

The Natural Widths of the K -Series of $W(74)$

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(Received June 28, 1934)

By means of a two-crystal x-ray spectrometer of high resolving power at short wave-length, the full widths at half maximum of the K -series of $W(74)$ have been measured. The observed widths W_O in the $(1,+1)$ position of the crystals have been corrected to true widths W_T by use of the formula $W_T = W_O - W_R$ where W_R is the width of the rocking curve of the crystals in the $(1,-1)$ position.

It is shown that, in the short wave-length region under consideration the $(1,-1)$ rocking curves obey the Hoyt equation. By using Weisskopf's equation for the shape of a spectral line, the above correction formula results. The following (corrected) full widths at half maximum (in volts) are obtained: $K\alpha_2$, 43.3; α_1 , 43.0; β_3 , 50.0; β_1 , 48.6; γ_2 , 37.0; γ_1 , 37.0; δ_2 , 34.0; δ_1 , 34.

I. INTRODUCTION

SEVERAL determinations of the widths of the lines in the K -series of $W(74)$ have been previously reported. The authors¹ made an estimate of the true width of $W K\alpha_1$ by extrapolation to higher orders of the apparent true width obtained by means of a two-crystal spectrometer with the crystals in the $(2,+2)$, $(3,+3)$ and $(4,+4)$ positions, respectively, using, to correct for the effect of the crystals, the Schwarzschild formula²

$$W_T = (W_O^2 - W_R^2)^{\frac{1}{2}} \quad (1)$$

where $W_T \equiv$ true width of the line; $W_O \equiv$ observed width; and $W_R \equiv$ width of rocking curve in parallel positions. This formula is now known to be incorrect. Barnes and Palmer³ arrived at about the same value for *each* of the positions $(1,+1)$, $(2,+2)$, $(3,+3)$ using a correction formula, derived from the Hoyt equation⁴ for the shape of a spectral line or a "rocking curve," viz:

$$W_T = W_O - W_R. \quad (2)$$

Williams⁵ has given the *uncorrected* widths of the K -series of $W(74)$, exclusive of $K\delta$ and the authors⁶ have announced preliminary data on the natural widths of these lines. These previously reported results for $K\alpha_1$ are summarized in Table I.

* The senior author acknowledges with thanks assistance from the Heckscher Research Council of Cornell University.

¹ F. K. Richtmyer and S. W. Barnes, Phys. Rev. **37**, 1695 (1931).

² Schwarzschild, Phys. Rev. **32**, 162 (1928); Ehrenberg and Mark, Zeits. f. Physik **42**, 807 (1927).

³ S. W. Barnes and L. D. Palmer, Phys. Rev. **43**, 1050 (1933).

⁴ Archer Hoyt, Phys. Rev. **40**, 477 (1932).

⁵ John H. Williams, Phys. Rev. **40**, 791 (1932).

⁶ F. K. Richtmyer and S. W. Barnes, Phys. Rev. **43**, 1049 (1933).

TABLE I. Width* of the $K\alpha_1$ line of $W(74)$.

Observers	Correction for crystals	W_R for crystals used	Width of $K\alpha_1$
Williams ⁵	None	9''-10''	$W_O = 0.19 \times X.U.$
Richtmyer ¹ and Barnes	$W_T = (W_O^2 - W_R^2)^{\frac{1}{2}}$ extrapolated to higher orders	9.6''	$W_T = 0.154$
Richtmyer ⁶ , ³ Barnes, Palmer	$W_T = W_O - W_R$	9.6''	$W_T = 0.15$

* $W \equiv$ full width at half maximum; $w \equiv$ half width at half maximum.

II. APPARATUS

A 60-cycle, 200 kv transformer, supplied with power from a 220-volt, 12 kva generator direct connected to a constant-speed, 60 kva synchronous motor, furnishes the high voltage which is rectified by kenotrons and smoothed out by condensers so that the ripple does not exceed a few percent. The voltage across the x-ray tube is read by an electrostatic voltmeter; and the tube current is measured by a galvanometer arranged to act as a null instrument. Tube voltage and tube current are maintained constant, by manual control, to about 0.1 percent.

