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K-Fluorescent-X-Ray Relative-Intensity Measurements*

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Measured values of the relative intensities of several K-fluorescent x rays are reported for 28 elements ranging from calcium through plutonium. Solid-state Si(Li) and Ge(Li) spectrometers and a Bragg-diffraction spectrometer were used in making the measurements. Fluorescence was excited in thin samples by higher-energy x rays. Corrections were made to the measured relative intensities for sample absorption, air absorption, and spectrometer efficiency. The accuracy of most of the measurements is ± 2 to 5%. The results are compared with those of other experimenters and with the Scofield calculations.

INTRODUCTION

Several recent experimental determinations of relative intensities of K emission lines have been reported.[1-6] Most of these papers describe measurements made for a relatively small number of characteristic x rays or for relatively few elements. The purpose of the present work is to provide experimental measurements of the intensities of several K emission lines relative to the $K\alpha_1$ intensity for a large number of elements from $Z = 20$ through $Z = 94$. Thin samples were used as fluorescers so that corrections for x-ray absorption would be minimized. Three spectrometers were used in these measurements. A Bragg-diffraction spectrometer with high-resolution Soller slits was used to measure $K\alpha_2$-to-$K\alpha_1$ ratios for x-ray energies less than 50 keV; a Si(Li) spectrometer was used to measure $K\beta$-to-$K\alpha$ ratios for x-ray energies less than 20 keV; and a Ge(Li) spectrometer was used to make all of the higher-energy measurements. Peak areas, rather than peak heights, were used in analyzing the data. Corrections for sample absorption, air absorption, and spectrometer efficiency were applied to the measured relative intensities.

APPARATUS

The high resolution required to separate the $K\alpha_1$ and $K\alpha_2$ lines for the lighter elements was obtained with a GE XRD-6 spectrometer utilizing a LiF crystal. The geometry used with this device is shown in Fig. 1. The direct beam from the 75 kVCP, 35-mA tungsten-target x-ray tube was incident on the sample. Fluorescent x rays produced in the sample exit at 90° to the direct beam through a Soller slit. After being diffracted by the LiF crystal, these x rays pass through a second Soller slit, and are detected by a NaI (Tl) counter. The scintillation crystal was covered with 1μ of Al and 0.001 in. of Be. Amplified pulses from this counter passed through a single channel analyzer to a scaler whose count was recorded on a teletypewriter. The full width at half-height of monoenergetic peaks observed with this spectrometer after allowing for the inherent width of the x-ray lines was 0.2° in 2θ. The first four diffraction orders of the LiF (200) set of planes were used in making the measurements reported here.

A Si(Li) spectrometer was used to measure $K\beta$-to-$K\alpha$ ratios over the energy region of 3.6 to 20 keV and to measure $K\alpha_2/K\alpha_1$ and $K\beta_2/K\beta_{1,3}$ at higher energies. ($K\beta_2$ is used to denote the sum of the intensities of x rays resulting from transitions between the K and N shells and between the K and O shells. $K\beta_{1,3}$ denotes the sum of the intensities of x rays resulting from transitions between the K and M shells.) The crystal dimensions were 6.2 mm in diam by 5 mm thick. The resolution of this spectrometer was 230 eV (FWHM) at 6 keV. The experimental geometry used with the Si(Li) spectrometer is shown in Fig. 2. For fluorescent x rays below 10 keV, the samples were illuminated by the direct beam from a 14 kVCP, 100-mA zirconium-target x-ray tube. The entire experimental geometry was housed in a vacuum chamber in order to eliminate problems associated with air attenuation. For higher-energy fluorescent x rays, the samples were illuminated by the direct beam from a 75 kVCP, 35-mA tungsten-target x-ray tube. Prefilters were used between the x-ray tubes and the samples to remove low-energy radiations characteristic of the tube target. The samples were placed at a 45° angle with respect to the direct beam, and fluorescent x rays emitted at 90° to the direct beam were detected by the collimated Si(Li) detector. The amplified output pulses from this detector were fed into a 1024 channel analyzer. The pulse-height spectrum was printed and was recorded on a punched paper tape.

