Effect of chemical combination

Chemical combination seems to have very little effect on the width of the K absorption edge. Most of the compounds of iodine investigated show a width nearly equal to that of the element. The compounds of bromine have very nearly the same width. The only exceptions are the IBr vapor, which has a slightly narrower width, and CH_3Br, which has a larger value for its width. The absorption edge of bromine vapor is the narrowest bromine edge found.

The shift found for HBr, 1.2 volts, compares favorably with that found by Hanawalt,[9] 1.5 volts, using photographic methods. The value of the shift found for CH_3Br, 1.3 volts, agrees with the value found by Stephenson,[5] 1.1 volts. The shift found for KBr, 4.5 volts, is of the same order of magnitude as that found by Hanawalt[9] for AgBr, 4.1 volts. Stephenson[5] finds a lower value for KBr and remarks that the effect of chemical combination on the position of the bromine edge seems to be less than that indicated by Hanawalt's data. Our data support Hanawalt's results.

It was thought desirable to check the effect of the thickness of the screen on the position and width of an absorption edge. Data were obtained on three different screens of solid iodine in which the transmission on the long wave-length side of the edge varied from 0.70 to 0.40. It was found that there is no change either in the position of the absorption limit or in its width, as the thickness of the screen is varied between these limits. Richtmyer and Barnes[3] show that the position and the width of an edge should vary with the thickness of the screen, but for the magnitude of variation of the thickness of the screens used for measurements of absorption limits, the change to be expected is too small to measure.

In conclusion, the writer wishes to thank Professor Bergen Davis for suggesting this problem, and for his interest and advice throughout the course of the investigation.

APRIL 15, 1937 PHYSICAL REVIEW VOLUME 51

X-Ray Fluorescence Yields

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The x-ray fluorescence yield for the K shell of atoms has been measured for a number of elements ranging from nickel to tin by an ionization chamber method similar to that developed by A. H. Compton. The results show an increase in the fluorescence yield with atomic number and are compared with those calculated by Massey and Burhop using relativistic wave mechanics and also with those calculated by Burhop from nonrelativistic wave mechanics. The fluorescence yield for the L_{III} shell of lead, thorium and uranium has been determined using suitable exciting radiation. An increase in the yield with atomic number is found.

INTRODUCTION

THE x-ray fluorescence yield, w_K, for the K shell of an assemblage of similar atoms is defined as the ratio of the number of fluorescence K quanta emitted per unit time to the number of atoms ionized in the K shell per unit time. Similar definitions may be applied to any one of the shells of an atom. It might be expected from the simple Bohr atomic theory that every atom ionized in the K shell would necessarily emit a K series quantum of radiation and that therefore this ratio would be unity. However, experiments have shown that this ratio is always less than unity although it increases with increase in the atomic number of the emitting atom. This phenomenon may be explained in either of two ways; first, by assuming that every atom ionized in the K shell emits a K series quantum but that in some of the atoms these quanta are photoelectrically absorbed in the parent atom with the ejection of an electron from an outer shell. The second explanation is that an atom ionized in the K shell may return to a state of lower energy either by a transition of an outer electron to the K shell with the emission of a K series quantum of radiation, or by a radiationless transition in which the surplus energy available when an outer electron falls into the K shell is transferred to another electron of the atom and this electron thereby ejected from the atom. These ejected electrons are often referred to as Auger electrons since Auger discovered them and explained their origin.

If from a number of similar atoms ionized in the K shell there are n_f fluorescence K quanta emitted per unit time and n_A Auger electrons emitted per unit time the fluorescence yield, w_K, for these atoms is given by:

$$w_K = n_f / n_A + n_f, \tag{1}$$

since $n_A + n_f$ is the number of atoms ionized in the K shell per unit time.

There is another quantity called the *internal conversion coefficient*, I_K, which is often used in relation to this phenomenon. It is defined as the ratio of the number of Auger electrons emitted per unit time to the number of atoms ionized in the K shell per unit time, or

$$I_K = n_A / n_A + n_f. \tag{2}$$

From the definitions of fluorescence yield and internal conversion coefficient it follows that $w_K = 1 - I_K$.

