 are displaced from their predicted positions by an amount which seems to be larger than the errors of measurement. This is especially surprising when we consider that from the M_1 and M_2 levels originate such lines in the L series as α_1 , α_2 and β_1 . These are strong lines and their wave-lengths should be accurately known. This shows the desirability of obtaining direct experimental values of the absorption wave-lengths M_1 and M_2 for those elements between bismuth and tungsten.

⁹ Millikan and Sawyer, Phys. Rev. **12**, 167 (1918)

On the whole, these results agree with the energy diagrams given in Sommerfeld's book¹⁰ and the article by Bohr and Coster. They differ in a few points which require further study.

Finally it is a pleasure to thank Mr. J. B. Dempster who did the excellent mechanical work on the apparatus and especially Professor G. W. Stewart who suggested the problem and under whose direction the work has been carried on.

UNIVERSITY OF IOWA,
February 1, 1925.

¹⁰ Sommerfeld, loc. cit.⁷ p. 513