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Relative Intensities and Transition Probabilities of the *K*-Series Lines of the Elements 24 to 52 by the Ionization Chamber Method

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Experiments on the ionization currents produced by x-ray lines of wave-lengths 2.29, 1.93 and 1.66A entering a double ionization chamber filled with methyl iodide, methyl bromide, argon, air, and sulphur dioxide have been carried out. The current ratios obtained when corrected for the fraction of the direct beam absorbed in the front chamber were found not to vary by more than 1.5 percent in these gases. The conclusion is reached that the ionization chamber is a suitable instrument for measuring relative intensities of x-ray lines of different wave-lengths in the region 0.4 to 2.3A. The relative intensities of the *K*-series lines of twenty elements from Cr (24) to Te (52) were examined under controlled conditions and on correction for various factors yield a variation of relative intensity with atomic number. α_2/α_1 remains constant at approximately 0.50 throughout the range. β_1/α_1 rises steeply from a value of 0.161 at Co (27) to 0.274 at Sr (38) then less rapidly to 0.306 at Te (52). β_2/α_1 rises steeply from a value of 0.0036 at Zn (30) to 0.0450 at Zr (40) and then in a more linear fashion to 0.0735 at Te. Equations obtained from measurements on the absorption coefficients of various materials are:

Mica $\mu=36.56\lambda^{2.76}$ from 0.4 to 2.3A
Cellophane $\mu=3.52\lambda^{2.66}$ from 0.6 to 2.3A
CH_3Br $\mu/\rho=19.2\ \lambda^{2.79}$ from 1.1 to 2.3A
CH_3I $\mu/\rho=65.46\lambda^{2.62}$ from 0.4 to 0.9A.

A treatment is given and discussed for the absorption of the x-rays within the target. The resultant correction is small and on application to the observed relative intensities the ratio of the transition probabilities for the *K*-series lines of these elements is obtained.

PART I

Introduction

THE first part of this paper deals with a test of the method of measuring the relative intensities of x-ray spectrum lines by an ionization chamber in the wave-length region 2.286 to 1.656A.

When one attempts to measure relative intensities by this method the question arises: are the ionic saturation currents caused by the x-rays entering the gas contained in the ionization chamber proportional to the actual intensity of the x-rays? For light gases the principal ionization is caused by the action of the photoelectrons and recoil electrons and it is only in heavier gases excited by a frequency greater than their *K* frequency, or in very heavy gases their *L* frequency, that the fluorescence radiation plays an important rôle. Many experiments[1] have been performed with air and other gases in the wave-length region 0.5 to 1.5A to measure the energy, ϵ, expended by a β-ray in the formation of a pair of ions. These researches lead to various values of ϵ, but all of them show no appreciable variation of ϵ with λ. Any such variation would invalidate measurements of the relative intensity of two x-ray beams of different wave-lengths by the ionization method. However, if ϵ is constant the conclusion is reached that the ionic saturation currents observed in an ionization chamber, where all the x-ray energy is transformed into β-ray energy and all the β-rays reach the end of their ionizing range before striking the boundaries of the chamber, will yield a true measure of the intensities of x-ray beams in the above wave-length region.

Recently Allison and Andrew[2] have attacked this problem in the wave-length region 0.6 to 1.5A, using a double ionization chamber and various gases. As it is not practicable to use such light gases as air because of the small absorption of x-ray energy, one must consider the effects resulting from the use of heavier gases. Fluorescence radiation may be excited in the gas itself or

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[1] Stockmeyer, Ann. d. Physik **12**, 71 (1932); O. Gaertner, Ann. d. Physik **3**, 322 (1929); **10**, 825 (1931); Crowther and Bond, Phil. Mag. **6**, 401 (1928), Steenbeck, Ann. d. Physik **87**, 811 (1928).

[2] Allison and Andrew, Phys. Rev. **38**, 441 (1931).

primary radiation may be scattered, and these radiations may escape to the walls of the chamber without being absorbed. Allison and Andrew have restated very clearly the corrections of Martin and Compton[3] to be applied in these cases. Their results showed that an ionization chamber of proper design gives a true measure of the relative intensity of x-ray spectrum lines.

If ϵ is independent of λ the expression for the relative power, $P_{\alpha\beta}$, of two lines α and β can be expressed in the form:

$$P_{\alpha\beta}=I_\alpha F_\beta R_\beta / I_\beta F_\alpha R_\alpha \equiv I_{\alpha\beta} F_{\beta\alpha} R_{\beta\alpha}, \tag{1}$$

where I is the ionic saturation current,

$$F\equiv(1-e^{-\mu l}), \tag{2}$$

and

$$R=1-\frac{\tau_K}{\mu} w_K \lambda \sum_i \frac{f_i}{\lambda_i} e^{-\tau_i r}-\frac{\sigma}{\mu} e^{-\tau r}. \tag{3}$$

From Eq. (2) we see that F is the fraction of the energy removed from the x-ray beam in passing through the chamber of length l when filled with a gas which has an absorption coefficient μ. This factor could be measured experimentally by means of a second chamber placed directly behind the first. In Eq. (3) R is the expression for the loss of energy due to two causes; first, the conversion of energy into fluorescence radiation and the incomplete absorption of this radiation before reaching the boundaries of the chamber, and second, the scattering of the primary radiation and loss of such scattered radiation to the walls. In this equation τ_K is the absorption coefficient of the fluorescence radiation in the gas, w_K is the Auger[4] coefficient, f_i is the fractional part of the total number of quanta emitted having the wave-length λ_i of the ith line of the fluorescence series, r is the effective radius of the chamber, and σ is the scattering coefficient of the gas for the primary wave-length λ.