The x-ray tube is a commercial-type, tungsten tube, fitted with a linear filament and kept on the pumps. The anode is cooled by a water-oil-water-cooling system.

The two-crystal spectrometer, direct reading as to wave-length, has been briefly described by the authors⁷ and, more fully, in a paper now in press.⁸

The ionization chamber is 31 inches long and 6 inches in diameter; and, following the suggestion

⁷ F. K. Richtmyer and S. W. Barnes, Phys. Rev. **35**, 1428 (1931).

⁸ Barnes and Richtmyer, Rev. Sci. Inst. **5**, October (1934).

of A. H. Compton,⁹ contains a "squirrel-cage" type of grid to reduce the disturbing effect of alpha-particles. The chamber is filled with methyl bromide at a pressure slightly less than one atmosphere. Ionization currents are measured by a two-tube bridge circuit¹⁰ employing a pair of FP-54 tubes.

The slits limiting the vertical divergence of the x-ray beam are 1 cm high and 120 cm apart. The maximum possible angle of divergence ϕ is thus 0.016 rad. Actually ϕ is considerably less than this since the focal spot is only 0.5 cm high and is 150 cm from the second slit.

The calcite crystals, our pair 3A+3B, have been ground and etched and when prepared gave a (1, -1) rocking curve width¹¹ of 2.8 seconds of arc (full width) at $\lambda=0.208\text{A}$. No (1, -1) rocking curves have been taken recently but, since there has been no measurable increase in the observed widths of lines in the (1, +1) position of these crystals, it is assumed that their characteristics have remained constant.

III. CORRECTING THE OBSERVED WIDTHS OF LINES FOR THE EFFECT OF THE CRYSTALS

On the assumption that the distribution of energy in an x-ray line as well as the so-called reflection curve of a pair of crystals in the (1, +1) position for strictly monochromatic, unidirectional radiation both follow the Gaussian error curve, Ehrenberg and Mark² derived Eq. (1) for the true width W_T of a spectral line. It is now known that this equation is not in agreement with experiment. For example, if Eq. (1) be correct, it should give identical values of W_T for any given line in the several orders. Allison and Williams¹² found that W_T for $K\alpha_1$ of Mo(42), as computed from Eq. (1) was some 13 percent less for the (2, +2) position than for the (1, +1) position of the crystals. Column 6 of Table II of the present paper shows a similar discrepancy of 13 percent for $W K\alpha_1$, as measured by crystals 3A+3B in the two orders. Furthermore, as was mentioned by Allison,¹³ rocking curves in the parallel as well

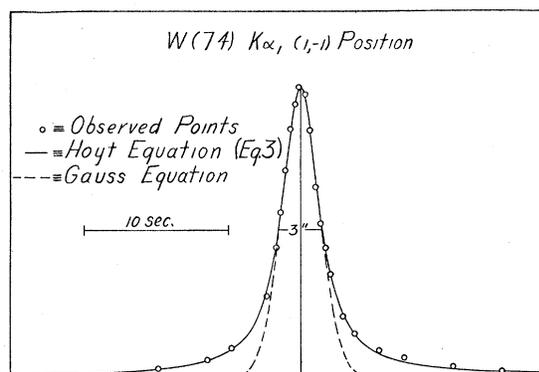


FIG. 1a. Rocking curve in the (1, -1) position for crystals 3A+3B at $\lambda=0.208\text{A}$, showing that the observed data agree with the Hoyt equation.