Two methods have been used for experimentally determining the fluorescence yield. In the one introduced by Auger[1] a Wilson cloud chamber is used and electron tracks counted. This method is necessarily limited to gases. A second method adopted by A. H. Compton[2, 3] uses an ionization chamber. This is the method used in this experiment.

The object of this investigation was to determine the variation of fluorescence yield with atomic number. Although many similar investigations have been carried out the somewhat divergent results seemed to justify a repetition of the experiments. Berkey[4] reported a maximum fluorescence yield for molybdenum, atomic number 42. No such maximum has been found in the present work.

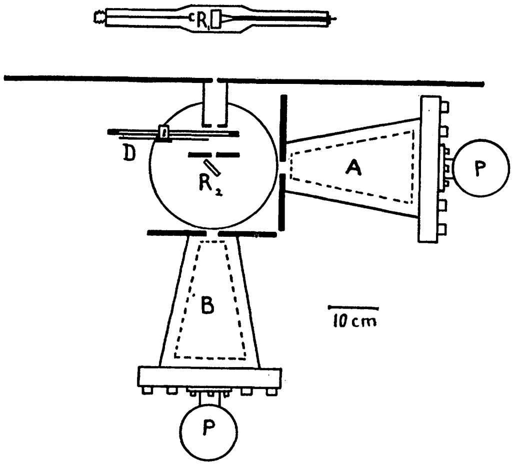

FIG. 1. Arrangement of apparatus.

THEORY

Suppose a beam of monochromatic x-rays of wave-length λ' falls at an angle of 45° on a solid radiator thus exciting K fluorescence radiation of average wave-length λ''. If P' is the power in the primary incident beam and P'' the power emerging from the radiator in a solid angle Ω at a mean angle of 45° with the radiator, then, as is shown elsewhere,[2]

$$w_K = \frac{1}{\Omega} \times \frac{r}{r-1} \times \frac{\mu' + \mu''}{\mu'} \times \frac{\lambda''}{\lambda'} \times \frac{P''}{P'}, \tag{3}$$

where μ' and μ'' are the coefficients of absorption in the radiator of the primary and secondary fluorescence beams respectively and r is the K absorption jump. Eq. (3) is a simplified form of Eq. (7.09) found on page 486 of *X-Rays in Theory and Experiment.* This simplification consists in using average values for the wave-lengths and absorption coefficients. The fraction $r - 1/r$ represents the ratio of the amount of the primary beam absorbed in the K shell to that absorbed in the atom as a whole. The solid angle Ω depends on the geometrical arrangement of the apparatus and is equal to $A/4\pi r^2$, where A is the area of the ionization chamber window. (See Fig. 1.)

In the measurement of P' and P'' a correction

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[1] P. Auger, Ann. d. Physik **6**, 183 (1926); Comptes rendus **180**, 65 (1925).

[2] A. H. Compton, Phil. Mag. **8**, 961 (1929).

[3] Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1936) p. 479.

[4] D. K. Berkey, Phys. Rev. **45**, 437 (1933).

must be made for the absorption and for the scattering of these radiations by the gas in the ionization chamber. The fraction f of the x-rays absorbed in the chamber is given by $f=1-e^{-\mu l}$ where μ is the absorption coefficient of the gas for the x-rays of the particular wave-length involved and l is the length of the ionization chamber. Of the fraction f of the x-rays absorbed in the chamber only a portion Rf produces ions. The fraction R is given by the equation[5]

$$R=1-\left(\frac{r-1}{r}e^{-\mu x_a}w_K\frac{\tau_K}{\mu}\frac{\lambda}{\lambda''}\right)_{\text{argon}}-\left(\frac{\sigma}{\mu}e^{-\mu' x}\right)_{\text{argon}}. \quad (4)$$