Allison and Andrew's results showed that even under the most unfavorable conditions, i.e., when the two lines lie on opposite sides of the K absorption limit of the gas filling the chamber, the relative intensities can be accurately determined and checked with those obtained under more favorable conditions.

Measurements

Since the purpose of the present experiment was to measure the relative intensities of x-ray spectrum lines of longer as well as of the same wave-lengths as had been previously examined, it was advisable to test the constancy of ϵ with λ in the region 1.5 to 2.3A. This was done with the apparatus and method of Allison and Andrew.[2] In order to obtain a source of x-rays yielding two lines of comparable intensity and reasonable wave-length separation targets of chromium-iron and iron-nickel alloys were used. The $K\alpha$-lines of wave-lengths 1.656, 1.933 and 2.286A were thus available. By observing the ratio of the intensity of Cr $K\alpha$ to Fe $K\alpha$ and Fe $K\alpha$ to Ni $K\alpha$ one can test whether there is any *significant* change of ϵ with λ by observing if these ratios remain constant when the ionization chamber is filled with different gases and the appropriate corrections are made. As in the work of Allison and Andrew[2] the F values were observed directly by measuring the intensity ratio in the back chamber after the beams had traversed the length of the front chamber when the latter was first filled with the gas at a given pressure and later evacuated.

The results are shown in Tables I and II. All the measurements were made at 25 kv and each result is the average of four determinations.

TABLE I. *Tests with the Kα-lines of Cr and Fe. λ2.286 and 1.933A.*

Gas	Pressure	I_{CrFe}	F_{FeCr}	R_{FeCr}	P_{CrFe}
CH_3Br	15.92 cm	0.9480	0.966	1.00	0.916
Argon	22.55	0.9505	0.960	1.00	0.912
Air	74.40	1.2715	0.721	0.99	0.907
CH_3I	2.85	0.9362	0.9715	1.00	0.909
SO_2	50.18	0.9287	0.9840	1.00	0.914

TABLE II. *Comparison of the Kα-lines of Fe and Ni. λ1.933 and 1.656A.*

Gas	Pressure	I_{FeNi}	F_{NiFe}	R_{NiFe}	P_{FeNi}
CH_3Br	22.55 cm	0.6985	0.9675	1.00	0.676
Argon	43.48	0.6992	0.9685	1.00	0.677
Air	74.88	0.9925	0.6870	0.99	0.675
CH_3I	6.07	0.6912	0.9888	1.00	0.673
SO_2	65.82	0.6927	0.9786	1.00	0.676

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[3] Martin, Proc. Roy. Soc. (London) **A115**, 420 (1927); Compton, Phil. Mag. **8**, 961 (1929).

[4] Auger, Ann. de Physique **6**, 183 (1926).

Hicks[5] has disclosed a source of error in ionization chamber measurements due to a faulty design of the front window. If the pressure of the gas is so high that an appreciable fraction of the ions are created in the layer of gas directly behind the window, and these ions are not collected and measured, an error would arise for beams of greatly different wave-lengths. In order to test this point with the present chamber, P_{CrFe}, as in Table I, was examined as a function of pressure. The results are shown in Table III. The results for the higher pressures are for one set of readings only so that the variation is within experimental error. It seems that if the collector is sufficiently close to the charged window that approximately all of the ions formed by the two beams are collected, the effect of the unequal absorption does not introduce an error.

TABLE III. *P_{CrFe} as a function of pressure of CH_3Br.*

Pressure (cm)	15.92	33.0	51.9	72.5
F_{FeCr}	0.966	0.999	1.00	1.00
P_{CrFe}	0.916	0.897	0.915	0.903

Conclusions

These results were obtained under more favorable conditions than those of Allison[2] in that no fluorescence x-rays of sufficient hardness to reach the walls were excited. Also in no case did the lines investigated overlap any absorption limit of the gas. The most critical test of the method in this wave-length region is the measurements with air where the F factor deviates largely from unity.

Recently Gaertner[1] has determined the energy expended by a β-particle in the formation of a pair of ions. For argon over a range of incident x-rays of wave-lengths 0.345 to 1.38A the energy required per ion pair was constant within the limits of the experiment.

One can therefore conclude that an ionization chamber of proper design will give a true measure of the relative powers of two x-ray beams of different wave-lengths between 0.4 and 2.3A when the appropriate corrections are applied.

PART II

Introduction

The second part of this paper deals with measurements on the relative intensities of the K-series lines of twenty elements from atomic numbers 24 to 52 and the calculation of the transition probabilities for these lines from these observations.

