# K Fluorescence Yield of Several Metals

CHARLES E. ROOS\*

## The Johns Hopkins University, Baltimore, Maryland, and The University of California, Riverside, California

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The K fluorescence yield  $(w_K)$  of iron, nickel, copper, and zinc has been measured by the solid angle method. By varying the solid angle subtended by a sample foil at a NaI(Tl) crystal one can distinguish between the collimated primary beam and the isotropically emitted fluorescent x-rays. The following new values were obtained: iron  $-0.308 \pm 0.015$ , nickel  $-0.366 \pm 0.011$ , copper  $-0.410 \pm 0.012$ , and zinc -0.446 $\pm 0.012$ . In addition, the values for the K fluorescence yield of zirconium, niobium, molybdenum, rhodium, palladium, silver, cadmium, and tin reported earlier, have been redetermined. With the single exception of the value for zirconium, these new values agree quite closely with the earlier values. The average change is approximately 1% or about one third of the previously estimated error. The redetermined values of  $w_K$  are as follows: Zr -0.70±0.02, Nb -0.73±0.02, Mo -0.73±0.02, Rh -0.786±0.015, Pd -0.790±0.015, Ag  $-0.821\pm0.019$ , Cd  $-0.827\pm0.015$ , Sn  $-0.846\pm0.012$ . A phosphorescence of the NaI(Tl) crystals with a decay time of  $8\pm 2$  milliseconds was found, while no sign of a reported 0.2-millisecond decay was observed.

## INTRODUCTION

HE K fluorescence yield  $(w_K)$ , or ratio of K x-rays to K-shell vacancies, is a measure of the Auger<sup>1</sup> effect and is of interest not only for detailed interpretations of x-ray spectra but also for many investigations with radioactivity. The value of  $w_K$  can be used to measure the relative transition probability for K capture and positron emission from the same energy states. This ratio permits a check on features of  $\beta$ -decay theory since it is independent of the nuclear matrix elements. The K fluorescence yield can also be used in certain cases to prove the existence of K capture and is quite useful in studies of internal conversion. It provides a method for the determination of the K/L ratios for low-energy K conversion lines and can be used to determine the K conversion coefficients. The applications to low-energy  $\beta$ -ray spectroscopy and nuclear physics have been discussed by Bergström and Radvanyi.2

More than 50 different investigators have measured the K fluorescence yield. They each examined 1 to 13separate elements and most of these values are listed in one or more of the recent summaries of Burhop,<sup>3</sup> Broyles *et al.*,<sup>4</sup> and Gray.<sup>5</sup> Unfortunately, many of these determinations are inconsistent and the different measured values of several elements differ by more than 20%. The last six years have seen the development of several precision methods. The magnetic spectrometer can measure directly the Auger electrons and has thus determined  $w_K$  for the elements of high atomic number (>46) with precisions of 1 to 8%. The proportional counter has also been extensively used to measure  $w_K$  for the noble gases. The third precision method was made possible by the development of the NaI(Tl) scintillation counter.

The solid-angle difference method, first described in an earlier paper,<sup>6</sup> measures the fluorescent radiation from a sample foil pressed in contact with an NaI(Tl) scintillation crystal. It differs in several important aspects from the older direct x-ray methods, which have been used by a number of observers<sup>7-17</sup> to measure some earlier values of the K fluorescence yields. They measured the secondary or fluorescent radiation from a thick target. The detector, usually an ionization chamber, was placed at  $90^{\circ}$  to the main beam where it intercepted approximately 0.1% of the fluorescent x-rays. The absorption coefficients for the primary and secondary beams had to be obtained from measurements on different samples or from x-ray absorption tables. Even slight contamination of the absorption samples with high-Z elements, small variations in foil thickness, or a slightly chromatic beam would result in substantial changes in the measured absorption coefficients. One major advantage of the solid-angle difference method is the possibility of using the same part of the same foil for both the absorption and fluorescence measurements. The new method also detects 20 to 30% of the total secondary radiation and thus enjoys a very high signalto-noise ratio.

