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## The Natural Widths of the $K\alpha$ X-Ray Doublet from 26Fe to 47Ag

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The full widths at half maximum of the  $K\alpha_1$  and  $K\alpha_2$  lines of 14 elements from 26Fe to 47Ag have been investigated with the double spectrometer in the (1, 1) position. The calcite crystals used had been previously studied in the (1, -1) position and shown to give results agreeing

well with those to be expected from a perfect calcite crystal. The reported widths are uncorrected for the effects of overlapping of the lines, vertical divergence of the x-ray beam, or diffraction pattern widths of the crystals. They are, in X—units

	26Fe	27Co	28Ni	29Cu	30Zn	32Ge	38Sr	40Zr	41Cb	42Mo	44Ru	45Rh	46Pd	47Ag
$K\alpha_2$	1.06	0.95	0.82	0.77	0.58	0.46	0.36	0.35	0.31	0.32	0.29	0.29	0.29	0.29
$K\alpha_1$	1.00	0.81	0.64	0.58	0.51	0.43	0.35	0.33	0.33	0.29	0.29	0.29	0.28	0.28

The  $K\alpha_1$  lines of Fe, Co, Ni, Cu, Zn and Ge are definitely asymmetrical, the center lying to the long wave-length side of the maximum ordinate. Pronounced difference in

width of  $K\alpha_1$  and  $K\alpha_2$  and asymmetrical lines are found in and near the region of the periodic table where the  $M_{IV}M_V$  shells are filling with electrons.

### INTRODUCTION

THE experiments reported here were performed with the double crystal x-ray spectrometer, which was first applied to experiments of this type by Ehrenberg and Mark and Davis and Purks in 1927. Since that time the study of line breadths and shapes in the x-ray region by this method has been taken up by many investigators.<sup>1</sup> For these measurements the

crystals must be placed in a position of finite dispersion, which is the case in which the reflecting surfaces are not parallel. The horizontal divergence of monochromatic radiation reflected from crystal *A* is then greatly reduced by the selectivity of the Bragg law, and to a first approximation we may consider the radiation incident on *B* as having been collimated for each wave-length by the action of *A*. The monochromatic rocking curves would thus have widths close to those given by the diffraction pattern and perfection of the crystal grating, and since the actual widths observed are much greater than this, they must be interpreted as natural widths of the lines. All the results reported here have been obtained with the crystals in the (1, 1) position according to the notation of Allison and Williams.<sup>2</sup> The crystals used were the

<sup>1</sup> Ehrenberg and Mark, *Zeits. f. Physik* **42**, 807 (1927). Ehrenberg and von Susich, *Zeits. f. Physik* **42**, 823 (1927). Davis and Purks, *Proc. Nat. Acad. Sci.* **13**, 419 (1927). Davis and Purks, *Proc. Nat. Acad. Sci.* **14**, 172 (1928). Purks, *Phys. Rev.* **31**, 931 (1928). S. K. Allison, *Phys. Rev.* **34**, 176 (1929). Allison and Williams, *Phys. Rev.* **35**, 149 (1930). Allison and Williams, *Phys. Rev.* **35**, 1476 (1930). Mark and von Susich, *Zeits. f. Physik* **65**, 253 (1930). Spencer, *Phys. Rev.* **38**, 618 (1931). Richtmyer and Barnes, *Phys. Rev.* **43**, 1049A (1933). Bearden and Shaw, *Phys. Rev.* **43**, 1050A (1933).

<sup>2</sup> Allison and Williams, *Phys. Rev.* **35**, 149 (1930).

calcites IIIA, IIIB, whose rocking curves in the (1, -1) position have been studied for a wide range of wave-lengths<sup>3</sup> and found to agree well with the theory of reflection by a perfect calcite crystal.

#### PRELIMINARY ADJUSTMENTS AND TESTS

The narrow rocking curves in the (1, -1) position which agree with the calculations for diffraction from a perfect calcite crystal have always been obtained from freshly cleaved surfaces. It is therefore of interest to inquire whether or not the reflecting power of these surfaces changes with time. Before beginning, and after completion of the experiments reported here, the (1, -1) curves for Cu  $K\alpha_1$  were taken on the crystals. Thus the half width at half maximum of the rocking curve from crystals III has been under observation from November 19, 1931, to March 4, 1933. The data are given in Table I.