Several attempts have been made by many workers[6] to measure the relative intensities of some lines in the K-series of certain isolated elements. These experiments have led to the conclusion that the relative intensity of the doublet α_1, α_2 is two to one, and also indicate that the relative intensity of β_2 to β_1 increases with atomic number. Duane and Stenström[6] give the relative intensities in tungsten of α_2/α_1, β_1/α_1, and β_2/α_1 as 0.50, 0.35, and 0.15, respectively. Allison and Armstrong[6] presented a collection of results on the relative intensity of β_2/β_1 for four elements as measured by Duane and his associates. The value of this ratio in W, Rh, Mo, Cu, is respectively 0.43, 0.15, 0.13, 0.024.

The only comprehensive work on this problem has been done by H.-T. Meyer[7] who photographed the spectra and analyzed the intensities with a microphotometer. The difficulties inherent in the photographic determination of relative intensities and the disagreement with the meager ionization measurements led to the present study of this problem.

Apparatus

Power was supplied by a 5 kva 540 cycle synchronous motor generator to a transformer, kenetrons and condensers. The voltage was measured by an electrostatic repulsion type voltmeter. A tube of the type described by Allison[8] was adapted to facilitate the use of interchangeable targets of standard design. The cathode rays made an angle of 45° with the target and the x-rays observed emerged at right angles to the electron beam. The x-rays left the tube through

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[5] Hicks, Phys. Rev. **38**, 572 (1931).

[6] M. Siegbahn and A. Žáček, Ann. d. Physik **71**, 187 (1923); Y. H. Woo, Phys. Rev. **28**, 427 (1926); Duane and Stenström, Proc. Nat. Acad. Sci. **6**, 477 (1920); Allison and Armstrong, Phys. Rev. **26**, 701, 714 (1925).

[7] H.-T. Meyer, Wissenschaftliche Veroffentlichungen aus dem Siemens-Konzern **7**, 108 (1929).

[8] S. K. Allison, Phys. Rev. **30**, 245 (1927).

a mica window 2.3×10^{-3} cm thick and were collimated by slits 0.08 mm wide and 25.4 cm apart. On reflection from a calcite crystal calibrated for reflecting power (Allison's[9] crystal VB, values of R in Table II) they entered the ionization chamber through a cellophane window 2.5×10^{-3} cm thick. The total air path was 41.5 cm. The ionization chambers were similar to those used by Allison and Andrew[2] and allowed the direct measurement of the fraction of the energy absorbed in the front chamber by measurements of the energy entering the back chamber. The ionization currents were measured by the rate of deflection method with a Compton electrometer.

Measurements

Measurements were made on the relative intensities of the K-series lines of twenty elements from Cr (24) to Te (52). For the elements Cr to Ge methyl bromide at suitable pressures was used in the ionization chamber. For the elements Sr to Pd a chamber 28.1 cm long was filled with methyl iodide to measured pressures in the neighborhood of 20 cm, and for the elements Pd to Te a chamber 56.5 cm long was similarily filled with methyl iodide. In this manner no fluorescence radiation of sufficient hardness to reach the walls of the chamber was excited and the intensities measured were independent of the R factor given by Eq. (3). The F factor as in Eq. (2) for the gas was observed directly by means of the back chamber and as a further check the absorption coefficients for CH_3Br and CH_3I were measured for the appropriate wave-lengths.

The measurements for any one element were obtained at a predetermined voltage (usually kept as low as possible) and consisted in general of four determinations of the ratios α_2/α_1, and β_2/β_1, and seven determinations of β_1/α_1. The value of β_1 includes the unresolved β_3. Readings were taken at 7.5″ intervals over the peak of the lines. The method of determining these ratios was to compare the peak intensities less the base intensities of each line. Since the resolved lines were of the same width, the ordinate of the peak was taken as the measure of the intensity. In the case of the partially resolved lines α_1 and α_2 (totally resolved except for low atomic numbers) these ordinates were corrected by the method suggested by Allison and Armstrong.[6] The angular divergence of the x-ray beam was sufficiently large to give an observed width of line much greater than the natural wave-length widths as observed in recent unpublished work by Allison with a double crystal spectrometer.

Absorption coefficients for mica and cellophane were also obtained for the α_1 and β_1 lines of a number of elements.

Results

The collected results on the observed relative intensities and the calculated corrections to be applied to these results are shown in a logarithmic form in Table IV. The correction factors and the relative intensities refer to α_2/α_1, β_1/α_1, and β_2/α_1. I_λ/I_{α_1} is the observed ratio of intensities F_i, F_a, F_m, F_w, F_c are, respectively, the correction factors for the differential absorption in the gas filling the ionization chamber, the air path, the mica of the tube window, the cellophane of the chamber window, and the ratio of the coefficients of reflection of the calcite crystal. P_λ/P_{α_1} is the resultant ratio of the intensities of two wave-lengths leaving the surface of the target.

As has been previously stated, the F_i factor was observed directly by measurements with the rear chamber and was checked by calculations from the measured absorption coefficients of the gases CH_3Br and CH_3I. The variation of these absorption coefficients with wave-length can be expressed as:

$$CH_3Br \quad \mu/\rho = 19.2\lambda^{2.79} \text{ from 1.1 to 2.3A,} \qquad (4)$$

and

$$CH_3I \quad \mu/\rho = 65.46\lambda^{2.62} \text{ from 0.4 to 0.9A.} \qquad (5)$$

These equations are sufficiently accurate to introduce only a negligible error in the resultant correction factors.

The F_a factor was calculated for the 41.5 cm air path from Table 10 in H.-T. Meyer's[7] paper.