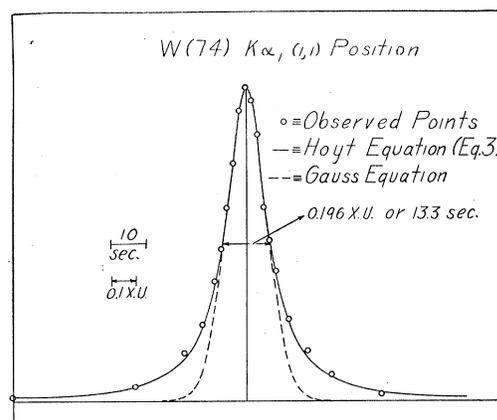


FIG. 1b. The $K\alpha_1$ line of W(74) as obtained by crystals 3A+3B, showing that the observed shape of the line agrees with the Hoyt equation.

as in the anti-parallel positions do not, in general, follow the Gaussian error curve upon which Eq. (1) is based. This is shown also by Figs. 1(a) and (b), in which the circles represent the observations on $W K\alpha_1$ in the (1, +1) and in the (1, -1) positions, respectively, and the dotted line represents the Gauss curve. The full line, which, in each case, is seen to agree well with the experimental data, is the plot of the Hoyt equation⁴

$$y = a/[1 + (x/b)^2], \quad (3)$$

where a is the maximum ordinate and b is the half width at half maximum; and $x=0$ when $y=a$.

Now, Weisskopf¹⁴ has shown that the true

⁹ A. H. Compton, Phys. Rev. **7**, 646 (1916).

¹⁰ L. A. DuBridge, Phys. Rev. **37**, 392 (1931).

¹¹ F. K. Richtmyer, S. W. Barnes and K. V. Manning, Phys. Rev. **44**, 311 (1933).

¹² Allison and Williams, Phys. Rev. **35**, 1477 (1930), Table V.

¹³ Allison, Phys. Rev. **38**, 203 (1931).

¹⁴ Weisskopf, Phys. Zeits. **34**, 1 (1933).

shape of a line is given by the equation

$$J(\nu) = b/\pi[(\nu_0 - \nu)^2 + b^2], \quad (4)$$

where $J(\nu)$ represents the probability of the emission of energy of frequency ν ; ν_0 is the most probable frequency; and b is the half width at half maximum of the curve $J(\nu)$ vs. ν . By rearrangement it is easily shown that Eq. (4) is identical in form with Eq. (3),^{14a} which, for the range of wave-lengths herein considered, replaces the Gauss error curve in the assumptions of Ehrenberg and Mark. We may then derive Eq. (2) as follows:

Let $\Phi_{1,1}(\xi_B)$ represent the "rocking curve" of the pair of crystals A and B in the (1,+1) position for unidirectional, monochromatic radiation of wave-length λ incident upon crystal A ; where ξ_B is the angle by which the setting of crystal B differs from the Bragg angle θ appropriate to λ , effects of refraction being neglected. Let $\Psi(\xi_B)$ represent the actual distribution of energy through the line. And let $f(\omega)$ represent the distribution of energy through the line as observed by use of crystals A and B . Then

$$f(\omega) = \int_{-\infty}^{+\infty} \Psi(\xi_B) \Phi_{1,1}(\omega - \xi_B) d\xi_B. \quad (5)$$

We cannot observe $\Phi_{1,1}$ directly but we may

^{14a} In Eq. (3) b and x , and likewise b in Eq. (4), are measured in frequency units. If b and x are to be measured in wave-length units—call them b_λ and x_λ , respectively—Eq. (3) becomes

$$y = a/[1 + (\lambda x_\lambda / \lambda_0 b_\lambda)^2], \quad (3a)$$

where λ_0 is the wave-length for maximum energy in the line, and λ is the wave-length corresponding to x_λ . If the line is narrow, the ratio λ/λ_0 may be set equal to unity for all values of λ for which y has a measurable value. That is, an equation of the type (3) should give the shape of a narrow line whether the plot be on a wave-length, or a frequency, scale. If, however, the line is wide and is symmetrical on a frequency plot, the asymmetry on a wave-length plot may become appreciable.

As was shown by Hoyt,⁴ the area under the curve of Eq. (3), i.e., the intensity I of the line, is

$$I = \pi a b_\nu, \quad (a)$$

where $b_\nu \equiv b$ of Eq. (3).