TABLE I. Widths in (1, -1) position; crystals III.

Date	Line	Half width at half maximum
Nov. 19, 1931	Mo $K\alpha_1$	2.6 sec.
Nov. 25, 1931	Cu $K\alpha_1$	4.9
Jan. 2, 1932	Mo $K\alpha_1$	2.6
Aug. 24, 1932	Cu $K\alpha_1$	4.9
Mar. 4, 1933	Cu $K\alpha_1$	5.1

From Table I it is concluded that no significant change in the surfaces of these crystals

$$\Phi(\xi_B) = \int_{-\phi_m}^{\phi_m} \int_{-\alpha_m}^{\alpha_m} \left(1 - \left|\frac{\phi}{\phi_m}\right|\right) \left(1 - \left|\frac{\alpha}{\alpha_m}\right|\right) F\left(\alpha - \frac{\phi^2}{2} \tan \theta\right) F\left(\xi_B - \alpha - \frac{\phi^2}{2} \tan \theta\right) d\alpha d\phi. \quad (1)$$

The above equation applies to the case in which the slits limiting the vertical and horizontal divergence of the beam consist of rectangular apertures.  $\alpha_m$  and  $\phi_m$  are the maximum horizontal and vertical divergences, respectively. If  $L_H$  is the distance between the slits limiting the horizontal divergence, each of equal width  $a$ , then  $\alpha_m = a/L_H$ , and an analogous definition holds for  $\phi_m$ .  $\phi$  and  $\alpha$  represent the vertical and horizontal divergence of any ray in the bundle

<sup>3</sup> S. K. Allison, Phys. Rev. 41, 1 (1932).

has taken place over this period. They have been kept in a desiccator except at times when runs were in process, and great care has been taken not to touch the reflecting surfaces.

In the parallel positions, if the crystal faces lie in the axes of rotation, and if these axes are parallel, the slit height does not add to the breadth of the rocking curve. This is not the case in positions of finite dispersion such as (1, 1), and the dimensions of the apparatus and height of the slits must be considered. Fig. 1

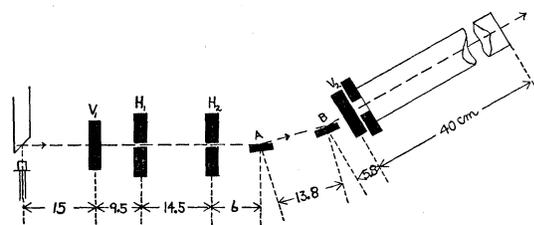


FIG. 1. Important dimensions in the double spectrometer. The axes of rotation of crystals  $A$  and  $B$  are perpendicular to the plane of the figure.  $V_1$  and  $V_2$  are slits limiting the vertical divergence of the x-ray beam,  $H_1$  and  $H_2$  are corresponding slits for the horizontal divergence.

shows important distances in the spectrometer, which was shown as Fig. 1 in a previous publication of the author.<sup>3</sup> It is seen that the slits limiting the vertical divergence were 49.6 cm apart, whereas the slits limiting the horizontal divergence were separated by 14.5 cm. If strictly monochromatic radiation were available for double spectrometer experiments, the rocking curves in the (1, 1) position would be given by

passing through all the slits, and can have values from  $-\phi_m$  to  $\phi_m$ , or  $-\alpha_m$  to  $\alpha_m$ , respectively. The function  $F$  is the diffraction pattern function from a single crystal, which, if perfect crystals are used, would be Darwin's formula as modified by Prins, which appears as Eq. (13) in a previous publication of the author.<sup>3</sup>  $\theta$  is the Bragg angle, and  $\xi_B$  represents the deviation of crystal  $B$  from some reference angle in the vicinity of the rocking curve. The equation in the form (1) applies to an experiment in which crystal  $A$  is left stationary and  $B$  is turned.