The F_m factor was calculated from direct measurements of the absorption coefficients of mica which gave

$$\text{Mica} \quad \mu = 36.56\lambda^{2.76} \text{ from 0.4 to 2.3A.} \qquad (6)$$

The F_w factor was similarly calculated from measurements on cellophane which gave

$$\text{Cellophane} \quad \mu = 3.52\lambda^{2.66} \text{ from 0.6 to 2.3A.} \qquad (7)$$

TABLE IV.

Element Press. Kv	Line	Log I_λ/I_{α_1}	Log F_i	Log F_a	Log F_m	Log F_w	Log F_c	Log P_λ/P_{α_1}	P_λ/P_{α_1}
Cr (24)	α_2	$\bar{1}.71676$	0	$\bar{1}.99638$	$\bar{1}.99852$	0.00032	0	$\bar{1}.71198$	0.5152
20.00 31.8	β_1	$\bar{1}.48982$	0.00303	$\bar{1}.83803$	$\bar{1}.91819$	$\bar{1}.99211$	0.01072	$\bar{1}.25190$	0.1786
Fe (26)	α_2	$\bar{1}.70243$	0	$\bar{1}.99747$	$\bar{1}.99878$	0.00015	0	$\bar{1}.69883$	0.4998
33.00 26.0	β_1	$\bar{1}.35793$	0.00303	$\bar{1}.89790$	$\bar{1}.94709$	$\bar{1}.99498$	0.02119	$\bar{1}.22212$	0.1668
Co (27)	α_2	$\bar{1}.69966$	0	$\bar{1}.99765$	$\bar{1}.99891$	0.00012	0	$\bar{1}.69634$	0.4970
40.00 26.0	β_1	$\bar{1}.31069$	0.00303	$\bar{1}.91871$	$\bar{1}.95684$	$\bar{1}.99585$	0.02119	$\bar{1}.20559$	0.1605
Ni (28)	α_2	$\bar{1}.69740$	0	$\bar{1}.99819$	$\bar{1}.99900$	0.00010	0	$\bar{1}.69469$	0.4951
50.00 25.0	β_1	$\bar{1}.35334$	0.00303	$\bar{1}.93222$	$\bar{1}.96464$	$\bar{1}.99651$	0.02202	$\bar{1}.27176$	0.1870
Cu (29)	α_2	$\bar{1}.69871$	0	$\bar{1}.99855$	$\bar{1}.99913$	0.00009	0	$\bar{1}.69648$	0.4971
62.00 25.0	β_1	$\bar{1}.35989$	0.00346	$\bar{1}.94660$	$\bar{1}.97128$	$\bar{1}.99717$	0.02160	$\bar{1}.29995$	0.1995
Zn (30)	α_2	$\bar{1}.70329$	0	$\bar{1}.99870$	$\bar{1}.99923$	0.00008	0	$\bar{1}.70130$	0.5027
73.00 25.0	β_1	$\bar{1}.35218$	0.00389	$\bar{1}.95655$	$\bar{1}.97566$	$\bar{1}.99760$	0.02857	$\bar{1}.31550$	0.2068
	β_2	$\bar{3}.59522$	0.00389	$\bar{1}.95352$	$\bar{1}.97388$	$\bar{1}.99750$	0.03203	$\bar{3}.55604$	0.0036
Ge (32)	α_2	$\bar{1}.70001$	0	$\bar{1}.99890$	$\bar{1}.99939$	0.00006	0	$\bar{1}.69836$	0.4993
73.00 31.0	β_1	$\bar{1}.38130$	0.01494	$\bar{1}.97049$	$\bar{1}.98318$	$\bar{1}.99826$	0.02979	$\bar{1}.37796$	0.2397
	β_2	$\bar{2}.12566$	0.01494	$\bar{1}.96918$	$\bar{1}.98166$	$\bar{1}.99820$	0.03282	$\bar{2}.12246$	0.0132
Sr (38)	α_2	$\bar{1}.70346$	$\bar{1}.99896$	$\bar{1}.99946$	$\bar{1}.99965$	0	0	$\bar{1}.70153$	0.5030
19.50 30.5	β_1	$\bar{1}.38543$	0.04493	$\bar{1}.98932$	$\bar{1}.99330$	$\bar{1}.99944$	0.02531	$\bar{1}.43773$	0.2740
	β_2	$\bar{2}.55962$	0.05225	$\bar{1}.98827$	$\bar{1}.99252$	$\bar{1}.99940$	0.02748	$\bar{2}.61954$	0.0416
Zr (40)	α_2	$\bar{1}.70364$	$\bar{1}.99752$	$\bar{1}.99957$	0	0	0	$\bar{1}.70073$	0.5020
19.90 34.0	β_1	$\bar{1}.37107$	0.05918	$\bar{1}.99202$	$\bar{1}.99454$	$\bar{1}.99957$	0.02202	$\bar{1}.43840$	0.2744
	β_2	$\bar{2}.57529$	0.06948	$\bar{1}.99114$	$\bar{1}.99402$	$\bar{1}.99953$	0.02375	$\bar{2}.65321$	0.0450
Cb (41)	α_2	$\bar{1}.70018$	$\bar{1}.99704$	$\bar{1}.99960$	0	0	0	$\bar{1}.69682$	0.4975
