THE K AND L ABSORPTION AND EMISSION SPECTRA OF TUNGSTEN

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Abstract

Both the absorption and emission spectra were photographed simultaneously on the same plate, using a special float-operated mechanism to turn the crystal very slowly so as to obtain the faint lines between β_2 and β_5. The *absorption wave-lengths* were found to be: LA_1, 1.2122A; LA_2, 1.0716A; LA_3, 1.0217A; KA, .17802A. Table I gives the *emission wave-lengths* of 28 L emission lines including the four new lines β_{15} (1.2432), β_{16} (1.2166), γ_{12} (1.0748) and n (1.0699), and of the $K\beta_3$ line (.18525) which is the line found by DeBroglie. *Comparison with the Bohr theory.* The agreement of the emission frequencies computed from the energy levels with the measured wave-lengths is better than 1/10 per cent, except for β_{15} and β_{16}. The lines β_{10}, β_9, γ_{12}, and γ_{11}, however, correspond to transitions between energy levels which are not predicted by the selection principle, and lines β_8 and n are not in agreement with the accepted energy levels. While Ln may be due to an impurity, β_8 is probably a tungsten line.

THIS work is an investigation of the absorption and emission spectra of tungsten under the same experimental conditions. Both spectra were obtained simultaneously on the same photographic plate in order to make certain the relative positions of the absorption limits and the emission lines.

Experimental Method

A medium focus tungsten target Coolidge tube was used as a source of x-rays. The x-rays were analyzed by means of a rock salt crystal and the spectra were recorded on photographic plates. The apparatus is essentially that used by Dershem[1] with the substitution of an accurately constructed crystal table, a narrow slit of 0.005 cm width, and a new rotator for the crystal.

The crystal table is shown in Fig. 1 and consists of a spindle fitted in bearings as shown. This spindle is removable and additional spindles make it possible to change crystals without remounting each time.

The crystal was rotated through a small angle by means of levers attached to a float in a tank of water, the level of which was raised by means of a small stream of water and lowered by the use of an intermittent syphon. The advantage of this method is that the crystal can be set for a particular line and a prolonged exposure taken with the as-

[1] Dershem, Phys. Rev. **11**, 461 (1918)

surance that the crystal will not rotate too far. The rotation can be made as slow as desired and the angle kept as small as a quarter of a degree. The fine slit greatly prolongs the time of exposure but enables greater resolving power to be obtained. The fine slit and the rotator made it possible to obtain the group of faint lines between β_2 and β_5.

While working with the L series it was necessary to keep the voltage so low that no appreciable second order continuous radiation would affect the plate at the same point.

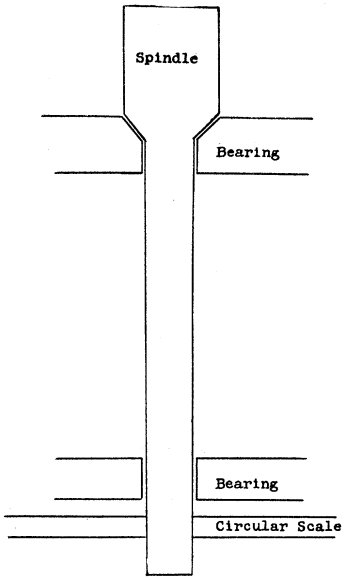

Fig. 1. Crystal table.

The work on the K series was done in the third order using 110,000 volts, effective value. The first and second order radiations were removed by absorbing screens.

The absorption bands were obtained by placing a screen of tungsten oxide in the path of the beam before it entered the spectrometer. This in no way interferes with the production of the emission spectra but does interfere with the analysis as emission lines are close to the absorption bands.

The method of measuring the plates is that developed by Dershem[1] in which a correction is made for the width of the slit. Measurements of faint emission lines and absorption bands were always made relative to strong emission lines.

Corrections

With the method employed there are two chief sources of error.

(a) If the plate is not perpendicular to the line of collimation it can be shown from geometrical considerations that θ is given by the following formula

$$D \tan 2\theta = d\sqrt{(1+m^2)} \pm \sqrt{d^2(1+m^2)+D^2m^2},$$

where θ is the glancing angle, d the distance from the crystal to the plate, D the distance between the lines as photographed on both sides of the line of collimation, and m the tangent of the angular displacement of the normal to the plate from the line of collimation. Since this correction is small, m may be determined with sufficient accuracy by means

of two known lines. In a manner similar to the above it can be shown that

$$2(1-p)m=(1+p)(m_1+m_2)\pm\sqrt{(1+p)^2(m_1+m_2)-4(1-p)^2m_1m_2}$$

where p is the ratio of the distances between the two lines on opposite sides of the line of collimation, m_1 and m_2 the value of $\tan\theta$ for the two known lines.

(b) If the face of the crystal is not in the axis of rotation an amount equal to $\delta/\sin\theta$ must be added to or subtracted from the distance from the axis of rotation to the plate in order to obtain the distance from the crystal to the plate, where δ is the displacement of the face of the crystal from the axis of rotation. Since for small values of θ, $\sin\theta$ is small this correction is important.

