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The Intensities of the *K*-Series X-Ray Lines of Tungsten and Platinum

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Measurements of the relative intensities of the $K\alpha$ and $K\beta$ lines of $_{74}$W and $_{78}$Pt have been made with a double crystal spectrometer, high pressure argon ionization chamber, and FP-54 Pliotron amplifier by measuring with a planimeter the areas under the curves of the lines graphed against Bragg angle. The results in the $_{78}$Pt spectrum, which are the more reliable, are: on the basis 100 for the intensity of $K\alpha_1$: $K\alpha_2=52$, $K\beta_3=10.2$, $K\beta_1=20.0$, $K\beta_5=0.38$, $K\beta_2=7.8$, $K\beta_4=0.8$, $(O_{\text{II}}O_{\text{III}}-K)=1.2$. Although the intensity of the quadrupole line $K\beta_5$ relative to $K\beta_1$ is in good agreement with the calculated value of Massey and Burhop, the predicted decrease in the relative intensity of this line at lower atomic numbers does not seem to be experimentally verified. The observed relative intensities of the stronger dipole lines seem to agree satisfactorily with the calculations of Pincherle and of Massey and Burhop.

MOST of the measurements of x-ray line shapes and intensities have been made only for elements of low atomic weights or were made photographically with x-ray spectrographs. This research was undertaken to study the *K*-series lines of heavy elements with a double-crystal spectrometer and ionization chamber, to look for anomalies and check against computed values for the intensities of regular and non-diagram lines.

I. THE TUBE AND SPECTROMETER

The x-ray tube, described previously,[1] was made at the Ryerson Laboratory, with metal ends, body of Pyrex piping, hot cathode and with target surrounded by metal shield with aluminum window. Electrodes were 48 mm apart. The measurements on the $K\alpha$ lines of tungsten were made with an earlier tube having similar electrodes spaced about 37 mm apart and a glass envelope of 3″ diameter throughout closed by large wax joints at the end. Tungsten target surfaces were tilted 30° with the perpendicular to the cathode beam; platinum, $22\frac{1}{2}$°.

Power for the tube was supplied by a synchronous motor and 540-cycle generator, a transformer, 2 kenotrons and two 0.050-mf filter condensers in the usual voltage doubling circuit. A calibrated electrostatic voltmeter was connected between the target and ground and a 2- and 4-ma calibrated meter mounted at the tube indicated electron current. The filament current required repeated adjustments and both the voltage and current across the tube were continuously observed and maintained constant by rheostats at the observer's position near the spectrometer.

The double crystal x-ray spectrometer designed by S. K. Allison[2] was used with calcite crystals in (1, 1) position. The entrance slit to the ionization

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* With the Gaertner Scientific Corporation, Chicago, at time of this research. Now with U. S. Department of Agriculture, Leland, Mississippi.

[1] W. Kliever, Rev. Sci. Inst. **10**, 126 (1939).

[2] S. K. Allison, Phys. Rev. **41**, 1 (1932).

chamber was 5 cm from the crystal B axis. Lead shields were placed about 1 mm from and perpendicular to the crystal faces to eliminate diffuse scattered radiation, especially that from crystal A. Both crystals were rotated, and thus a constant spot on the target was used as a source. The spectrometer arm carrying crystal B is geared to rotate at double the speed of crystal A. The ionization chamber slit was sufficiently wide so that the chamber did not need to be moved during related measurements except when comparing $K\beta$ lines with $K\alpha_1$.

One slit only was used to limit the rays, the other being set slightly wider. Since the collimating property of the two crystals serves to select a parallel bundle of rays, *viz.*, all those rays which have an angle of incidence equal to one-half the angle between the crystal faces, it follows that, using two slits of equal width, the full aperture of the slits is used only when the rays selected by the crystal enter exactly parallel with the line of the slits. Otherwise the beam will be limited by one side of one slit and the opposite side of the other slit, and the horizontal aperture will be less than the slit widths and will vary if there is an error in crystal rotation. Under conditions of 0.3 mm slits 138 mm apart the width would be reduced about $\frac{1}{4}$ percent for an accumulated error of only 1 second in the motion of crystal A.

The vertical aperture was 2.2° except during the earlier determinations on the tungsten $K\alpha$ lines when it was 1.1°.