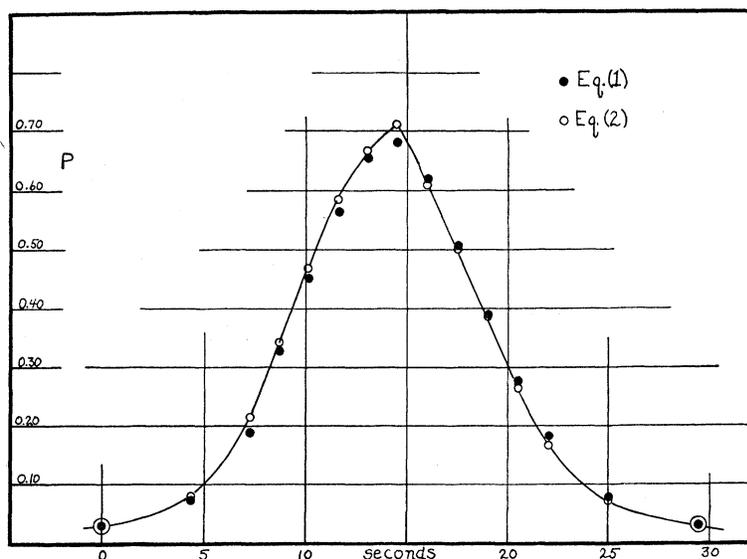


FIG. 2. The calculated effect of a vertical and horizontal divergence of maximum angle  $4 \times 10^{-3}$  on the shape of a (1, 1) monochromatic rocking curve of wave-length 1.537Å. Prins' form of the single perfect crystal diffraction pattern is used, and the calculations apply only to the  $\sigma$ -polarized component of the beam. The ordinates are ratios of the power reflected from  $B$  to that incident upon it from  $A$ . The zero of abscissae represents a setting of the spectrometer in which the central ray makes an angle  $\arcsin \lambda/2d$  on both crystals. The curve is drawn through points calculated without taking account of divergence of the beam. The solid circles show the corrected curve, which has its center of gravity slightly displaced to larger glancing angles.

If we neglect the effect of vertical divergence, Eq. (1) becomes

$$\Phi(\xi_B) = \int_{-\infty}^{\infty} F(\alpha)F(\xi_B - \alpha)d\alpha. \quad (2)$$

In passing from Eq. (1) to Eq. (2) the limits of integration of  $\alpha$  have been extended to  $\pm \infty$ , and the variation in the intensity of the incident beam with horizontal divergence is neglected. This is justified by the fact that these unobservable monochromatic curves would extend over a very small angular range. The functions  $(1 - |\alpha/\alpha_m|)$  and  $(1 - |\phi/\phi_m|)$  which appear in Eq. (1) represent the intensity of the incident beam as a function of horizontal and vertical divergence, respectively, assuming a uniform distribution on the focal spot and that both slits have the same widths or heights.

With the cooperation of Mrs. G. S. Monk of Ryerson Laboratory, calculations of the shape of the (1, 1) rocking curves at the wave-length of  $\text{Cu } K\alpha_1$  have been carried out. The calculations were made for a value of  $\phi_m$  of  $4 \times 10^{-3}$ ,

which corresponds to two slits limiting the vertical divergence 50 cm apart, and each slit 2 mm high. A like value was assumed for  $\alpha_m$ , although this has a negligible influence on the shape of the curve. The  $F$  functions were those of Prins, using the constants given for this wave-length in a recent paper by Parratt.<sup>4</sup> The  $F$  functions depend upon the polarization of the beam, and the present calculations have only been carried out for the  $\sigma$ -component, that is, the component polarized so that its electric vector lies in a plane perpendicular to the plane of incidence. The resultant rocking curves are shown in Fig. 2. It is interesting to note<sup>5</sup> that if the  $F$  functions are not symmetrical, the (1, 1) rocking curve also lacks symmetry, in contrast to the (1, -1) curves which are symmetrical irrespective of the nature of the diffraction patterns, so long as these are the same for the two crystals.

<sup>4</sup> Parratt, Phys. Rev. **41**, 561 (1932).

<sup>5</sup> I have received many ideas about these curves from conversations with Professor Carl Eckart of this laboratory, also from the paper of Laue, Zeits. f. Physik **72**, 472 (1932).