The total spectrometer efficiency (photopeak plus escape peak) shown in Fig. 3 was measured at 10 energies between 1.5 and 60 keV. The lower-en-

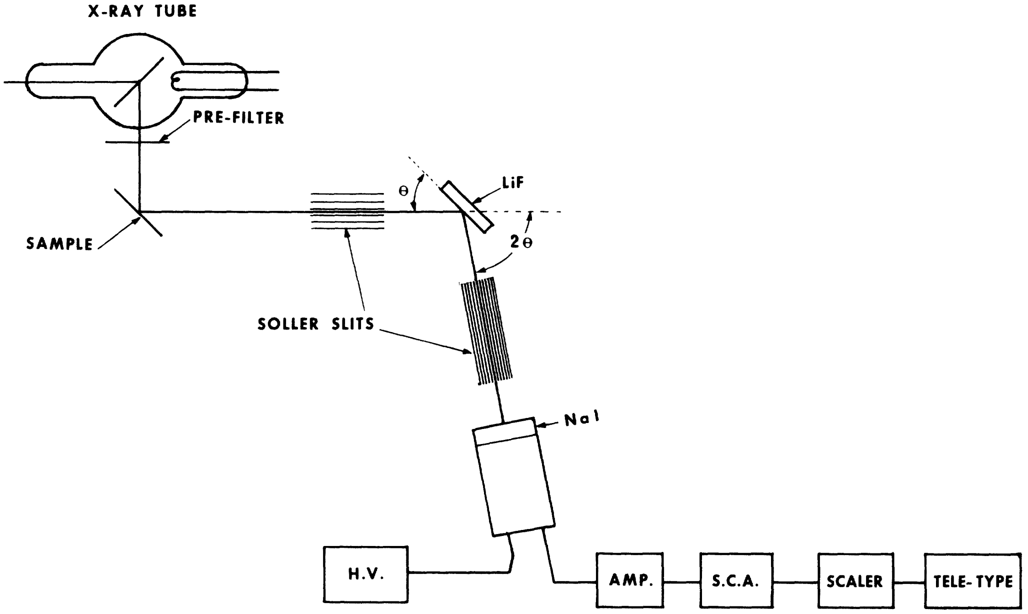

FIG. 1. Experimental geometry for Bragg-diffraction spectrometer.

ergy efficiencies were measured by comparing the Si(Li) detector with a xenon ionization chamber,[7] and higher-energy efficiencies were measured by using radioisotope sources and a NaI(Tl) counter. The lower-energy efficiencies follow the transmissivity of the 0.0012-in. Be window which covers the Si(Li) detection crystal. The absorption of the x rays by the conducting and dead layers of the crystal were found to be negligible.

A Ge(Li) spectrometer was used in the higher-energy (> 20 keV) measurements. The crystal, which was covered with a 0.005-in. Be foil, had a sensitive depth of 5 mm and a diameter of 10 mm. Its resolution was 570 eV(FWHM) at 14 keV. The experimental geometry and electronics used with this detector were the same as shown in Fig. 2. Figure 3 contains a plot of the Ge(Li) efficiency which was measured with radioisotope sources and NaI(Tl) counters. The measured efficiency follows the transmissivity of the Ge crystal. Two x-ray machines were used to excite sample fluorescence. Samples with atomic number less than 70 were placed in the direct beam of a 75 kVCP, 35-mA x-ray machine, and heavier element samples were illuminated by the beam from a 300 kVCP, 15-mA machine. Air absorption and detector window and dead layer absorption were negligible at the x-ray energies for which the Ge(Li) spectrometer was used.