The crystals were split calcite one of which was etched 3 sec. in dilute HCl according to the method developed at Cornell University.[3] The full rocking curve width at half-maximum for parallel position is about $8\frac{1}{2}$ sec. of motion of crystal B only. A different pair of crystals used for the 74 W $K\alpha$ lines had similar resolving power for narrow slits but was found unsuited for use with the wide slits used on $K\beta$ lines.

II. IONIZATION CHAMBER AND AMPLIFIER

The ionization chamber was of steel of 25 mm diameter and 198 mm length internally, built for high pressure. The ends are bolted to flanges which are screwed to the cylindrical body. The inner electrode is a 1.6 mm rod off center by 3.2 mm and insulated by amber, with surrounding grounded guard ring. The entrance window is 3.2 mm off center opposite the rod, covered by Celluloid with rubber gasket. The chamber body is insulated from the spectrometer, shielded by a 3.2-mm grounded lead housing, and charged to 90 volts above ground by an Edison storage battery. The ionization current was found satisfactorily constant from 30 to over 200 volts. Stability was improved by connecting a 4-mf condenser between chamber and ground and a 1-megohm resistor between chamber and battery. The chamber was built by T. M. Hahn and is generally similar in design to the steel chamber described by Williams.[4]

An FP-54 Pliotron and L. and N. type R galvanometer were used in the well-known DuBridge and Brown circuit,[5] modified according to Fig. 1*f* of Penick[6] (modified Barth circuit). The tube was mounted in an evacuated, grounded metal case, with the additional precaution of a P_2O_5 drying tube. The ionization current conductor was supported only at the Pliotron grid cap and at the chamber electrode, and was entirely contained in the vacuum. A key operated through a sylphon permitted grounding the grid or applying known voltages. The wires to the tube base were soldered to the prongs of the tube, the latter passing out of the vacuum through rubber gaskets. The entire circuit including lead wires was carefully shielded, and all batteries were contained in a double wall, heat insulated steel box.

The sensitivity of the circuit was 2×10^{-16}A/mm with the 8×10^{10} ohm grid resistor used, and deviations from linearity were found negligible.

III. CORRECTIONS TO READINGS

1. *Zero drifts* were determined by periodically closing a lead shutter at the spectrometer slits and taking zero readings which thus take account of such factors as stray radiation, variations in batteries, amplifiers, etc. The zero readings were

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[3] K. V. Manning, Rev. Sci. Inst. **5**, 316 (1934); F. K. Richtmyer, S. W. Barnes and K. V. Manning, Phys. Rev. **44**, 311 (1933).

[4] J. H. Williams, Rev. Sci. Inst. **3**, 586 (1932); T. M. Hahn, Phys. Rev. **46**, 149 (1934).

[5] L. A. DuBridge and H. Brown, Rev. Sci. Inst. **4**, 532 (1933).

[6] D. B. Penick, Rev. Sci. Inst. **6**, 116 (1935).

plotted against the number of readings, and the interpolated value subtracted from each reading before plotting.

2. The *sensitivity* of the amplifier, when less than its maximum was determined by comparing the reading at some point on the background spectrum with that at full sensitivity, other conditions remaining equal. All results have been computed for 100 percent sensitivity by dividing the measured values by the sensitivity. It should be mentioned here as a possible help to others that it would have been advantageous had the sensitivity of the amplifiers been adjustable in steps instead of continuously, so that settings could be repeated and more thoroughly calibrated.

3. *Absorption* by materials between the target and ionization chamber requires some correction which has been applied only to the computed ratios of more intense lines. If a material of thickness x and density ρ absorbs 2 rays of wavelengths λ_1 and λ_2 and intensities I_1 and I_2 before and I_1' and I_2' after absorption, if the respective mass absorption coefficients are μ_1 and μ_2, and if we let $I_1/I_2=R$ (the true ratio) and $I_1'/I_2'=R'$ (measured ratio), then

$$R=\frac{I_1}{I_2}=\frac{I_1'e^{\mu_1 x}}{I_2'e^{\mu_2 x}}=R'e^{(\mu_1-\mu_2)x}.$$

Only the absorption by the aluminum window and Pyrex wall of the tube was found appreciable. Absorption coefficients for aluminum were interpolated from curves plotted from data in the appendix of Compton and Allison's book on x-rays.[7] From the same data the mass absorption coefficients for Pyrex were computed from an analysis supplied through the courtesy of Corning Glass Works with the following results: W $K\alpha_1$, 0.241; W $K\alpha_2$, 0.247; W $K\beta_1$, 0.214; W $K\beta_2$, 0.209; Pt $K\alpha_1$, 0.215; Pt $K\alpha_2$, 0.220; Pt $K\beta_1$, 0.195; Pt $k\beta_2$, 0.193.