TABLE I

Wave-lengths in Angstroms

L SERIES

α_2	1.4844	β_{15}	1.2432	β_{10}	1.2099	A_2	1.0716
α_1	1.4733	β_2	1.2421	β_9	1.2027	n	1.0699
η	1.418	β_8	1.2364	γ_5	1.1299	γ_2	1.0659
β_4	1.2988	β_7	1.2217	γ_1	1.0964	γ_3	1.0599
β_6	1.2875	β_{16}	1.2166	γ_8	1.0786	γ_{11}	1.0444
β_1	1.2793	β_5	1.2133	γ_{12}	1.0748	γ_4	1.0266
β_3	1.2602	A_1	1.2122	γ_6	1.0723	A_3	1.0217

K SERIES

Comparison lines				Measured			
α_2	.21352	β	.18436	β_3	.18525	A	.17802
α_1	.20885	γ	.17940				

Using Dershem's method for locating the lines, the penetration into the crystal does not introduce an error for the method depends on locating the edge of the line as reflected from the face of the crystal.

EXPERIMENTAL RESULTS

Table I shows the experimental results on the emission and absorption in the L and K series. The absorption limits are indicated by the letter A with appropriate subscript. In the L series the following lines were measured carefully and the results taken as standards for the measurements of all other lines: α_1, β_1, β_2, γ_1, γ_3, and γ_4. The comparison lines in the K spectrum are indicated in Table I. Because of the presence of the reference lines the results obtained on two or more plates varied only in the last significant figure shown. The line l does not appear because of the absorption in the glass walls of the tube. The lines β_{15}, β_{16}, γ_{12}, and n are new lines for the L series of tungsten.

Discussion of Results

Fig. 2 presents the results in the well known form of energy levels as recently published by Bohr and Coster.[2] Table II gives the corresponding frequencies of the energy levels. The K and L frequencies were obtained directly from the measurements made on the wave-lengths. The other

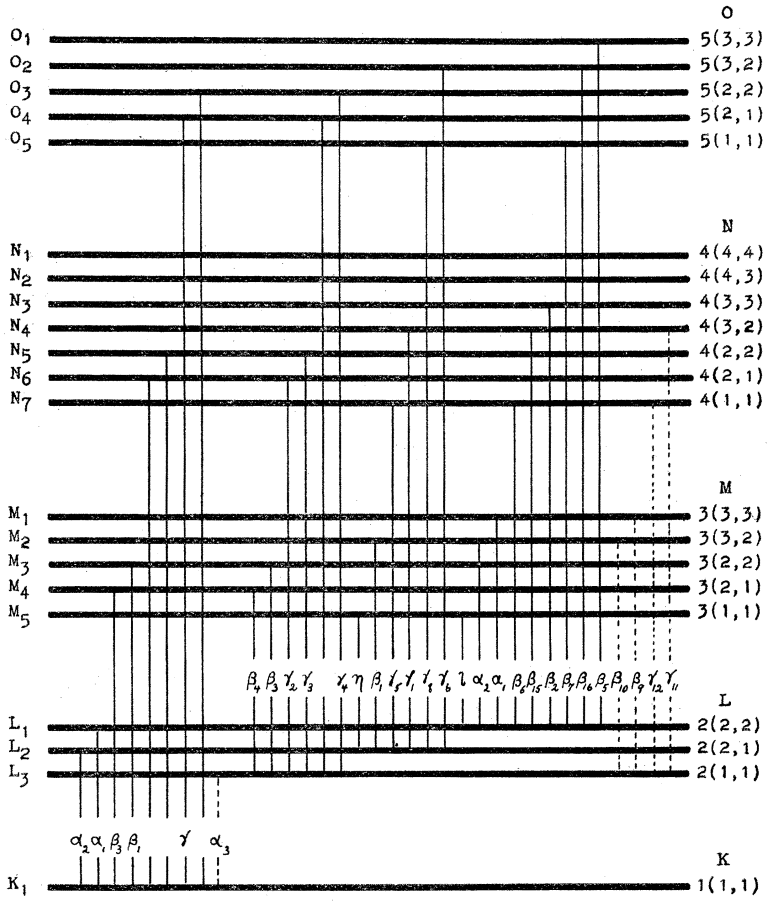

Fig. 2. Energy level diagram for tungsten showing the K and L series. Solid lines are transitions predicted by the selection principle. Broken lines are other transitions.

frequencies were calculated from the K and L absorption frequencies and the frequencies of the emission lines. The solid lines between the energy levels of Fig. 2 represent transitions predicted by the selection principle.[3]

[2] Bohr and Caster, Zeits. f. Phys. **12**, No. 6 (1923)

[3] Bohr, Phil. Mag. June 1922

The broken lines represent other transitions found. The notation is that of the line produced by the transition. If there is no symbol the line has not been found. The symbols at the left of the horizontal lines are the usual notations of the energy levels; those at the right are the notations of Bohr and Coster [the symbol 4(2,1) corresponds to the energy level having the total quantum number 4, the "grund" quantum number 2 and the azimuth quantum number 1].