SAMPLES

Table I is a list of the sample elements, their chemical form, and their thickness. Most of the samples were deposited on 0.0005-in. Be (2.5 mg/cm^2), the effects of which were negligible on the results of these experiments. A few of the sam-

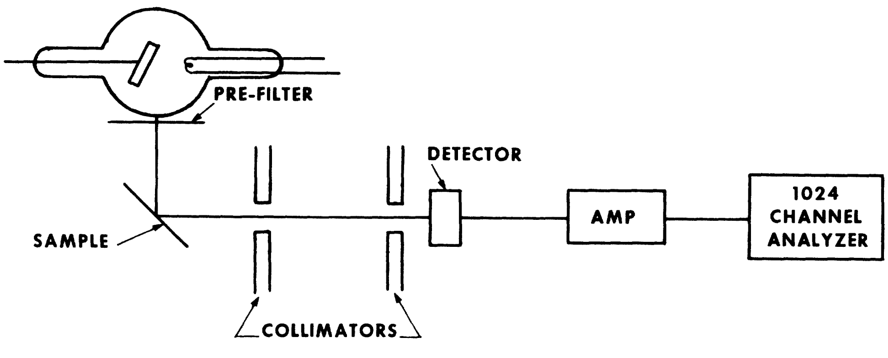

FIG. 2. Experimental geometry for solid-state spectrometer.

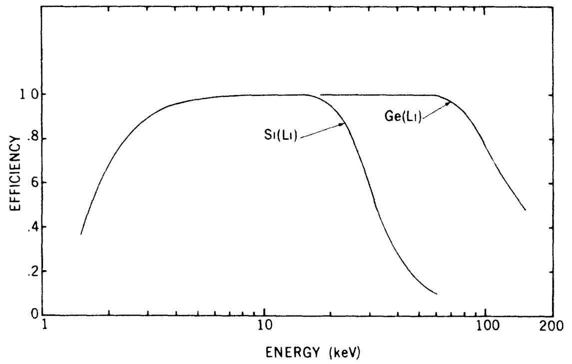

FIG. 3. Solid-state spectrometer efficiencies vs x-ray energy.

ples (Mo and Pu) were in the form of foils. The Pu foil was covered with 0.0004-in. Ni foil for health protection. The criterion for determining the sample thickness was that it should transmit 90% of its *Kα* radiation. In most cases the actual thickness was fairly close to this nominal value. Sample thicknesses were determined by measuring the weight and area of the sample material deposited on the Be foil. Uniformity in thickness was assumed. All samples were made of materials whose purity was 99% or higher.

TABLE I. Samples.

Element	Material	Material thickness (mg/cm^2)
Ca	CaF_2	0.90
Ti	Ti	0.50
Cr	Cr	1.04
Fe	Fe	1.56
Cu	Cu	1.43
Ge	Ge	1.47
Se	Se	1.9
Rb	RbF	3.9
Zr	Zr	2.7
Mo	Mo	3.8
Rh	Rh	3.6
Ag	Ag	3.9
Sn	Sn	3.4
I	NaI	9.0
Ba	BaF_2	9.3
Ce	CeO_2	0.5
Sm	Sm	8.8
Gd	Gd	9.0
Ho	Ho	9.3
Yb	Yb	8.9
Ta	Ta	9.2
Ir	Ir	28
Au	Au	18.5
Pb	Pb	20
Bi	Bi	21
Th	Th	149
U	U	20
Pu	Pu	55

EXPERIMENTAL PROCEDURE

The intensities of x-ray emission lines which lay closest together in energy were measured using the Bragg spectrometer described above. The $K\alpha_2/K\alpha_1$ intensity ratios were measured with this system for the elements Fe through Gd listed in Table I as were the $K\beta_2/K\beta_{1,3}$ ratios for Rb through Gd. Data were taken as follows. The sample under study was loaded and the x-ray machine was turned on and allowed to warm up for 1 h. The high voltage was set well above the *K* edge of the element under study, and the tube current adjusted to give a reasonable count rate. The detector electronics were adjusted so that the single channel analyzer passed the entire photopeak associated with the *K* x rays from the sample. A rapid scan was then made over the angular region of the *Kα* and *Kβ* peaks to determine which diffraction order would yield the best compromise between resolution and count rate. In most experiments different diffraction orders were used for the *Kα* and the *Kβ* regions. From the strip-chart record of this scan, the angular region to be studied, the counting times, and the angular intervals between data points were determined. The angular region generally included 2 or 3° in 2θ on each side of the *Kα* and *Kβ* peaks so that the background count rate under the peaks could be interpolated. Angular increments of 0.02° were used between data points in most of the runs so that approximately 20 count rates were measured over each peak. Sufficiently long counting times were used so that errors due to counting statistics were negligible in the measured intensities of the $K\alpha_1$, $K\alpha_2$, and $K\beta_{1,3}$ peaks. Counting times varied from 40 to 200 sec. but were constant for a given run. Peak count rates were measured before and after each step scan to verify the stability of the x-ray