TABLE I. *Sample data taken in an experimental run. Voltage on x-ray tube, 108 kv. Current through x-ray tube, 0.77 ma. Slit width, 0.06 cm. Sensitivity of amplifier, 75 percent of maximum.*

X-Ray Line	Area (Arbitrary Units)	Area Ratio $K\alpha_2/K\alpha_1$	Atmospheres Pressure in Chamber	Absorption Correction in Percent			Final Intensity Ratio
				Al	Pyrex	Chamber	
Pt $K\alpha_1$	492.7						
$K\alpha_2$	247.3	0.507	83.1	—	0.4	−2.2	0.498
$K\alpha_1$	482.7						
$K\alpha_2$	275.6						
$K\alpha_2(M)$	261.4	0.542	83.1	—	0.4	−2.2	0.532

(M) indicates average of the two preceding determinations of area.

TABLE II. *Intensity of $K\alpha_2$ on the scale $K\alpha_1=100$.*

Element	Experiment	Theory Pincherle	Theory Massey and Burhop
$_{74}$W	47	52	—
$_{78}$Pt	52	—	—
$_{79}$Au	—	—	48

No attempt is made to correct for absorption of rays in the target.

4. *Ionization chamber corrections.* Correction has been made with the aforementioned coefficient data for the unabsorbed rays. The maximum photoelectron range has been estimated as 0.2 cm for Pt $K\beta_2$ and 45 atmospheres (hardest ray and lowest pressure used) from the formula[8] $x=v^2/b$ where v = photoelectron energy in electron kilovolts and $b=610\times 45$. Thus the photoelectrons should be completely absorbed. Fluorescent radiation is assumed largely used in the Auger effect. Scattered radiation, modified and unmodified, has been neglected in its effect on line intensity ratios, because no convenient methods of correcting for it were found.

Considerable diffuse scattering by the calcite crystals was observed, which necessitated careful shielding. This may have affected the intensity ratios, but no corrections were attempted for this factor.

IV. RESULTS

Table I shows a sample of the data taken in an experimental run. The intensities are taken (before correction) as proportional to the areas under the curves with Bragg angle as abscissae, as measured with an Ott planimeter.

The $K\alpha$ line intensities

Considerable interest is attached to measurements of the intensities in the K series of heavy elements, because of the chance to detect relativistic effects, if present. The nonrelativistic

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[7] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (Van Nostrand, 1935).

[8] Reference 7, page 494.

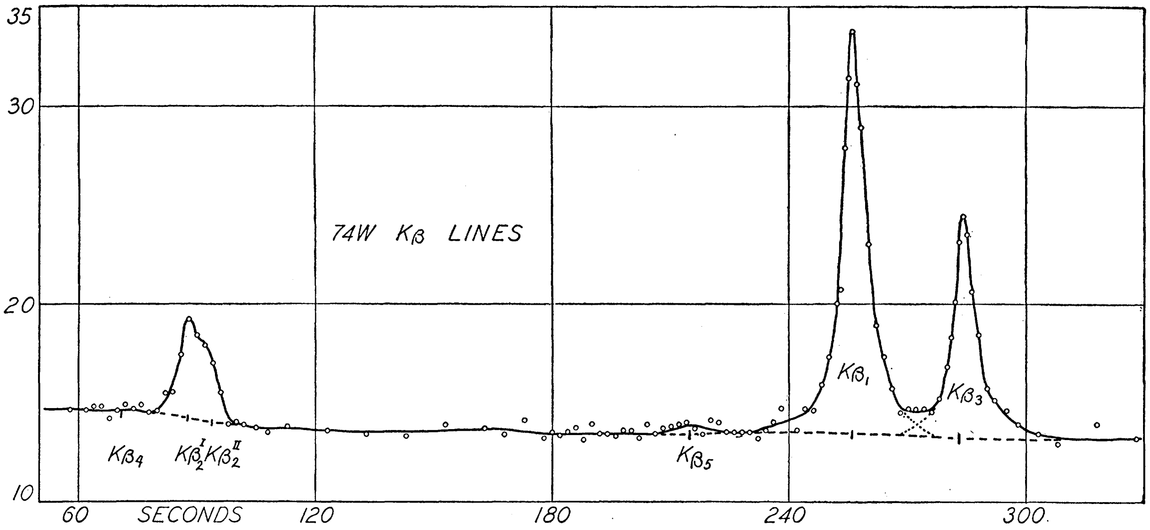

FIG. 1. Intensity curve of $_{74}$W $K\beta$ lines. The short cross lines on Figs. 1 and 2 give the positions of the x-ray lines according to Ingelstam, as measured from $K\beta_2{}^{I}$ and $K\beta_3$.