The ratio of R of the intensities of two lines is

$$R = I_1/I_2 = (ab_\nu)_1/(ab_\nu)_2. \quad (b)$$

If, however, R be determined by comparing the areas obtained from wave-length plots, Eq. (b) becomes

$$R = (\lambda_2/\lambda_1)^2 \cdot (ab_\lambda)_1/(ab_\lambda)_2. \quad (c)$$

That is to say, the ratio of the areas of two lines determined from wave-length plots must be multiplied by $(\lambda_2/\lambda_1)^2$ to give the relative intensities of the lines.

use as its equivalent the rocking curve in the (1,-1) position, i.e., $\Phi_{1,-1}$ as may be shown by the following argument:

Allison has shown¹⁵ that the rocking curve $\Phi_{1,1}$ for a pair of identical crystals is given by

$$\Phi_{1,1}(\xi_B) = \int_{-\infty}^{+\infty} F(\alpha) F(\xi_B - \alpha) d\alpha, \quad (6)$$

where $F(\alpha)$ represents the ratio of the x-ray energy (per second) reflected from either crystal when set at angle α from the Bragg angle, to that reflected when $\alpha=0$; ξ_B is the angle by which crystal B differs from parallelism to crystal A when for it $\alpha=0$. The curve $\Phi_{1,-1}$ for the (1,-1) position is correspondingly given by

$$\Phi_{1,-1}(\xi_B) = \int_{-\infty}^{+\infty} F(\alpha) F(\alpha - \xi_B) d\alpha. \quad (6a)$$

As pointed out by Allison,¹⁵ irrespective of the nature of the F function, $\Phi_{1,-1}$ must be symmetrical—in agreement with experiment. But if F is unsymmetrical then $\Phi_{1,1}$ cannot be symmetrical. We observe, however, that for $W K \alpha_1 f(\omega)$ of Eq. (5) is symmetrical, not only for the (1,1) position but for (2,2) and (3,3). It is, of course, possible that for any given order an unsymmetrical $\Phi_{1,1}$ might combine with a correspondingly unsymmetrical Ψ in Eq. (5) to give a symmetrical $f(\omega)$; but this could hardly be so for several orders, since the relative effect of the crystal diffraction on $f(\omega)$ is less for the higher orders. (See Table II.) We conclude,

TABLE II. Values of W_T for $W K \alpha_1$.

Order	W_O	W_R	W_T		
			by Eq. (2)	by Eq. (1)	
<i>By crystal pair 3A+3B</i>					
1, +1	13.3"	3.0"	10.3"	0.151 X.U.	0.191 X.U.
2, +2	21.9"	1.6"	20.3"	0.148	0.155
3, +3	34.5"	3.2	31.3	0.151	0.166
<i>By crystal pair 1A+1B</i>					
1, +1	19.7"	9.6"	10.1	0.149	0.252

therefore, that within the limits of error of experiment¹⁶ the F functions are symmetrical and

¹⁵ Allison, Phys. Rev. **44**, 63 (1933), Eq. (2).

¹⁶ It should be pointed out that for $W K \alpha_1$ and for our crystals $3A+3B$, $W_T \approx 3W_R$. Any marked asymmetry in $\Phi_{1,1}$ would be more readily observed than when, as is the case for longer wave-lengths, W_R is relatively much smaller.

therefore $\Phi_{1,1}$ is symmetrical and equal to $\Phi_{1,-1}$.

We can now solve Eq. (5) by inserting values of $\Psi(\xi_B)$ and of $\Phi_{1,1}(\omega - \xi_B)$ as follows:

$$\Psi(\xi_B) = h/[1 + (\xi_B/w_T)^2] \quad (7a)$$

in accordance with the conclusions of Weisskopf¹⁴ where h is the maximum ordinate of the energy distribution curve for the line in question and w_T its half width at half maximum; and

$$\Phi_{1,1}(\omega - \xi_B) = a/[1 + ((\omega - \xi_B)/w_R)^2] \quad (7b)$$

where a is the maximum ordinate and w_R the half width at half maximum of the (1, -1) rocking curve of the crystals used. Integration then leads to

$$f(\omega) = A/[1 + (\omega/(w_R + w_T))^2], \quad (8)$$

where A is the maximum ordinate. As shown in Fig. 1a, Eq. (8) is in agreement with experiment. The half width at half maximum, namely w_0 , of the curve $f(\omega)$ is given by

$$w_0 = w_R + w_T.$$

Letting $W_0 = 2w_0$, $W_R = 2w_R$ and $W_T = 2w_T$ we have the equation

$$W_T = W_0 - W_R$$

in agreement with Eq. (2) above.