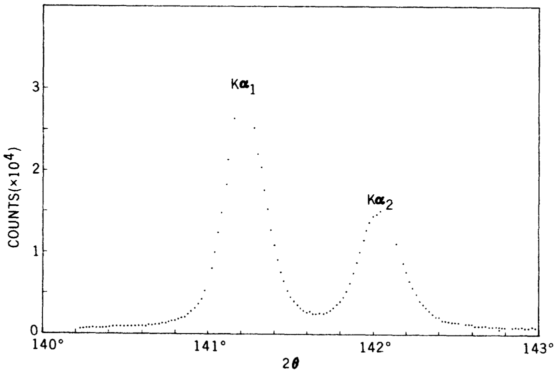

FIG. 4. Copper *Kα* x-ray spectrum as measured with the Bragg spectrometer (germanium diffraction crystal).

beam intensity. All counts and counting times were typed out by the teletypewriter.

The same experimental procedure was used with the solid-state spectrometers. Using the geometry shown in Fig. 2, the x-ray machine was turned on and adjusted so that the total count rate was approximately 1000 counts/sec. Dead time in the multichannel analyzer was negligible. The amplifier gain was adjusted so that the photopeaks and escape peaks associated with the various *K* emission lines from the sample were distributed about the center of the pulse height spectrum. The system was operated for a sufficiently long counting time (400–2000 sec) so that errors due to counting statistics in the more intense peaks were negligible.

DATA ANALYSIS

All data were analyzed by adding the counts taken at equal intervals in a given peak, i.e., by using the peak area rather than the peak height. Figure 4 is a plot of the copper $K\alpha$ spectrum from the Bragg spectrometer. The two peaks are fairly well resolved, but there are contributions under each peak from the other. Background under the peaks was assumed to be a linear interpolation of the count rates at the extreme right and left of the portion of the spectrum shown in the figure. After subtracting the background from all counts, the contribution to each measured count rate from the other peak was estimated by assuming that each peak had the same shape and by assuming that the ratio of the line widths were those measured.[8]

The relative area of each peak was determined by adding the counts between those two points where the count rate was a predetermined fraction of the peak count rate. The ratios obtained with the diffraction spectrometer were corrected for the Lorentz polarization factor and for the transmissivity of the NaI(Tl) detector window. The scintillator was opaque to the x rays for which it was used. The diffraction efficiency for a perfectly mosaic crystal is proportional to the cube of the wavelength of the radiation.[8] However, for the geometry used here, it is also inversely proportional to the absorption coefficient of the crystal which is very nearly proportional to the cube of the wavelength.[9] Hence, for the cases under consideration, the dependence of the diffraction efficiency on the wavelength very nearly vanishes and was neglected for the small wavelength separation of the

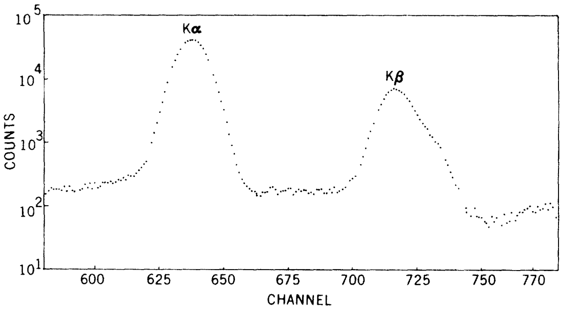

FIG. 5. Zirconium *K* x-ray spectrum as measured with Si(Li) spectrometer.