wave functions are certainly inadequate for the representation of these states in which the K electrons are bound with energies of approximately 70 kev. Massey and Burhop[9] have made calculations of x-ray intensities in which a rough approximation to a rigorous relativistic treatment has been introduced, and similar calculations have been made by L. Pincherle.[10] Massey and Burhop state that the relativistic treatment does not alter appreciably the nonrelativistic value of 0.500 for $K\alpha_2/K\alpha_1$, even in $_{92}$U. A previous experimental value of 0.500 was found by Duane and Stenström[11] in $_{74}$W. Table II summarizes the results on the $K\alpha$ lines.

No definite evidence of $K\alpha_3$ ($L_{\text{I}}-K$) was obtained, although some of the curves taken on tungsten showed slight irregularities in the expected region. According to Massey and Burhop, this line should be about as strong as $K\beta_5$ in $_{79}$Au.

The $K\beta$ line intensities

Since the advent of high resolving power spectrometers for x-rays, the β-group in the K series has been reexamined and several new, faint lines reported.[12] Since this work was begun, an excellent monograph by Ingelstam[13] has appeared, in which accurate measurements of the wave-lengths of the K lines of the heavy elements have been made with a high resolving power photographic spectrograph. Some visual estimates of intensities are made in this work.

Figures 1 and 2 show the present results on the $K\beta$ lines of $_{74}$W and $_{78}$Pt. Comparison of the curves shown on the $K\beta_2$ ($N_{\text{II}}N_{\text{III}}-K$) doublet with Fig. 23*a* of Ingelstam's monograph, and Fig. 4 of Richtmyer and Barnes[14] indicates that the resolving power was comparable to, but slightly lower than, that of the two other researches.

TABLE III. *Intensities of the $K\beta$ lines of $_{74}$W and $_{78}$Pt, based on the scale $K\alpha_1 = 100$.*

Symbol	Transition	$_{74}$W λ in x.u. Ingelstam	$_{74}$W Observed Intensity	$_{78}$Pt λ in x.u. Ingelstam	$_{78}$Pt Observed Intensity	Theoretical Intensity Pincherle $_{74}$W	Theoretical Intensity Massey Burhop $_{79}$Au
$K\beta_3$	$M_{\text{II}}-K$	184.795	9.6	164.157	10.2	11	13
$K\beta_1$	$M_{\text{III}}-K$	183.991	18.1	163.334	20.0	21	29
$K\beta_5{}^{II}$	$M_{\text{IV}}-K$	182.882	0.25	162.364	0.38	—	0.19
$K\beta_5{}^{I}$	$M_{\text{V}}-K$	182.711		162.203		—	0.41
$K\beta_2{}^{II}$	$N_{\text{II}}-K$	179.232	1.7	159.053	3.0	2.5	—
$K\beta_2{}^{I}$	$N_{\text{III}}-K$	179.049	3.1	158.863	4.8	4.5	—
$K\beta_4$	$N_{\text{IV}}N_{\text{V}}-K$	178.55	0.036	158.48	0.8	—	—
—	$O_{\text{II}}O_{\text{III}}-K$	178.073	0.04	157.922	1.2	1.5	—

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[9] H. S. W. Massey and E. H. S. Burhop, Proc. Camb. Phil. Soc. **32**, part 3, p. 461 (1936).

[10] L. Pincherle, N. Cimento **10**, 344 (1933).

[11] W. Duane and W. Stenström, Proc. Nat. Acad. Sci. **6**, 477 (1920).

[12] A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment* (Van Nostrand, 1935), pp. 632, 639.

[13] E. Ingelstam, Die K-Spektren der Schweren Elemente, Nova Acta Regiae Societatis Scientiarum Upsaliensis, Ser. IV, **10**, No. 5 (1937).