An obvious test of Eq. (2) is the constancy of the values of W_T which it yields for any given line in several orders, and with different pairs of crystals. Table II gives data for W $K\alpha_1$, as measured in these orders by crystal pair 3A + 3B; and also by crystal pair 1A + 1B in first order. A plot of the data in columns 1, 5 and 6 of Table II is shown in Fig. 2. The superiority of Eq. (2) is

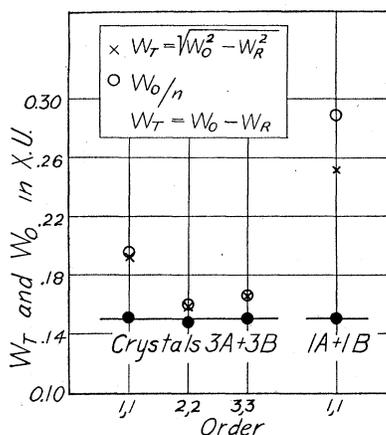


FIG. 2. The true width, W_T of $K\alpha_1$ of W(74) as computed (1) by the Schwarzschild formula and (2) by the equation based on the Hoyt formula, for crystals 3A + 3B in three orders and for crystals 1A + 1B in the first order.

evident. It is therefore used in determining W_T for the K lines of W(74). But it should be emphasized that when $\Phi_{1,-1}$ departs noticeably from the form of Eq. (3)—as for example¹⁷ at wave-lengths in the neighborhood of 1A,—Eq. (2) cannot be used.

RESULTS

The observed values W_0 of the width of the several lines of the K -series of W(74) and also the values of the true width W_T as computed by use of Eq. (2) are shown in Table III. The two components of the doublet $K\alpha_{1,2}$ are separated far enough so that the influence of either component on the observed shape of the other may be neglected; and the values of W_0 may be read directly from the line as observed. The

TABLE III. Widths of the lines of the K series of W(74) (in the (1, +1) position of the crystals 3A + 3B). $W_R = 3.0 \pm 0.2$ sec. of arc for the (1, -1) position of crystals 3A + 3B.

Line of W(74)	W_0 in (1, +1) position		Sec. of arc	$W_T = W_0 - W_R$	Volts
	X.U.	Sec. of arc.			
$K\alpha_2$	0.210 ± 0.002	13.9 ± 0.14	10.9 ± 0.3	0.160 ± 0.004	43.3 ± 1
α_1	0.196 ± 0.001	13.3 ± 0.07	10.3 ± 0.2	0.151 ± 0.003	43.0 ± 0.9
β_3	0.183 ± 0.003	12.4 ± 0.20	9.4 ± 0.3	0.138 ± 0.004	50.0 ± 1.5
β_1	0.178 ± 0.003	12.1 ± 0.20	9.1 ± 0.3	0.133 ± 0.004	48.6 ± 1.5
γ_2	0.140 ± 0.004	9.5 ± 0.27	6.5 ± 0.3	0.095 ± 0.005	37.0 ± 2.0
γ_1	0.140 ± 0.004	9.5 ± 0.27	6.5 ± 0.3	0.095 ± 0.005	37.0 ± 2.0
$\delta_{1,2}$	0.16 ± 0.01	10.2 ± 0.6	7.2 ± 0.6	0.106 ± 0.01	41.0 ± 3.7

¹⁷ Allison, reference 13. Also unpublished data by the authors.