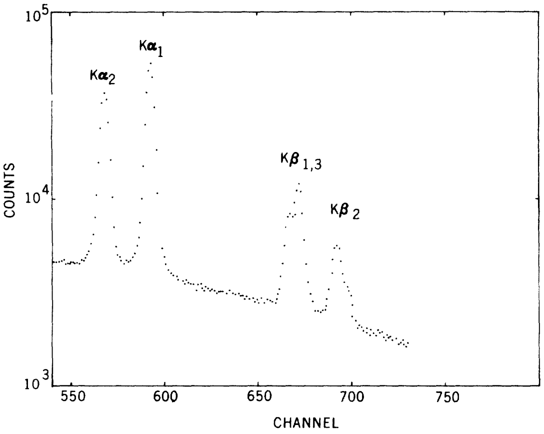

FIG. 6. Plutonium *K* x-ray spectrum as measured with Ge(Li) spectrometer.

TABLE II. Measured *K* x-ray relative intensities.

Element	Z	α_1	α_2	$\beta_{1,3}$	β_2
Ca	20	100		12.8 ± 0.4	
Ti	22	100		13.2 ± 0.4	
Cr	24	100		13.5 ± 0.4	
Fe	26	100	50.7 ± 1.0	20.5 ± 0.6	
Cu	29	100	51.1 ± 1.0	20.9 ± 0.7	
Ge	32	100	50.6 ± 1.0	22.7 ± 0.7	
Se	34	100	52.3 ± 1.1	23.9 ± 0.7	
Rb	37	100	51.0 ± 1.0	23.9 ± 0.7	2.5 ± 0.1
Zr	40	100	52.3 ± 1.1	24.9 ± 0.7	3.7 ± 0.2
Mo	42	100	52.8 ± 1.1	26.5 ± 0.8	4.3 ± 0.2
Rh	45	100	51.9 ± 1.1	27.6 ± 0.8	4.6 ± 0.2
Ag	47	100	52.4 ± 1.1	28.4 ± 0.8	4.9 ± 0.3
Sn	50	100	53.1 ± 1.1	29.8 ± 0.9	5.5 ± 0.3
I	53	100	54.1 ± 1.1	30.1 ± 0.9	6.0 ± 0.3
Ba	56	100	53.3 ± 1.1	30.4 ± 0.9	7.1 ± 0.4
Ce	58	100	53.6 ± 1.1	30.3 ± 0.9	8.0 ± 0.4
Sm	62	100	56.0 ± 1.1	32.1 ± 0.9	7.5 ± 0.4
Gd	64	100	55.0 ± 1.1	31.0 ± 0.9	8.7 ± 0.4
Ho	67	100	56.4 ± 1.1	32.0 ± 0.9	8.8 ± 0.5
Yb	70	100	56.9 ± 1.1	32.7 ± 1.0	8.9 ± 0.5
Ta	73	100	57.5 ± 1.1	32.7 ± 1.0	9.0 ± 0.5
Ir	77	100	57.8 ± 1.1	33.6 ± 1.1	9.6 ± 0.5
Au	79	100	58.4 ± 1.2	33.3 ± 1.1	9.8 ± 0.5
Pb	82	100	58.9 ± 1.2	33.3 ± 1.1	9.8 ± 0.5
Bi	83	100	59.6 ± 1.2	33.7 ± 1.1	10.1 ± 0.5
Th	90	100	61.7 ± 1.2	34.7 ± 1.1	11.5 ± 0.6
U	92	100	63.3 ± 1.2	33.8 ± 1.1	11.3 ± 0.6
Pu	94	100	64.1 ± 1.3	34.1 ± 1.1	12.0 ± 0.6

$K\alpha$ doublet.

The validity of the assumed diffraction efficiency was checked experimentally by comparing values of the $K\beta/K\alpha$ ratios for Ti and Cr measured using the diffraction spectrometer with those obtained from the Si(Li) spectrometer. The agreement was good. The Lorentz polarization correction was less than 2% for all of the $K\alpha$ and $K\beta$ ratios measured with the Bragg spectrometer. Corrections were applied for absorption of the x rays by the sample and by the air, using published attenuation coefficients.[10,11]