Comparing Eq. (4) with that given by Allison and Andrew on page 496 of *X-Rays in Theory and Experiment* it will be seen that again average values have been taken for wave-lengths and absorption coefficients. This averaging makes a negligible error and considerably simplifies the calculations. The second term of Eq. (4) represents that part of the incident beam of wave-length λ which produces argon fluorescence radiation of wave-length λ'' which is not absorbed in the chamber. Since the fluorescence yield for argon is small ($w_K=0.07$) and any argon fluorescence radiation produced has such a long wave-length that it is nearly all absorbed in the chamber, it follows that the second term is in this case negligibly small. The third term represents that fraction of the beam which is removed from the chamber by scattering and hence does not produce any ionization current. Since the ratio of scattering to total absorption, σ/μ, increases as the wave-length of the absorbed radiation decreases this term becomes of importance for short wave-length x-rays.

APPARATUS

A nearly homogeneous beam of x-rays was obtained by using the fluorescence rays from a radiator R_1 placed just above the window of an x-ray tube, Fig. 1. This beam of x-rays passed through a series of circular holes whose diameter was 0.62 cm and fell on the radiator R_2 whose fluorescence yield was to be determined. The radiator R_2 was placed at the center of the table of an x-ray spectrometer at an angle of 45° to the incident beam. The fluorescence rays from R_2 entered the ionization chamber placed in position A and the resulting ionization current was measured. This was compared with the ionization current obtained with the ionization chamber in position B and the radiator R_2 removed.

Since the power P' of the primary beam which enters the ionization chamber in position B is several hundred times greater than the power P'' of the fluorescent beam entering the chamber in position A some device was necessary to bring the two beams to approximately the same power. At first the power in the primary beam was reduced by using thin absorbers of silver, but this was found unsatisfactory owing to the difficulty of measuring accurately the thickness and the absorption coefficients of the silver absorbers. A rotating disk D with an adjustable radial slot was then tried. This proved a very satisfactory means of reducing the power in the primary beam. The amount transmitted through the radial slot was found to increase uniformly with the angular opening of the slot for angles greater than 1°. When the radial slot was less than 1° the results were not reliable due presumably to edge effects of the slot. Throughout the experiments the slot was fixed at an angular opening of 1° thus reducing the power in the primary beam by 1/360. When further reduction was necessary aluminum absorbing screens were also used. The rotating disk D was placed on an arm so that it could be easily removed when not in use.

When investigating the fluorescence yields of elements of low atomic number up to selenium (34) an x-ray tube having a silver target and a radiator of molybdenum was used. Power for the x-ray tube was furnished by a motor generator set delivering current at 540 cycles to a transformer the high voltage from which was rectified and smoothed out by condensers. This equipment was designed by Professor S. K. Allison for providing constant current and voltage for x-ray use. Suitable ionization currents were obtained when the x-ray tube was operated at 40 kilovolts and 10 milliamperes. For the investigation of elements of higher atomic number from zirconium

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[5] S. K. Allison and V. Andrew. Phys. Rev. **38**, 441 (1931).

(40) to tin (50) the silver target x-ray tube was replaced by one having a tungsten target. The radiator R_1 was then silver, tin or barium oxide depending on the element whose fluorescence yield was being investigated. The tungsten target tube was operated at about 65 kilovolts and 7 milliamperes.

The ionization chamber was of a conical shape to receive the divergent beam from R_2. Inside an earthed steel case and separated from it by about 1.5 cm was placed a conical grid of copper wire (shown dotted in Fig. 1) which was kept at about 140 volts and which formed the ionization chamber proper. Inside the conical grid were placed two collecting electrodes connected directly to an FP-54 vacuum tube. The chamber was arranged so that the x-ray beam never struck the collecting electrodes or the side walls of the grid. The window of the ionization chamber was 2.55 cm in diameter and was covered with heavy Cellophane. The length of the chamber was 23.7 cm and its front window was 12.7 cm from the center of the spectrometer.