### EXPERIMENTAL PROCEDURE

The use of a solid detector such as the NaI(Tl) crystal of a scintillation counter enables one to vary

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  <sup>15</sup> E. Arends, Ann. Physik 22, 281 (1935).
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<sup>\*</sup> Present address: The University of California, Riverside, California.

California. <sup>1</sup> P. Auger, Compt. rend. 180, 65 (1925). <sup>2</sup> I. Bergström, in *Beta- and Gamma-Ray Spectroscopy* edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1955), p. 624; P. Radvanyi, Ann. Physik 10, 584 (1955). <sup>3</sup> E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, Cambridge, 1952), p. 45. <sup>4</sup> Broyles, Thomas, and Haynes, Phys. Rev. 89, 715 (1953). <sup>5</sup> P. R. Gray, Phys. Rev. 101 (1306 (1956))

<sup>&</sup>lt;sup>5</sup> P. Ř. Gray, Phys. Rev. 101, 1306 (1956).



FIG. 1. Crystal mounting and sample holder. In position No. 1 the scintillation counter detects very few of the fluorescent x-rays, while in position No. 2 it subtends an effective solid angle of  $2\pi$  steradians. When the sample is moved out of the beam in position No. 3 the direct beam is measured.

the solid angle subtended by the counter from almost  $2\pi$  to effectively zero. Since the primary x-rays which eject the K electrons from the sample foil were well collimated and the fluorescent radiation was emitted isotropically, this large change in solid angle enabled one to distinguish between the primary and fluorescent radiation. From the ratio of the fluorescent to the direct primary beam (no sample) the K fluorescence yield can be obtained.<sup>6</sup>

The combination sample holder and scintillation crystal mounting used for the new measurements presented in this paper is shown in Fig. 1. This mounting enabled one to make a series of measurements without disturbing the position or settings of the scintillation counter. With the foil holder in position No. 1 only the primary x-rays which are not absorbed by the sample foil are observed. In position No. 2 both the nonabsorbed primaries and the fluorescent x-rays are observed. When the holder is in position No. 3, it is out of the path of the beam and the direct monochromatic primary x-rays are measured. The foil holder was aligned so that the x-rays struck the same region of the sample foil in both positions No. 1 and No. 2. The crystal mounting was designed to absorb less than 2% of the 6-kev x-rays, while giving high resolution. Two sheets of 0.25-mil Mylar film with an evaporated aluminum coating were stretched over the NaI(Tl) crystal, where they served both as a reflector and as a vapor barrier to protect the crystal from moisture.

### CRYSTAL PHOSPHORESCENCE AND NOISE

The tail of the pulse-height spectra of 15-kev x-rays, shown in Fig. 2, was investigated with a mechanical chopper and found to be an unreported phosphorescence of the NaI(Tl) crystal, amounting to 2.4% of the total integrated light detected by the phototube. The pulseheight spectrum of a chopped 15-kev x-ray beam was normalized to the same photopeak as the direct beam. The difference between these spectra is seen to be zero except for the phosphorescence to the left of the solid line. The scaling circuits accepted pulses from the phosphorescence during the 8 milliseconds that the chopper was open. The difference curve is, therefore, not quite as large as the phosphorescent portion of the direct spectrum. A variety of different chopping speeds were used, and from the different heights of the difference curves the decay time for this phosphorescence was found to be  $8\pm 2$  milliseconds. This result is contrary to a phosphorescence reported by Harrison<sup>18</sup> in a different set of crystals. These had a decay time of 200 microseconds, and an intensity of 8% of the total light. An electronic gating circuit showed an absence of any 200 microsecond decay in our crystals. This seems to indicate that slight differences in thallium content or some trace impurity can shift the decay time by a factor of forty times. This phosphorescence occurs in the region where one might hope to detect low-energy x-rays (1-2 kev), and it may well set the lower limit for x-ray detection by the NaI(Tl) scintillation counter. Since the decay time is long these pulses should correspond to single photons emitted by the crystal.