Figure 5 is a plot of the K x-ray spectrum of zirconium taken with the Si(Li) spectrometer. The resolution of this instrument is not sufficient to separate the $K\alpha_1$ and the $K\alpha_2$ lines or to resolve the $K\beta$ lines of this element. The $K\beta/K\alpha$ ratio was obtained by subtracting the background and adding the counts in the silicon escape peak to those in the photopeak. Corrections were applied to these intensities for the detector efficiency (Fig. 3) and for the effects of the absorption of x rays by the sample and by the air. From this $K\beta/K\alpha$ ratio and from the $K\alpha_2/K\alpha_1$ and the $K\beta_2/K\beta_{1,3}$ ratios measured with the diffraction spectrometer, the intensities of the three lines relative to the $K\alpha_1$ intensity were calculated. For peaks which were not well resolved, the contribution of one peak to another was removed in the same manner as that described above for the Bragg spectrometer. Figure 6 is a plot of the plutonium K emission spectrum as taken with the Ge(Li) spectrometer. All four of the peaks are well resolved. In this energy region germanium escape peaks were not detectable, and the background under a given peak was obtained from an interpolation of the scattered continuum. These higher-Z data were corrected for detector efficiency (Fig. 3) and sample absorption. Air absorption was negligible.

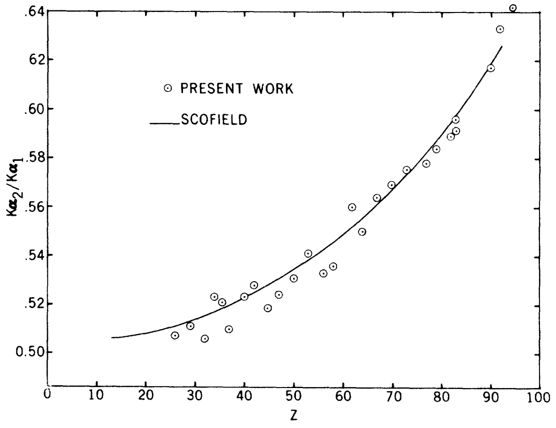

FIG. 7. $K\alpha_2/K\alpha_1$ intensity ratio vs atomic number.

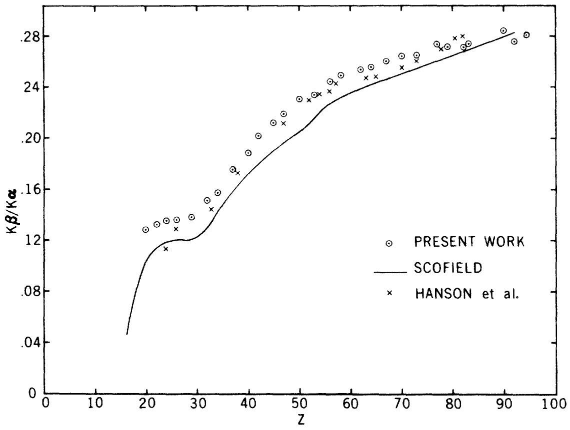

FIG. 8. $K\beta/K\alpha$ intensity ratio vs atomic number.

RESULTS

The results of the present measurements are listed in Table II. Figure 7 is a plot of the $K\alpha_2/K\alpha_1$ ratio as a function of atomic number. The present results agree with the calculations of Scofield.[12] They are also in agreement with the measurements of Nelson and Saunders[2] for $Z > 50$ and with the values reported by Salem and Wimmer.[4] Figure 8 is a plot of the measured $K\beta/K\alpha$ ratio as a function of atomic number. The disagreement between these measurements and the Scofield calculations is considerably outside experimental error. The present measurements, however, are in fairly good agree-