20.20 35.5	β_1	$\bar{1}.37291$	0.06521	$\bar{1}.99322$	$\bar{1}.99515$	0	0.01870	$\bar{1}.44519$	0.2787
	β_2	$\bar{2}.60591$	0.07720	$\bar{1}.99242$	$\bar{1}.99476$	0	0.02000	$\bar{2}.69029$	0.0490
Mo (42)	α_2	$\bar{1}.70157$	$\bar{1}.99651$	0	0	0	0	$\bar{1}.69808$	0.4990
20.40 37.0	β_1	$\bar{1}.36736$	0.07262	$\bar{1}.99414$	$\bar{1}.99568$	0	0.01578	$\bar{1}.44558$	0.2790
	β_2	$\bar{2}.62242$	0.08546	$\bar{1}.99342$	$\bar{1}.99538$	0	0.01686	$\bar{2}.71354$	0.0517
Ru (44)	α_2	$\bar{1}.70387$	$\bar{1}.99616$	0	0	0	0	$\bar{1}.70003$	0.5012
20.00 38.0	β_1	$\bar{1}.37658$	0.08207	$\bar{1}.99555$	$\bar{1}.99634$	0	0.01620	$\bar{1}.46674$	0.2929
	β_2	$\bar{2}.64516$	0.09701	$\bar{1}.99498$	$\bar{1}.99610$	0	0.01725	$\bar{2}.75040$	0.0563
Rh (45)	α_2	$\bar{1}.70605$	$\bar{1}.99561$	0	0	0	0	$\bar{1}.70166$	0.5031
20.27 39.0	β_1	$\bar{1}.34635$	0.08955	$\bar{1}.99612$	$\bar{1}.99695$	0	0.01620	$\bar{1}.44517$	0.2787
	β_2	$\bar{2}.64695$	0.10555	$\bar{1}.99560$	$\bar{1}.99679$	0	0.01725	$\bar{2}.76214$	0.0578
Pd (46)	α_2	$\bar{1}.70018$	$\bar{1}.99843$	0	0	0	0	$\bar{1}.69861$	0.4996
20.40 40.0	β_1	$\bar{1}.35218$ $\bar{1}.39445$	0.09412 0.06221	$\bar{1}.99664$	$\bar{1}.99745$	0	0.01452	$\bar{1}.45491$ $\bar{1}.46527$	0.2850 0.2919
	β_2	$\bar{2}.70408$	0.07420	$\bar{1}.99616$	$\bar{1}.99733$	0	0.01542	$\bar{2}.78719$	0.0613
Ag (47)	α_2	$\bar{1}.70114$	$\bar{1}.99712$	0	0	0	0	$\bar{1}.69826$	0.4992
20.57 41.0	β_1	$\bar{1}.38435$	0.07004	$\bar{1}.99708$	$\bar{1}.99787$	0	0.01248	$\bar{1}.46182$	0.2896
	β_2	$\bar{2}.69948$	0.08330	$\bar{1}.99663$	$\bar{1}.99777$	0	0.01328	$\bar{2}.79046$	0.0617
Cd (48)	α_2	$\bar{1}.70209$	$\bar{1}.99585$	0	0	0	0	$\bar{1}.69794$	0.4988
20.52 41.5	β_1	$\bar{1}.39005$	0.07700	$\bar{1}.99739$	$\bar{1}.99826$	0	0.00945	$\bar{1}.47215$	0.2966
	β_2	$\bar{2}.71020$	0.09194	$\bar{1}.99700$	$\bar{1}.99820$	0	0.01002	$\bar{2}.80736$	0.0642
In (49)	α_2	$\bar{1}.70243$	$\bar{1}.99540$	0	0	0	0	$\bar{1}.69783$	0.4987
20.50 42.5	β_1	$\bar{1}.38417$	0.08314	$\bar{1}.99760$	$\bar{1}.99856$	0	0.00860	$\bar{1}.47207$	0.2965
	β_2	$\bar{2}.70742$	0.09892	$\bar{1}.99724$	$\bar{1}.99850$	0	0.00910	$\bar{2}.81118$	0.0647
Sn (50)	α_2	$\bar{1}.70239$	$\bar{1}.99502$	0	0	0	0	$\bar{1}.69714$	0.4979
20.33 42.5	β_1	$\bar{1}.37676$	0.08884	$\bar{1}.99795$	$\bar{1}.99888$	0	0.00945	$\bar{1}.47188$	0.2963
	β_2	$\bar{2}.73469$	0.10546	$\bar{1}.99761$	$\bar{1}.99885$	0	0.00995	$\bar{2}.84656$	0.0702
Sb (51)	α_2	$\bar{1}.70757$	$\bar{1}.99388$	0	0	0	0	$\bar{1}.70145$	0.5029
20.70 44.0	β_1	$\bar{1}.39270$	0.09272	$\bar{1}.99822$	$\bar{1}.99910$	0	0.00903	$\bar{1}.49177$	0.3103
	β_2	$\bar{2}.73314$	0.11059	$\bar{1}.99792$	$\bar{1}.99908$	0	0.00946	$\bar{2}.85019$	0.0708
Te (52)	α_2	$\bar{1}.70329$	$\bar{1}.99344$	0	0	0	0	$\bar{1}.69673$	0.4974
20.65 45.0	β_1	$\bar{1}.38382$	0.09587	$\bar{1}.99843$	$\bar{1}.99930$	0	0.00775	$\bar{1}.48517$	0.3056
	β_2	$\bar{2}.74555$	0.11499	$\bar{1}.99820$	$\bar{1}.99929$	0	0.00810	$\bar{2}.86613$	0.0735