The noise from the photomultiplier in the absence of the scintillation crystal apparently arose from the thermal emission of electrons from the photocathode and was approximately  $\frac{1}{3}$  of the phosphorescence. While cooling would reduce this noise, it was found to increase the response time of the NaI(Tl) crystal if the latter was in close contact with the photomultiplier. This is in agreement with the results of Bonanomi and Rossel<sup>19</sup> who reported that the response time can be increased



FIG. 2. The rapid rise in counting rate for low pulse heights is found to be predominantly due to a phosphorescence which has a decay time of  $8\pm 2$  milliseconds. The difference between the normalized chopped and the direct beams shows a portion of the pulse height spectrum of the phosphorescence. The scale has been expanded to the left of the solid line.

<sup>&</sup>lt;sup>18</sup> F. B. Harrison, Nucleonics 12, 24 (1954).

<sup>&</sup>lt;sup>19</sup> J. Bonanomi and J. Rossel, Helv. Phys. Acta 24, 310 (1951).

a hundred fold from  $10^{-6}$  second at 20°C to  $10^{-4}$  at  $-50^\circ\mathrm{C}.$ 

#### EXPERIMENTAL CORRECTIONS AND ERRORS

A series of at least five sets of measurements was made in each of the three positions of the sample holder. Since each set was quite reproducible it was not necessary to monitor the x-ray beam. Some possible corrections to these experimental ratios were: scattering effects, the fluorescent radiation detected with the  $0.02\pi$  solid angle in position No. 1, the differences in absorption by the crystal mounting of the primary and secondary radiation, and the differences in the detection efficiency of the scintillation counter.

The effect of scattering was measured by repeating the above procedure using wavelengths longer than the K edge of the sample foil. It was found to be negligible or less than 0.02%. The  $0.02\pi$  solid angle, in position No. 1, was chosen to permit the counter to receive most of the x-rays scattered through small angles. This relatively large solid angle required a 2 to 4% correction since the counter also detected some fluorescent radiation. The exact correction was calculated; it depends on the angular distribution of the fluorescent radiation leaving each sample. The differential absorption of the 0.5-mil aluminized Mylar film and the 1-mil layer of oil between the Mylar and the NaI(Tl) crystal introduces a correction of 1.4 to 2%. The primary x-rays have both a shorter wavelength and a shorter average path than the fluorescent x-rays.

The most important correction to the experimental ratios [(2-1)/3] for iron, nickel, copper, and zinc was the allowance for the variation in the detection efficiency of the scintillation counter. The iron  $K\alpha$  x-ray is only 6 kev and it is quite difficult to completely resolve these x-rays from the crystal phosphorescence and photomultiplier noise. The detection efficiency varied from 75% for 6-kev x-rays to 99% for 15 kev when only those pulses greater than the peak for 4-kev x-rays were utilized.

For a 6-kev x-ray the number of photocathode electrons appears to vary between zero and ten. The extrapolation, shown in Fig. 3, was based on the assumption that the photocathode electrons follow a Poisson distribution. The shape of the distribution curves indicate that on the average 1.2 kev of incident x-ray energy is required to produce one photocathode electron. This figure is in agreement with the work of West, Meyerhof, and Hofstadter<sup>20</sup> who measured 1 to 1.5 kev/electron.

The correction for the difference in detection efficiency of the primary and secondary x-rays was approximately 10% for copper, nickel, and zinc, while it was 23% for iron. Unless the pulse-height spectra are radically different from Poisson distributions this correction is correct to 20%. The total estimated error



FIG. 3. Pulse height spectrum for 6-kev x-rays. In the low pulse height region the phosphorescence obscures the measurement of the 6-kev line. The extrapolated curve was drawn by fitting a Poisson distribution to the rest of the experimental curve.

in the experimental ratios including statistics is 4% for iron and less than 3% for copper, nickel, and zinc.