The rear of the ionization chamber was made of a series of layers of wood, aluminum, iron and copper each about 3 mm thick. This prevented any x-rays which were not absorbed in the chamber from being scattered by the rear wall back into the chamber. The ionization chamber was capable of holding a pressure of 5 atmospheres though the actual pressure of the argon used in it depended on the wave-length of the x-rays being absorbed.

The wave-length λ' and λ'' for the primary and the fluorescence beams were calculated by taking the weighted mean of the α and β lines in accordance with the work of Williams.[6] The values of the K absorption jump r for each element investigated were taken from published data on absorption coefficients on the long and short wave-length side of the K absorption edge.

TABLE I. *Values used in calculations.*

R_1	R_2	λ'	λ''	$\frac{\mu'+\mu''}{\mu'}$	$\frac{r-1}{r}$	$\frac{R'}{R''}$	$\frac{f'}{f''}$	$\frac{i''}{i'}$	$\frac{P''}{P'}$	w_K
Mo	Ni28	0.695	1.635	2.25	0.881	0.967	0.431	0.65	0.000162	0.385
Mo	Cu29	.695	1.521	1.875	.879	.969	.435	.96	.00022	.41
Mo	Zn30	.695	1.42	1.87	.875	.970	.438	1.32	.000275	.48
Mo	Se34	.695	1.086	1.45	.866	.977	.507	2.76	.000555	.575
Sn	Zr40	.480	.770	1.525	.852	.95	.496	.464	.000605	.69
BaO	Zr40	.378	.770	1.985	.852	.905	.296	.497	.000368	.69
Sn	Mo42	.480	.695	1.405	.858	.96	.55	.535	.00078	.73
BaO	Mo42	.378	.695	1.77	.858	.91	.328	.595	.000495	.74
BaO	Rh45	.378	.600	1.56	.841	.92	.42	.613	.000664	.77
BaO	Ag47	.378	.545	1.432	.844	.93	.485	.66	.000837	.81
BaO	Cd48	.378	.523	1.39	.842	.936	.504	.668	.000875	.79
BaO	Sn50	.378	.480	1.316	.828	.95	.595	.64	.00101	.81

In determining the power in the primary and fluorescence beams P' and P'', respectively, it was necessary to make a correction both for absorption of the x-rays in the window of the ionization chamber and in the air between the radiator R_2 and the window. An attempt was made to determine if there was any scattered radiation present in the primary and fluorescence beams. This was done by making absorption measurements on the two beams. The results showed the scattered radiation in every case to be small and within experimental error. In the course of the investigation the pressure of the argon in the ionization chamber was changed several times so that the fluorescence yield for any one element was determined at several pressures of gas within the chamber. For a few elements the fluorescence yield was determined using primary radiation of several wave-lengths. No variation in the yield due to this factor was found. This is in accordance with the results of several previous investigators who found that the value of the fluorescence yield is independent of the wave-length of the exciting radiation. (Table I.)

The various primed quantities refer to the primary exciting radiation whereas the double primed quantities refer to the fluorescence radiation.

DISCUSSION OF RESULTS

Fig. 2 shows a plot of the collected results of the various authors listed in Table II. The circled dots represent the author's results. The full curve A is that given by Massey and Burhop[7] for the K fluorescence yield and was obtained from theoretical calculations of the K fluorescence yield using relativistic wave mechanics. The dotted curve B shows the earlier nonrelativistic calculations by Burhop of the K fluorescence

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[6] J. H. Williams. Phys. Rev. **44**, 146 (1933).

[7] H. S. W. Massey and E. H. S. Burhop. Proc. Roy. Soc. **153**, 661 (1936).