F_c, the ratio of the coefficients of reflection of the calcite crystal VB were measured directly by Allison[9] for several wave-lengths in this region. The values of R given in his Table II were plotted and a smooth curve through the points permitted interpolation to a reasonable accuracy. This application is not strictly correct for the calibration was carried out by means of a partially polarized beam from the first crystal, whereas in the present experiment the beam is unpolarized before reflection. The values of F_c are not changed appreciably by a proper treatment.

There is no significant variation of α_2/α_1 with atomic number, the average value for these twenty elements being 0.5003, in excellent agreement with the theory of Burger and Dorgelo[10] and with all previous experimental work.

The variation of the calculated values of P_{β_1}/P_{α_1} as a function of atomic number is shown graphically by the circles in Fig. 1. The crosses in this figure represent the results of H.-T. Meyer[7] using a gas tube, a rocksalt crystal, and a photographic-microphotometer method. The explanation for the decided lack of agreement between the present work and that of Meyer is perhaps to be found in the rather cumbersome photographic method. In the method of determining relative intensities of x-ray lines from a photographic plate, especially when the lines are very widely separated or lie on opposite sides of the silver or bromine K limit, it is necessary to make some rather bold assumptions which are open to doubt. The internal consistency of the results themselves seems to indicate that the ionization method is preferable.

The variation of β_2/α_1 is shown graphically in Fig. 2, with similar symbols, and it will be noted that the deviation from Meyer's results is in the same direction. His method is, of course, more powerful in the detection of the β_2 line when it almost disappears at Zn. He has continued his measurements on β_2 to lower atomic numbers but this line apparently disappears at Ni (28) and the further observations were on $K\beta_5$.

No attempt was made in this research to measure the relative intensity of any satellite lines.

As far as is known there are no theoretical predictions as to the variations of relative in-

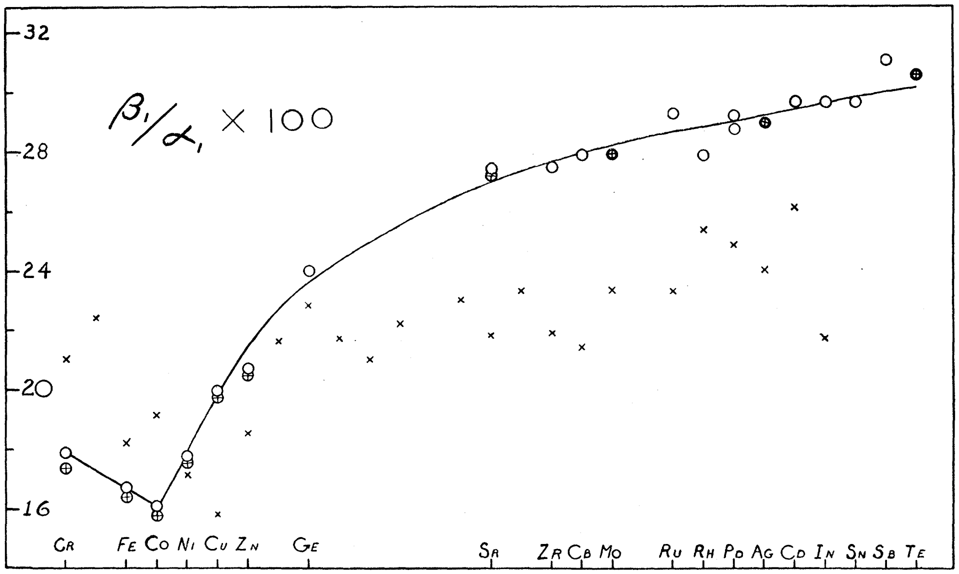

FIG. 1. Variation of the relative intensities and transition probabilities of β_1 to α_1 as a function of atomic number. The open circles are the values of the relative intensities of the two wave-lengths at the surface of the target, the circles containing crosses are the relative transition probabilities, and the crosses are the values of the relative intensities obtained by H.-T. Meyer.[7]

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

[10] Burger and Dorgelo, Zeits. f. Physik **23**, 258 (1924).