# CALCULATIONS OF K FLUORESCENCE YIELD

The relationship between the experimental ratios of the fluorescence x-rays to the primary beam, or  $(N/N_0)$ , and the K fluorescence yield  $(w_K)$  was derived in the earlier paper<sup>6</sup> and will only be outlined here. The number of K excited atoms is proportional to (r-1)/r $e^{-\mu_1 x}$  where r is the K jump ratio. A certain fraction  $(w_K)$  of the K excited atoms will emit K x-rays. The number of these K x-rays escaping from the foil will depend on their direction of travel  $(\theta)$ , the point where they were produced in the foil (x), and their absorption coefficient,  $\mu_j$ . The relationship between the fluorescence yield and the experimental ratio  $N/N_0$  is given by the expression:

$$\frac{N}{N_0} = \frac{\mu_1 w_k(r-1)}{2r} \sum_j C_j \int_0^t e^{-\mu_1 x} \int_0^{\pi/2} e^{-\mu_j(t-x) \sec\theta} \sin\theta d\theta dx,$$

where  $\mu_1$  is the absorption coefficient for the primary x-rays, and t is the thickness of the sample foil.  $C_j$  is the intensity of each line relative to the total intensity of the K series.

The above expression does not depend on the separate values of t,  $\mu_1$ , and  $\mu_j$ , but depends only on  $\mu_j t$  and  $\mu_1 t$  which are obtained directly. It is also quite insensitive to the values of  $\mu_1 t$  encountered in this experiment. Absorption measurements were made on the same region of the sample foils at the time the fluorescent measurements were obtained. The wavelengths corresponding to the principal K lines of each element were isolated from the general spectrum of tungsten by a calibrated 1.5-meter Bragg single-crystal spectrometer.

<sup>&</sup>lt;sup>20</sup> West, Meyerhof, and Hofstadter, Phys. Rev. 81, 141 (1951).

TABLE I. Summary of the more recent experimental determinations of the K fluorescence yield of the medium weight elements.

	Ζ	Solid angle diff. (This paper)	Other methods	
Α	18		$0.10 \pm 0.02^{a}$	
Cr	24		$0.262 \pm 0.002^{b}$	
Fe	26	$0.308 \pm 0.015$	$0.34 \pm 0.03^{\circ}$	
Ni	28	$0.366 \pm 0.011$	$0.40 \pm 0.03^{d}$	
Cu	29	$0.410 \pm 0.012$	$0.45 \pm 0.05^{\circ}$	$0.39 \pm 0.02^{f}$
Zn	30	$0.446 \pm 0.012$	$0.50 \pm 0.05^{g}$	
Kr	36		$0.68 \pm 0.02^{h}$	$0.62 \pm 0.03^{i}$
Zr	40	$0.70 \pm 0.02$	$0.69 \pm 0.03^{j}$	
$\mathbf{Nb}$	41	$0.73 \pm 0.02$		
Mo	42	$0.73 \pm 0.02$	$0.76 \pm 0.05^{k}$	
Tc	43		$0.70 \pm 0.03^{1}$	
Rh	45	$0.786 \pm 0.015$	$0.79 \pm 0.03^{m}$	
$\mathbf{Pd}$	46	$0.790 \pm 0.014$	$0.84 \pm 0.03^{n}$	
Ag	47	$0.821 \pm 0.015$	$0.83 \pm 0.06^{\circ}$	$0.83 \pm 0.03^{p}$
$\operatorname{Cd}$	48	$0.827 \pm 0.014$	$0.82 \pm 0.03^{m}$	$0.83 \pm 0.03^{p}$
In	49		$0.82 \pm 0.02^{f}$	$0.87 \pm 0.03^{1}$
Sn	50	$0.846 {\pm} 0.012$	$0.83 \pm 0.03^{q}$	
Xe	54		$0.85 \pm 0.04^{h}$	
Cs	55		$0.89 \pm 0.08^{r}$	
Ba	56		$0.866 \pm 0.005^{s}$	$0.90 \pm 0.05^{n}$
La	57		$0.94 \pm 0.02^{t}$	
Pr	59		$0.88 \pm 0.05^{u}$	