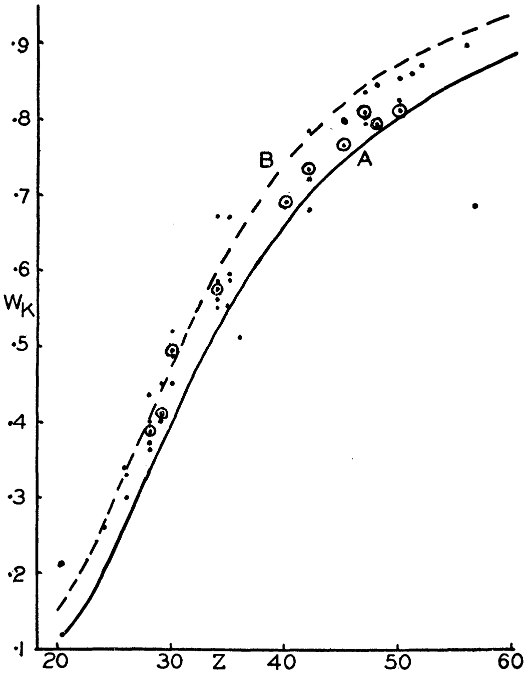

FIG. 2. Values of K fluorescence yields determined by various authors. The results of the present paper are encircled. Dotted curve gives nonrelativistic calculations by Burhop, the full curve gives the calculations of Massey and Burhop who used relativistic wave mechanics.

yields. These calculations are not exact as various approximations have to be made in order to evaluate certain integrals. The nonrelativistic curve* is not that given in this paper but is recalculated on the basis of an error pointed out in a later paper by Burhop.[8]

Thus we see that the data collected to date do not decide in favor of either curve, that is, between that based on the relativistic and that based on the nonrelativistic calculations. The author's results, however, definitely favor the relativistic calculations.

FLUORESCENCE YIELDS FOR THE L_{III} SHELLS OF LEAD, THORIUM AND URANIUM

The procedure in this experiment is the same as that for the determination of the fluorescence yields in the K shells, with the exception that now the radiator R_1 must be chosen so that the radiation which it emits has a wave-length in between the L_{II} and L_{III} absorption edges for the element R_2 under investigation. The radiation from molybdenum is such that it excites the radiation from the L_{III} shell of uranium but not from the L_{II} or any other shells in which the electrons have greater binding energy. In a similar manner suitable radiators were found for exciting the radiation from the L_{III} shells of thorium and lead. The Table III shows the data used in these experiments. The present value given in Table III for the fluorescence yield for the L_{III} shell of uranium is preferred to the author's earlier value[9] where silver absorbers were used to reduce the intensity of the primary beam. The present investigation showed that the

TABLE II. *Collected results of fluorescence yields in the K series.*

ELEMENT	AUGER	MARTIN[a]	COMPTON	HAAS[b]	LAY[c]	ARENDS[d]	BACKHURST[e]	STEPHENSON
18A	0.07							
20Ca				0.15	0.21			
24Cr				0.26	0.265			
26Fe		0.33			0.34	0.30		
28Ni		0.40	0.37		0.436	0.364		0.385
29Cu		0.45				0.401		0.41
30Zn		0.52			0.476	0.45		0.48
34Se		0.67	0.55		0.585	0.55		0.575
35Br		0.67	0.56					
36Kr	0.51							
40Zr								0.69
42Mo			0.68			0.724	0.785	0.735
45Rh							0.801	0.77
46Pd							0.835	
47Ag						0.795	0.838	0.81
48Cd							0.846	0.79
50Sn						0.825	0.855	0.81
51Sb							0.862	
52Te							0.872	
54Xe	0.70							
56Ba							0.900	

[a] L. H. Martin, Proc. Roy. Soc. **A115**, 420 (1927).
[b] M. Haas, Ann. d. Physik **16**, 473 (1932).
[c] H. Lay, Zeits. f. Physik **91**, 523 (1934).
[d] E. Arends, Ann. d. Physik **22**, 281 (1935).
[e] I. Backhurst, Phil. Mag. **22**, 737 (1936).

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* Concerning the nonrelativistic curve:

$$I_K = n_A/n_A + n_f, \qquad I_K = 0.42;$$

$n_f = 48.0 \times 10^{-3}$ (data for silver from Burhop's paper). This data gives $n_A = 34.8 \times 10^{-3}$. The error concerned the value of n_f which should have been four times as great as the value given above, i.e., $n_f = 192.0 \times 10^{-3}$. Using this value for n_f and the above value for n_A the calculated value for I_K for silver is 0.154. The relation between I_K and Z, the atomic number of the element, is given by Wentzel and Burhop as $I_K = 1/1 + bZ^4$ where b is a constant. Substituting in this equation $I_K = 0.154$ and $Z = 47$ for silver the constant b is found to be 1.127×10^{-6}. This value for b has been used in calculating the points for the dotted curve in Fig. 2.