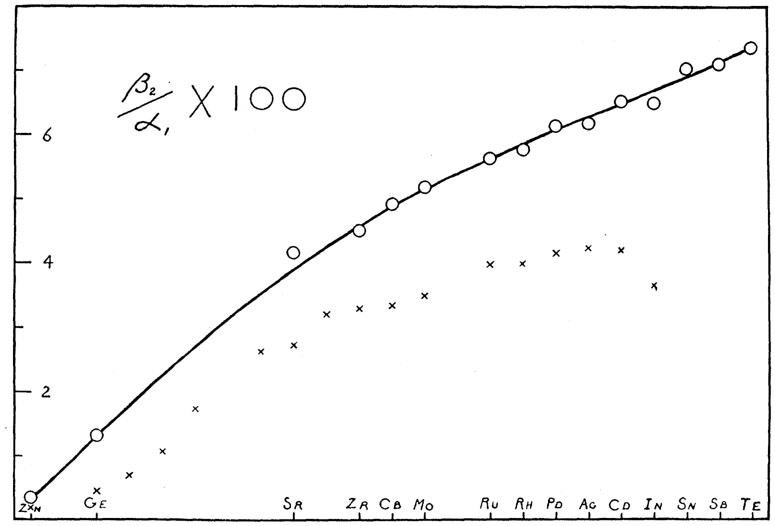

FIG. 2. Variation of the relative intensities of β_2 to α_1 as a function of atomic number. The circles are the present results and the crosses are the values of H.-T. Meyer.[7]

tensity with atomic number. The marked change of β_1/α_1 in the region 27 to 40 is not easily reconciled with the electron population of the M levels. The increased value of the ratio for Fe and Cr is presumably due to the presence of increasingly intense satellites of β_1. However in the case of β_2/α_1 the variation of the intensity ratio in the region 38 to 30 is indicated by the decreasing population of the N_{22} and N_{21} levels.

Corrections for the absorption within the target

The P_λ/P_{α_1} ratios obtained above will yield directly the relative transition probabilities in the various atoms if one can correct for the absorption within the target. As these values are of some theoretical significance it is worth while to attempt an approximate solution to the problem.

Fig. 3 shows the geometrical arrangement of the target with respect to the cathode rays and the observed x-rays. If we assume a perfectly smooth surface of the target material we can set up the following conditions. The intensity dP_λ, of x-rays observed of wave-length λ, arising from primary ionization by the impinging electrons in an element of electron path dx at a depth x is given by:

$$dP_\lambda = c_\lambda F(x) e^{-\mu_\lambda x} dx \tag{8}$$

where c_λ is a factor including the instrumental constants and the probability of the transition giving rise to the wave-length λ; $F(x)$ is the ionization probability for the impinging electrons at a depth x; and μ_λ is the absorption coefficient of the x-rays in the target material. The total intensity, P_λ, leaving the target at the appropriate angle is

$$P_\lambda = c_\lambda \int_0^{x_0} F(x) e^{-\mu_\lambda x} dx. \tag{9}$$

The limits of the integration are imposed by the maximum depth to which the electrons can penetrate the target material and yet retain sufficient energy to ionize the level in question. These limits are assumed to be given by the Thomson-Whiddington equation

$$x = (V^2 - V_x^2)/b, \tag{10}$$

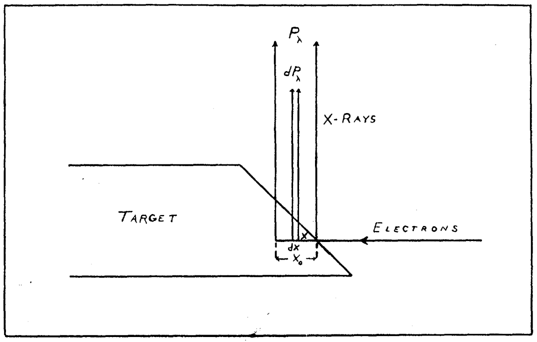

FIG. 3. Geometrical arrangement of the target and cathode beam in the x-ray tube.

where V is the initial voltage of the electrons, V_x is their voltage at the depth x, and V_0 is to be taken as the excitation potential of the level or the voltage at the depth x_0. Substituting from Eq. (10) in Eq. (9), we obtain

$$P_\lambda = \frac{2c_\lambda}{b} e^{-\mu_\lambda V^2/b} \int_{V_0}^{V} V_x F'(V_x) e^{\mu_\lambda V_x^2/b} dV_x. \tag{11}$$

Here $F'(V_x)$ is the ionization probability as a function of the electron voltage, as has been measured by Webster and his associates[11] with thin targets of silver. The best fitting equation given by them is

$$F'(V_x) = \frac{6k_\lambda}{(V_x/V_0)\{[\pi/2 \cos^{-1}(V_0/V_x)^{\frac{1}{2}}]^2 - 1\}}. \tag{12}$$

Substituting Eq. (12) in Eq. (11) we obtain

$$P_\lambda = K V_0 \frac{2c_\lambda}{b} e^{-\mu_\lambda V^2/b} \int_{V_0}^{V} \frac{e^{\mu_\lambda V_x^2/b} dV_x}{[\pi/2 \cos^{-1}(V_0/V_x)^{\frac{1}{2}}] - 1} \tag{13}$$

or for the ratio

$$\frac{P_\lambda}{P_\alpha} = \frac{c_\lambda'}{c_\alpha'} \frac{e^{-\mu_\lambda V^2/b}}{e^{-\mu_\alpha V^2/b}} \int_{V_0}^{V} \frac{e^{\mu_\lambda V_x^2/b} dV_x}{[\pi/2 \cos^{-1}(V_0/V_x)^{\frac{1}{2}}] - 1} \bigg/ \int_{V_0}^{V} \frac{e^{\mu_\alpha V_x^2/b} dV_x}{[\pi/2 \cos^{-1}(V_0/V_x)^{\frac{1}{2}}]^2 - 1}, \tag{14}$$

where c_λ'/c_α' is the true ratio of the transition probabilities of wave-lengths λ and α.