TABLE II. *Cu K $\alpha$  doublet curves at various slit widths.*

Line	Voltage	Location of crystal $A$	$\alpha_m$	$\phi_m$	Observed full width at half maximum
Cu $K\alpha_1(1, 1)$	46 kv	on $\alpha_1$	$2.2 \times 10^{-3}$	$> 10^{-2}$	43 sec.
"	46	"	2.2	$> 10^{-2}$	42
"	31	"	6.2	$4.0 \times 10^{-3}$	41
"	31	"	6.2	$1.0 \times 10^{-2}$	41
"	43	"	6.2	$1.0 \times 10^{-2}$	39
Cu $K\alpha_2(1, 1)$	46	on $\alpha_2$	$2.2 \times 10^{-3}$	$> 10^{-2}$	54 sec.
"	46	"	2.2	$> 10^{-2}$	55
"	43	"	6.2	$1.0 \times 10^{-2}$	52

Average angular width of  $\alpha_1$  41 sec. or 0.58 X.U.  
Average angular width of  $\alpha_2$  54 sec. or 0.77 X.U.

TABLE III. *Widths of the Cu K $\alpha$  doublet.*

Author	Orders	Cu $K\alpha_1$ Full width at half maximum	Remarks
Ehrenberg and von Susich (1927)	(1, 1)	0.70 X.U.	Corrected for (1, -1) width
Purks (1928)	(1, 1)	0.63	Crystals probably unreliable; uncorrected
Valasek (1930)	(1), (2)	0.38	Photographic spectrometer; corrected, but method doubtful. Cf. Table IV
Spencer (1931)	(2, 2)	0.60	uncorrected; "universal" spectrometer
Spencer (1931)	(1, 1)	0.61	" " "
Spencer (1931)	(1, 1)	0.69	uncorrected; old type spectrometer
Allison (1933)	(1, 1)	0.58	uncorrected
Cu $K\alpha_2$			
Purks (1928)	(1, 1)	0.63 X.U.	as above
Spencer (1931)	(2, 2)	0.75	uncorrected; universal
Allison (1933)	(1, 1)	0.77	uncorrected

It is seen that the corrections for slit height and width produce a very minor change in the curve calculated by Eq. (2), which neglects these effects. Of course, in the actual experimental curves obtained in the (1, 1) position, the monochromatic curves of these calculations are entirely covered by the large wave-length spread in a so-called monochromatic x-ray line, but it seems safe to say that if the effect of divergence of the beam on the calculated, truly monochromatic, rocking curve is negligible, it will also be negligible in the observed curve.<sup>6</sup> The conclusions thus arrived at from calculation were given an experimental test by running several curves on the Cu  $K\alpha$  doublet with various slit heights and slit widths. The adjustments of the double spectrometer used in these experiments

<sup>6</sup> However, if the spectral range covered is very wide, appreciable intensity may be reflected at some position from parts of the beam having horizontal divergences large enough to be affected by the function  $(1 - |\alpha/\alpha_m|)$ . A method of correcting for this is discussed later in this paper.

have been described in a previous paper.<sup>3</sup> Before the experiments were begun, crystal  $B$  was removed, and the slits limiting the horizontal divergence were made so narrow that  $\alpha_m$  was  $8.3 \times 10^{-4}$ ; about 2.9 minutes of arc. Using the instrument as a single crystal spectrometer, the setting of crystal  $A$  for the peak of Cu  $K\alpha_1$  could be readily located, and its setting for any other wave-length calculated. Table II shows the result of the experiments. In this table the values of  $\phi_m$  marked  $> 10^{-2}$  represent experiments performed before a slit limiting the vertical divergence was placed near the x-ray tube, so that the limiting value was governed by the size of the focal spot. These are the only experiments performed in connection with the work reported in this paper where such an uncertainty as to the limit of the vertical divergence existed, all the other runs being made with both vertical slits in place. The experiments on Cu  $K\alpha_1$  show that a sixfold variation in the value of  $\phi_m$ <sup>2</sup> produced no sig-

TABLE IV. Full width of  $Mo K\alpha_1$  at half maximum,  $\Delta\lambda$ .

Authors	Crystal	Orders	$\Delta\lambda$	Remarks
Ehrenberg and Mark (1927)	Diamond (111)	(1, 1)	0.41 X.U.	corr. for (1, -1) width
Ehrenberg and von Susich (1927)	Calcite (100)	(1, 1)	0.38	corrected
Mark and von Susich (1930)	Calcite (100)	(2, 2)	0.326	corrected
Mark and von Susich (1930)	Topaz (001)	(6, 6)	0.288	corrected
Allison and Williams (1930)	Calcite (100)	many	0.294	corrected
Valasek (1930)	Calcite (100)	(1)	0.26	photographic*
Spencer (1931)	Calcite (100)	(2, 2)	0.281	uncorrected
Allison (1933)	Calcite (100)	(1, 1)	0.29	uncorrected