[14] F. K. Richtmyer and S. W. Barnes, Phys. Rev. **46**, 352 (1934).

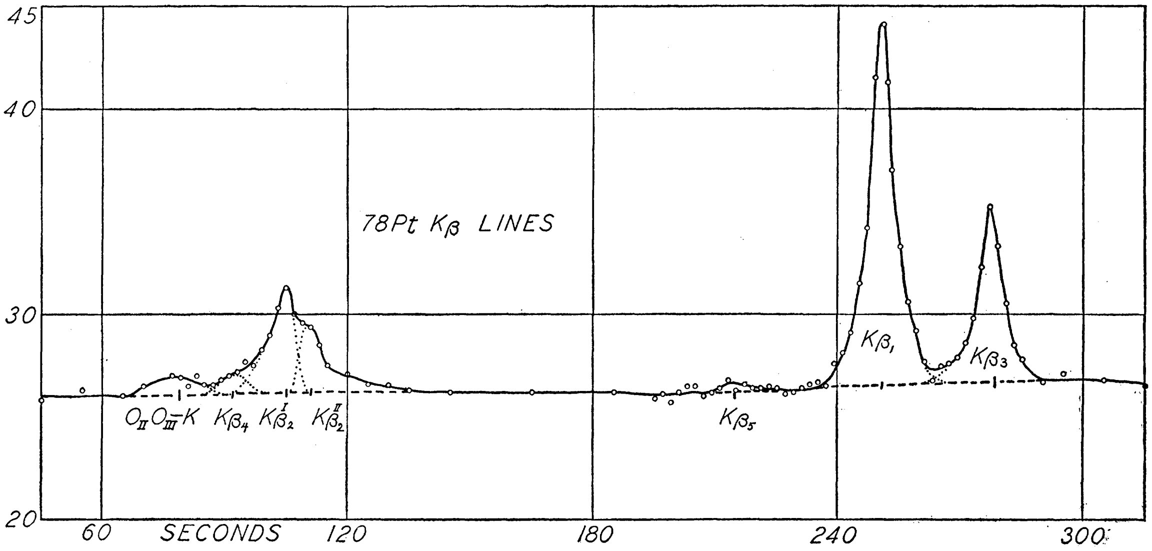

FIG. 2. Intensity curve of $_{78}$Pt K_β lines.

In addition to the diagram lines $K\beta_1$, $K\beta_3$ (M_{II}, $M_{III}-K$) and $K\beta_2^{I}$, $K\beta_2^{II}$ (N_{II}, $N_{III}-K$) which were known previous to Ingelstam's work, he reports evidence of $O_{II}O_{III}-K$, obtained first in $_{49}$In and observed in heavier elements also. In the $_{78}$Pt $K\beta$ spectrum given here, there is some evidence of a broad line in the required region. Ingelstam gives 157.922 x.u. as the wave-length; the maximum of the broad peak in the present work lies at 158.05 x.u. In the present work on tungsten, the corresponding line was not detected with certainty. Table III gives the results on the $K\beta$ lines.

The intensities given for the nondiagram lines $K\beta_5$ and $K\beta_4$ certainly have a large error, probably a factor of 2, because they lie so near the base-line. In the case of tungsten, the values seem less reliable than for platinum. The platinum curves were taken subsequent to the tungsten experiments, when the technique had been better developed.

If one takes the observed values of the intensity of Pt $K\beta_5$ with respect to Pt $K\beta_1$, namely 0.019, it agrees well with Massey and Burhop's value of 0.021 for this ratio. Although the intensity of this interesting quadrupole line agrees with Massey and Burhop's calculation at $_{78}$Pt, the meager experimental evidence available would seem to show that its intensity does not decrease with atomic number as they predict. At $_{44}$Ru, Wilhelmy[15] estimated $K\beta_5$ as 0.25 if $K\alpha_1$ is 100, whereas for $_{51}$ Sb according to Massey and Burhop's calculations, the line should have sunk to $\frac{1}{5}$ of its value at $_{78}$Pt, which means a value of 0.05–0.08 instead of Wilhelmy's 0.25.

The author wishes to express his thanks to Dr. S. K. Allison, under whose guidance the work was done, and to M. L. Dannis for assistance and for measuring the areas of the curves.

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[15] E. Wilhelmy, Phys. Rev. **46**, 130 (1934).