Since this equation is not integrable by ordinary means it must be evaluated graphically. The limit V is set by the experimental voltage shown in the first column of Table IV and the values of V_0 are taken from Table 225 in Siegbahn.[12] These voltages were transformed to relativistic velocities and the coefficient b became a in the Thomson Whiddington law

$$v^4 - v_x^4 = ax. \tag{15}$$

a was determined from an empirical equation given by Wissak[13]

$$a = 9.6 \times 10^{42} Z\rho/A, \tag{16}$$

where Z is the atomic number, A the atomic weight and ρ the density. μ was determined from Richtmyer's equation

$$\mu = 5.29\rho \times 10^{-4} \lambda^3 Z^{4.3}/A, \tag{17}$$

which holds between the K and L limits and was here presumed to yield absorption coefficients for wave-lengths up to 2.3A although it is known to be rigid only to 1.0A.

With these numerical values the equation has been solved in a graphical manner,[14] for the elements Cr, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag and Te. The largest correction is for Cr where V/V_0 has the largest value 5.18. The ratio of the integrals comparing the β_1 to the α_1 line is 0.975 and of the exponential factors outside the integral is 1.060. P_{β_1}/P_{α_1} must therefore be multiplied by 0.97 to give the ratio of the transition probabilities for these lines.

The resultant correction factors to be multiplied by P_{β_1}/P_{α_1} to yield $c_{\beta_1}'/c_{\alpha_1}'$ are given in Table V. The resultant values of $c_{\beta_1}'/c_{\alpha_1}'$ are shown graphically by the circles containing crosses in Fig. 1.

TABLE V. *Target corrections to yield ratios of transition probabilities.*

Element	Cr	Fe	Co	Ni	Cu	Zn	Sr	Mo	Ag	Te
F_t	0.97	0.98	0.98	0.99	0.99	0.99	0.99	1.00	1.00	1.00
$c_{\beta_1}'/c_{\alpha_1}'$	0.173	.163	.157	.185	.197	.205	.271	.279	.289	.305

The correction, F_t, to be applied due to the absorption in the target is thus seen to be surprisingly small and to the first approximation measurements on the relative intensities of *K*-series lines from thick targets of the heavier elements at voltages not much greater than the excitation voltages give the relative transition probabilities.

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[11] Webster, Hansen and Duvendack, Phys. Rev. **42**, 141 (1932).

[12] M. Siegbahn, *Spektroskopie der Rontgenstrahlen,* second edition.

[13] Wissak, Ann. d. Physik **5**, 507 (1930).

[14] I am indebted to Mrs. A. T. Monk for carrying out this graphical integration.

The treatment outlined above is very crude and it is perhaps worth while to point out the approximations and examine their effect on the results. A smooth target face is assumed whereas the roughness is large compared to the depth of penetration of the cathode rays (10^{-4} to 4×10^{-4} cm). This is possibly the largest error and might influence the correction factor considerably. Also any deposit on the target face was disregarded, for this was very small for a sufficiently "hard" tube. The treatment takes no account of the indirect production of characteristic radiation; i.e., a cathode ray may first excite a continuous spectrum quanta of shorter λ than the K limit, which in turn will fluoresce line radiation at a different depth within the target. However we know[15] that the ratio of the direct line radiation to the indirect line radiation remains constant at approximately two up to 180 kv in Pd. If it is assumed that the white radiation spreads out spherically from its excitation center and is converted into line radiation within 10^{-4} cm the correction from this source will be of a smaller order of magnitude. Furthermore no account has been taken of the diffusion of the incident electrons within the target, which tends to make the mean depth of penetration less than that calculated by the above method. It is conceivable that the last two factors may to some extent have a balancing effect. The expression for $F'(V_x)$ has been assumed to hold for the excitation function in an element of thickness dx within the target, whereas it is found experimentally to satisfy measurements from a thin surface layer. The values of "a" in the Thomson-Whiddington equation are in doubt since the available experimental values are not in good agreement. Furthermore these values for metals were obtained with the electron beam normally incident on a thin film instead of at 45° as in the present arrangement. E. J. Williams[16] has found the fourth power law to be expressed more accurately as:

$$v^{3.7}-v^{3.7}=ax. \tag{18}$$

The values of the absorption coefficients are supposed to hold for the range of wave-lengths 0.1 to 1.0A and are not accurately true for the longer wave-lengths.

It is felt that nothing very definite can be said about the effect of these assumptions other than that the roughness of the target sets a limit to the accuracy of the correction. In these experiments no attempt was made to polish the target, which was in general machined to a visible smoothness. The cathode beam did not pit the target to any visible extent except in the case of Cd and Sb.

The values in Table IV for P_λ/P_{α_1} may therefore be taken as the ratio of the intensities of the two wave-lengths leaving the surface of the target to within an estimated error of four percent and for the heavier elements they may be accepted as the ratio of the transition probabilities to within a slightly greater error.

In conclusion I wish to express my appreciation to Professor S. K. Allison for the use of his laboratory equipment and for the suggestion of this problem.

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[15] Hansen and Stoddard, Phys. Rev. **43**, 701 (1933).

[16] E. J. Williams, Proc. Roy. Soc. (London) **130**, 310 (1930).