[8] E. H. S. Burhop. Proc. Roy. Soc. **148**, 272 (1935).

[9] R. J. Stephenson. Phys. Rev. **43**, 527 (1933).

TABLE III. *Values used in calculating the fluorescence yields from L_{111} shells of atoms.*

R_1	R_2	λL_{11}	λL_{111}	λ'	λ''	$\frac{\mu'+\mu''}{\mu'}$	$\frac{r-1}{r}$	$\frac{i''}{i'}$	$\frac{P''}{P'}$	wL_{111}
Rb	Pb82	.8143	.9492	0.908	1.14	1.751	0.58	0.40	0.000214	0.32
Cb	Th90	.6293	.7600	.731	.925	1.796	.56	.97	.00026	.42
Mo	U92	.6913	.7208	.695	.876	1.81	.56	.325	.000274	.44

method of reducing the primary beam by silver absorbers was not capable of giving reliable results. Lay, using a photographic method for determining the power in the primary and fluorescence beams, gives a value of 0.41 for the fluorescence yield from the L_{111} shell of uranium.

The author is indebted to the Museum of Science and Industry of Chicago for the loan of a piece of uranium and to Professor S. K. Allison for many helpful discussions.

APRIL 15, 1937 PHYSICAL REVIEW VOLUME 51

The Energy Distribution of Photoelectrons Emitted by Calcium and Calcium Oxide*

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Measurements of the energy distribution of the photoelectrons emitted from calcium with the aid of a magnetic velocity analyzer using radiation of wave-length λ2536 have been made. Special care was taken to eliminate contact potentials and to ensure that the emission observed was that from pure calcium. Energy distribution curves were obtained for pure Ca, CaO, and for a number of stages intermediate between the oxide and the pure metal. The theories of Fowler, DuBridge, Mitchell, and Nottingham were found to compare favorably with the data for pure Ca on the high energy side, but to depart from the data at low energies. The photoelectric work function obtained for pure Ca was 3.21 electron volts. The failure of all attempts to fit the above theories to the data for the oxide indicates that the Sommerfeld theory of a metal is not applicable to CaO.

INTRODUCTION

THE appearance of a number of theories of the emission of photoelectrons in recent years has indicated the desirability of developing a method of distinguishing between the various theories and comparing them with the experimental data. Rudberg[1] has shown that the energy distribution curves provide a suitable basis for such a comparison. According to Rudberg, for high energies the energy distribution curves predicted by all the theories are dominated by the Fermi factor

$$1/1+\exp{(E-E_m)/kT},$$

where E is the energy, E_m is the maximum energy of emission when the temperature T is 0°K, and is defined by

$$E_m=h\nu-\varphi,$$

where φ is the photoelectric work function at the absolute zero of temperature, and ν is the frequency of the incident light. For small values of the energy the distribution function may be approximated by

$$kE^n,$$

where k is a constant. The exponent n differs for each theory and so may be used to differentiate between the theories.

Thus, though the high energy side of the energy distribution curve cannot be used to differentiate between various theories it may be used, in conjunction with the relation for E_m above, to obtain the value of the work function. The behavior of the distribution curve in the neighborhood of the origin determines the exponent n, and so may be used to compare the theories with the data.

A number of attempts have been made to use a uniform magnetic field to measure the energy distribution of photoelectrons. The first of these was by Ramsauer[2] in 1914. Ramsauer

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* Submitted to the faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science.

[1] Rudberg, Phys. Rev. **48**, 811 (1935).

[2] Ramsauer, Ann. d. Physik **45**, 961 (1914); **45**, 1121 (1914).