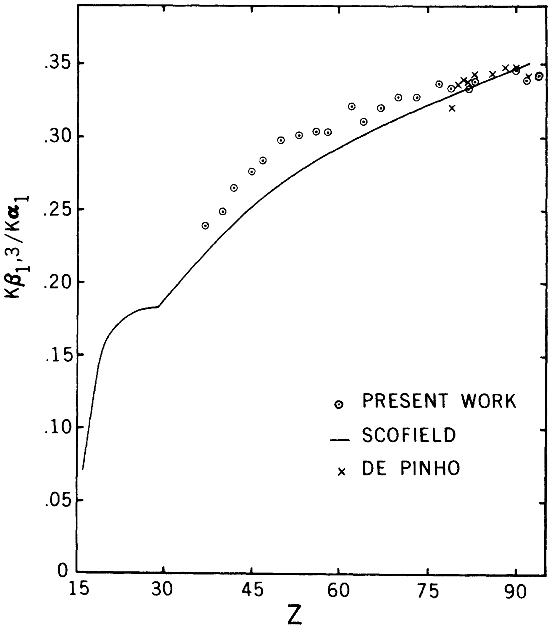

FIG. 9. $K\beta_{1,3}/K\alpha_1$ intensity ratio vs atomic number.

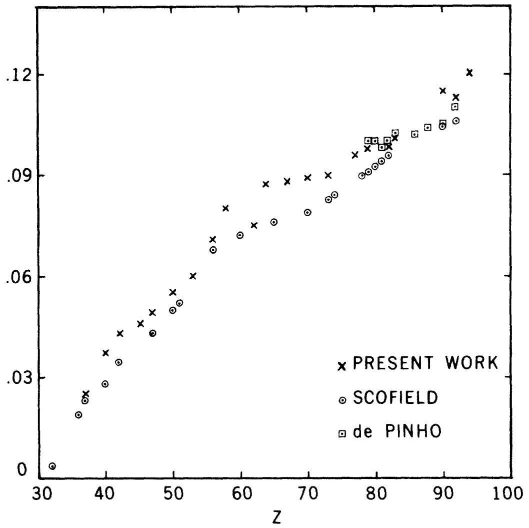

FIG. 10. $K\beta_2/K\alpha_1$ intensity ratio vs atomic number.

ment with the work of Hansen, Freund, and Fink. Figures 9 and 10 are plots of the $K\beta_{1,3}/K\alpha_1$ ratios and the $K\beta_2/K\alpha_1$ ratios, respectively, as a function of atomic number. Also plotted are the calculations of Scofield and the heavy element measurements of de Pinho.[5]

ERRORS

Possible sources of error include (a) analysis of unresolved peaks, (b) background determinations, (c) spectrometer efficiency, (d) sample and air absorption, and (e) counting statistics. Of these, the first two are the most important. These errors and estimates of their magnitude will be discussed below.

a. Analysis of unresolved peaks. The same technique was used in analyzing unresolved peaks in the output of all three spectrometers. The criterion was to construct two peaks with the same shape whose sum was the unresolved profile shown in the spectrum. All data contained within the same fraction (~ 95%) of each peak were added to give the relative intensity of that peak. For iron and copper the $K\alpha_1$ and $K\alpha_2$ peaks were seen to have different widths.[8] The copper spectrum shown in Fig. 4 is typical. Few of the spectra had worse resolution than that shown in this figure.

b. Background determinations. For the data from all three spectrometers, the background count rate under the peaks was interpolated from the count rates measured away from the peaks. For most of the measurements the background count rate was less than 10% of the peak count rate. The combined error introduced into the measured relative intensities due to background determination and the analysis of unresolved peaks is estimated to be ± 2% for the $K\alpha_2/K\alpha_1$ ratios, ± 3% for the $K\beta_{1,3}/K\alpha_1$ ratios, and ± 5% for the $K\beta_2/K\alpha_1$ ratios.

c. Spectrometer efficiency. Since the corrections for spectrometer efficiency were very small (1–2%) for the Bragg spectrometer the error in the measured ratios due to the application of this correction is negligible (< 0.5%). The ratios obtained in the higher-energy (low-efficiency) regions of both solid-state spectrometers could contain errors of as much as ± 2%.

d. Sample and air absorption. Corrections to the measured ratios for absorption of x rays by the sample and by air were in nearly all cases less than 5%. Errors due to these corrections are believed to be less than ± 1% for all reported ratios.

e. Counting statistics. Counting statistics introduced negligible error into all of the measurements except for some of the $K\beta_2/K\alpha_1$ ratios.

The total combined error was estimated for each measured ratio and is listed with that ratio in Table II.

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