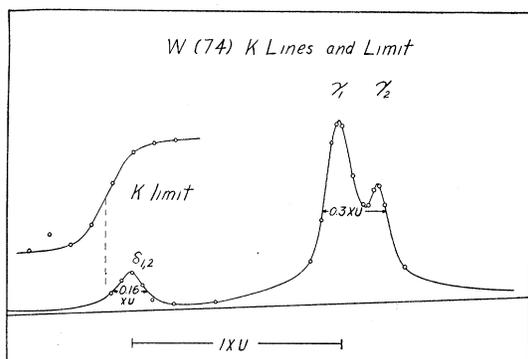


FIG. 3. The $K\gamma$ and the $K\delta$ doublet of W(74) as observed. The location of the K limit is sketched in from unpublished data.

same remark applies to $K\beta_{1,3}$ (Siegbahn's notation). The doublet $K\gamma_{1,2}$ however, is not fully resolved; and the doublet $K\delta_{1,2}$ ($K \rightarrow O_{II,III}$) appears as a single line—as is shown in Fig. 3. Parenthetically, the position and approximate width of the K -limit of W(74), about 37 volts, is shown in Fig. 3, from unpublished data by the authors. It is significant that it overlaps the doublet $K\delta_{1,2}$.

The method used in separating the components $K\gamma_1$ and $K\gamma_2$ is clear from Fig. 4. By a trial-and-error method two Hoyt curves (Eq. (3)) were drawn so that the sum of their ordinates gave the envelope that passes through the observed points.

It is to be observed that, expressed in volts, the widths of the components of a doublet are the same within the limits of experimental error. We were, however, somewhat surprised to find that the widths of the components of the $K\beta$ doublet are greater than those of either $K\alpha$ or $K\gamma$ —a circumstance which finds confirmation in more recent data by the authors, soon to be published, in which it is shown that the energy states $M_{II,III}$ are wider than either $L_{II,III}$ or $N_{II,III}$.

The width of the unresolved $K\delta_{1,2}$ line is put at 41.0 volts. By graphical extrapolation of data given in Siegbahn's *Spektroskopie der Roentgen-*

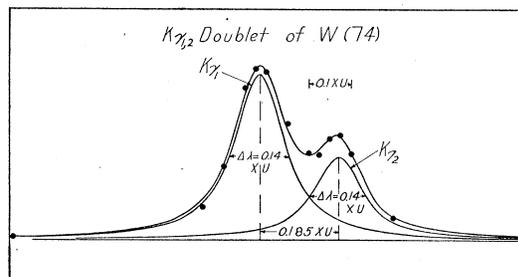


FIG. 4. The $K\gamma$ doublet is resolved into its components by use of two Hoyt curves.

strahlen, it is estimated that the limits O_{II} and O_{III} are separated by approximately 7 volts. If so, $K\delta_1$ and $K\delta_2$ should likewise be separated by some 7 volts. The widths of each of the lines $K\delta_1$ and $K\delta_2$ should therefore be about 34 ± 4 volts.

One concluding remark: The above measurements show that x-ray lines are far less "monochromatic" than are optical lines. The full widths at half maximum of the W K lines are of the order of 0.1 percent of their respective wave-length; whereas for optical lines the corresponding value is more nearly 0.0001 percent or less. From a systematic study of the widths and shapes of x-ray lines we may hope to obtain important information regarding the widths and shapes of the several x-ray energy states of the atom.

ADDENDUM

Our spectrometer is not calibrated to give absolute values of wave-length with high precision. It does however give acceptably precise values of small differences of wave-length. We therefore record the following:

From the graph of Fig. 4, we determine that the wave-length separation of $K\gamma_1$ and $K\gamma_2$ is 0.185 X.U. Siegbahn gives $N_{II} - N_{III} = 68$ volts for W(74) corresponding to 0.176 X.U.

From Fig. 3 we find that the difference in wave-length between $K\gamma_1$ and $K\delta_{1,2}$ is 1.00 ± 0.01 X.U. Siegbahn gives, for W(74), $N_{III} - O_{II,III} = 381$ volts, corresponding to 0.98 X.U.