(Proportional counter) references 25 to 29.

b) (Direct x-ray) references 7, 9, 10, 14.
 c) (Direct x-ray) references 7, 8, 10, 11, 14, 15.
 d) (Direct x-ray) references 7, 8, 11 to 15, 17.
 c) (Direct x-ray) references 7 to 11, 13, 15, 17.

<sup>6</sup> (Direct x-ray) references 7 to 11, 13, 15, 17.
<sup>7</sup> (Prop. counter) references 29.
<sup>8</sup> (Direct x-ray) references 7, 8, 10, 11, 13 to 15, 17.
<sup>h</sup> (Prop. counter) references 25, 26, 28.
<sup>i</sup> (Calculated from the L/K capture ratio) J. P. Welker and M. L.
Perlman, Phys. Rev. 100, 74 (1955).
<sup>i</sup> (Direct x-ray) reference 17.
<sup>k</sup> (Direct x-ray) reference 17.

 (Direct x-ray) references 10, 12, 13, 15 to 17.
 <sup>1</sup> (Mag. spect.) J. Laberrique-Frolow and P. Radvanyi, Compt. rend.
 242, 901 (1956). (Direct x-ray) references 16, 17,

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 (Direct x-ray) references 16.
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 (Mag. spect.) Huber, Humbel, Schneider, and de-Shalit, Helv. Phys. Acta 25, 3 (1952). Error has been estimated from similar measurements by the interdirection term. other investigators.

 q (Direct x-ray) references 15 to 17.
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(1954) (Mag. spect.) E. Kondaiah, Phys. Rev. 83, 471 (1951). Error has been

estimated from similar measurements by other investigators.

Four values of the K jump ratios<sup>21</sup> (r) were averaged and used to calculate r-1/r. While the individual determinations have a maximum variation of 11%, this introduces a change of 1.7% in r-1/r. The values of  $C_i$ , the relative intensity of the K lines, were obtained from the data of Williams.<sup>22</sup>

The resulting values of the K fluorescence yield are given in the third column of Table I. The values of the K fluorescence yields of the elements with atomic numbers between 40 and 50 were redetermined and are also included. With the single exception of zirconium the changes in the revised values averaged less than 1.1%, or one third of the originally estimated error.<sup>6</sup>

<sup>21</sup> A. H. Compton and S. K. Allison, X-rays in Theory and Experiment (D. Van Nostrand Company, Inc., New York, 1935), p. 528.

<sup>22</sup> J. H. Williams, Phys. Rev. 44, 146 (1933).

#### DISCUSSION

The values for the solid angle difference method, presented in Table I, include the data which were used to compute the fluorescence yields given in the original paper<sup>6</sup> and also in the preliminary report on the yields of iron, copper, nickel, and zinc.<sup>23</sup> In Table I these new values are compared with a summary of the experimental determinations of the K fluorescence yields of the medium weight elements. In view of the fact that there have been more than 100 separate measurements of  $w_K$  for these elements, the determinations have been classified by method and, where possible, averaged according to the error assigned to them by the original authors. Many of the individual values have been listed in some of the recently published summaries,<sup>3-5</sup> and the original references are, of course, given for all values used in each average. Table I includes the direct x-ray method for its historical interest, but has otherwise been restricted to the recent precision methods.

More than half of the measurements of fluorescence yield were obtained by some modification of the direct x-ray method<sup>7-17</sup> which usually measured the x-ray intensity with an ionization chamber. Unfortunately, most of these authors did not publish error limits. The listed errors are the standard deviation of the mean value of  $w_K$  for all elements where 6 or more different values have been published. For elements where fewer determinations were made, the error of each individual



FIG. 4. The recent determinations of the K fluorescence yield. The solid curve is the semiempirical curve of Burhop.