The selection principle states that the azimuth quantum number must change by ± 1 or 0 and that the "grund" quantum number must change by ± 1.[2]

TABLE II

Absorption frequencies $\times 10^{-18}$

K and L measured; M, N and O calculated

K_1	16.844	M_1	.4401	N_3	.0579	O_1	.0022
L_1	2.4738	M_2	.4548	N_4	.0629	O_2	.0053
L_2	2.7982	M_3	.5554	N_5	.1058	O_3	.0140
L_3	2.9349	M_4	.6261	N_6	.1220	O_4	.017
		M_5	.6814	N_7	.1448	O_5	.0189

A comparison of Table I with Fig. 2 shows that all but the β_8 and n lines are represented on the diagram. The n line is a new line and may be due to some impurity, although a comparison with tables failed to reveal its identity. The β_8 line has been found by Overn[4] and Siegbahn[5] and should be accepted as a line of tungsten. This line is hard to measure being very indistinct. Coster[6] has shown that it appears as β_{11} and β_{12} in elements of atomic numbers 47 to 51. Of the four lines of the L series β_9, β_{10}, γ_{11}, and γ_{12} not given by the selection principle, γ_{12} is a new line. A careful investigation failed to reveal the $K\alpha_3$ line of which Duane and Shimizu[7] found some indication. The results indicate that if it does exist it does not differ in wave-length from the α_2 line by more than .04 per cent, or else its intensity is so low that it is concealed by the general radiation. It is not predicted by the selection principle. The two other new lines are given by the selection principle.

β_{15} is so close to β_2 that it could not be completely resolved, but because of the difference in intensity the edges of both lines could be located and measured. The other new lines are very faint and close to lines already known. $K\beta_3$ is the line previously found by DeBroglie.[8] The wave-lengths obtained for the absorption bands are shorter than those

[4] Overn, Phys. Rev. **14**, 137 (1919)
[5] Siegbahn, Phil. Mag. Nov. 1919
[6] Coster, Phil. Mag. Sept. (1922)
[7] Duane and Shimizu, Phys. Rev. **14**, 67 (1919)
[8] De Broglie, Comptes Rendus, 1920

obtained by Duane, which are usually accepted as standard. These changes in wave-length are sufficient to alter the relative positions of the LA_1 and the LA_2 with respect to β_5 and γ_6, as is shown in Table III and of course visually on the plates themselves.

It is seen from Fig. 2 that all lines found as transitions between energy levels but not predicted by the selection principle involve (1,1) energy levels. This may be a coincidence but it may have significance.

No special attempt was made to obtain the relative intensities of the lines. The β_{15} is of medium intensity while the other new lines are very faint.

The fact that the lines β_{15}, β_{16}, and γ_{12} fit into the energy level diagram makes it seem reasonable that they are tungsten lines.

Since the absorption and emission spectra appear on the same plates it is impossible to say much regarding the structure of the absorption bands, some of the emission lines being very close to the absorption edges. However the edges were sharp and easily measured.

TABLE III

The shift in absorption wave-lengths

A_1	1.2140*	A_2	1.0730*	γ_4	1.0266
β_2	1.2133	γ_6	1.0723	A_3	1.024*
A_1	1.2122	A_2	1.0716	A_3	1.0217

The differences between the frequencies of the emission lines as computed (1) from the energy levels and (2) from the measured results are about .13 per cent for β_{15} and β_{16} and less than .10 per cent for the remainder with an average difference of .03 per cent.

CONCLUSIONS

The selection principle reduces the possible number of lines from fifty-one to twenty-one for the L series and from twenty to eight for the K series. Two of the new lines found agree with the selection principle, thus increasing the total number in agreement from eighteen to twenty for the L series, leaving one more line to be found. All lines in the K series are in agreement with the principle.

In addition to the lines given by the selection principle four were found in the L series which are not in agreement but which quantitatively correspond to transitions between energy levels. The $K\alpha_3$ line, found by Duane but not observed by the present photographic method, is not in agreement with the selection principle and is yet somewhat in doubt.

As an indication that the present energy levels are not sufficient there appear to be two lines in the L series which are not in agreement. One

*Values given by Duane and Shimizu[7]

of these is a new line and may be due to an impurity; the other is the β_8 line.

It is seen from the above that the energy levels as drawn do not satisfy all the measurements of what are undoubtedly tungsten lines, and that Bohr's selection principle would eliminate four lines which have been found. These disagreements emphasize the need for further experimental and theoretical work.

I wish to acknowledge indebtedness to the members of the staff of the physical laboratory at the University of Iowa for their interest in the work and especially to Professor G. W. Stewart who suggested the problem.

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