<sup>23</sup> C. E. Roos, Phys. Rev. 100, 1267(A) (1955).

investigator's measurements was estimated from the average of his deviations from the means of neighboring elements with 6 or more determinations. With this estimate of the error of each single measurement, the standard deviation of the weighted average could be obtained. Three measurements, which have been subject to specific criticism by other authors, were not included. The modifications and corrections to a few values given by Broyles, Thomas, and Haynes<sup>4</sup> were included. It should be noted that these estimated errors measure only the precision or consistency of the direct x-ray measurements.

The recently developed proportional counter method has been used by several authors.<sup>24-29</sup> It is particularly useful for the noble gases, but has also been used for copper and indium.<sup>29</sup> All recent proportional counter determinations were given equal weight in computing the averages, since most authors have assigned approximately the same error limits. The values listed in Table I, while obtained by five different methods, easily agree within the indicated error.

The calculated theoretical and the most direct experimental determinations of the K fluorescence yield. obtained within the last five years, are shown in Fig. 4. The solid curve is the semiempirical relationship of Burhop,<sup>30</sup>  $[w_K/(1-w_K)]^{\frac{1}{2}} = A + BZ + CZ^{\frac{3}{2}}$ . The constants A, B, and C have been evaluated by Burhop using least-squares fits to all of the then available experimental data. The first term represents the

- <sup>3</sup> Harrison, Crawford, and Hopkins, Phys. Rev. 100, 841 (1955).
   <sup>30</sup> E. H. S. Burhop, J. phys. radium 16, 624 (1955).

screening effect, the second the  $Z^4$  dependence of dipole transitions, while the last is due to the effects of relativity. Laberrique-Frolow and Radvanyi<sup>31</sup> have just recently recalculated these constants using a different weighting system and only the data of the last 10 years, including several new experimental values published since Burhop's original evaluation. While this revised curve gives an even closer fit to the solid angle values, it is not yet available in the general literature.

Two groups have recently calculated some theoretical values for  $w_K$ . The K fluorescence yields for argon and krypton, calculated by Rubenstein and Snyder,<sup>32</sup> seem a little high ( $\sim 3\%$ ) in comparison with most of the newer experimental determinations, but they are in close agreement with Heintze's values.28 The measured value for the K fluorescence yield of silver (0.821), obtained by the solid angle method, lies between the theoretical values of 0.85 calculated by Rubenstein and Snyder and 0.81 obtained from the work of Mokhov and Urin.33

### ACKNOWLEDGMENTS

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<sup>&</sup>lt;sup>24</sup> G. M. Insch, Phil. Mag. 41, 857 (1950).
<sup>25</sup> D. West and P. Rothwell, Phil. Mag. 41, 873 (1950).
<sup>26</sup> G. C. Hanna (A) and J. H. Kahn (Kr and Xe), cited by D. West, Progress in Nuclear Physics (Academic Press, Inc., New York, 1953), Vol. III, p. 43.
 <sup>27</sup> Bertolini, Bisi, and Zappa, Nuovo cimento 10, 1424 (1953).
 <sup>28</sup> J. Heintz, Z. Physik 143, 153 (1955).

<sup>&</sup>lt;sup>31</sup> J. Laberrique-Frolow and P. Radvanyi (private communication) [J. phys. radium (to be published)]. <sup>32</sup> R. A. Rubenstein and J. N. Snyder, Phys. Rev. **97**, 1653

<sup>(1955).</sup> <sup>33</sup> V. N. Mokhov and M. G. Urin, Zhur. Eksptl. i Teort. Fiz.

<sup>30, 209 (1955) [</sup>English translation: Soviet Physics JETP 3, 133 (1956)].