\* The correction to be applied to the photographic measurements of Valasek (Phys. Rev. 36, 1523 (1930)) has been discussed by the author (Phys. Rev. 38, 203 (1931)). According to the method of correction advocated, Valasek's results for  $Mo K\alpha_1$  should be nearer 0.38 X.U.

nificant effect on the full width at half maximum of the rocking curve. The widths observed for the copper lines may be compared with those of other observers, as in Table III. From this table it is seen that the widths obtained with this instrument agree with those obtained by Spencer on his "universal" double spectrometer to within about 3 percent.

A further check on the performance of the instrument and crystals was to compare the results on  $Mo K\alpha_1$  with the many experiments performed on this line by other observers. The value found in the present experiments was obtained at 43 kv, in the (1, 1) position, with  $\alpha_m = 4.8 \times 10^{-3}$  and  $\phi_m = 1.0 \times 10^{-2}$ . The uncorrected full width at half maximum was 20 seconds, corresponding to 0.29 X.U. Table IV shows a comparison of this value with other results.

In Table IV it is seen that the results of Mark and von Susich, Allison and Williams, and Spencer for  $Mo K\alpha_1$  are in good agreement with themselves and with the present results. This gives confidence that the apparatus was in proper adjustment and operating in a satisfactory manner. In Table V is shown information concerning operating conditions on the lines studied in the present research.

PREPARATION OF TARGETS

The x-ray tube used in these experiments was of a design previously described by the author.<sup>7</sup> All the targets were made of the same size, so that they could be interchanged. All the various substances used were attached to a copper base

TABLE V. Experimental conditions.

Element	Voltage	Current	$\alpha_m$	$\phi_m$
26Fe	36.5 kv	10 m.a.	$4.8 \times 10^{-3}$	$1.0 \times 10^{-2}$
27Co	35.2	10	"	"
28Ni	39.5	6.6	"	"
29Cu		see Table II	"	"
30Zn	39.5	7.4	"	$4.0 \times 10^{-3}$
32Ge	39.5	4.6	"	$1.0 \times 10^{-2}$
38Sr	36.5	5.0	"	"
40Zr	39.5	7.0	"	"
41Cb	39.7	6.0	"	"
42Mo	42.6	4.0	"	"
44Ru	39.5	6.0	"	"
45Rh	45.2	6.0	$3.4 \times 10^{-3}$	"
46Pd	45.2	6.9	"	"
47Ag	45.2	8.5	"	"

by one method or another. These bases were made from  $\frac{3}{4}$  inch solid copper rod, on which a face was cut at  $45^\circ$  to the long axis. In most cases, a circular depression,  $\frac{5}{16}$  inch in diameter and  $\frac{1}{8}$  inch deep was cut in this face, and the element placed in this cavity. The rod was then bored out for water-cooling, and a sleeve turned down on it so that it fit snugly into a standard brass jacket, carrying the water cooling pipes. It is essential to obtain good thermal junction between the target substance and the copper, especially if the melting point is low, or the substance readily gives off gas when warmed. In the case of Fe, Co, Ni, Ru, Rh, Pd, Ag, disks were prepared of the correct dimensions and silver soldered into the depression in the copper. Zn was melted and poured into such a depression with a little acid flux so that it wet and adhered to the copper. Ge was melted in a hollow copper cylinder whose inside diameter was  $\frac{5}{16}$  inch, and which was closed to the air. The Ge adhered to the copper, and a section was sawed out and soft soldered onto a standard diameter copper

<sup>7</sup> S. K. Allison, Phys. Rev. 30, 245 (1927).

shank. In the case of Sr, a nickel cup whose outside diameter was  $\frac{5}{16}$  inch was stamped out of sheet and small pieces of metallic strontium inserted. The cup was provided with a lid which could be spot-welded so that it was nearly airtight. This arrangement was at once placed in a glass tube, which was then evacuated, and the Sr melted with an induction furnace. The molten strontium made good thermal contact with the nickel, and after cooling, the nickel cup was quickly soldered into the standard copper target. Zr and Cb were obtained in sheets which were spot-welded to nickel sheets, and then the nickel soldered with silver solder to the copper face, no depression having been made. Copper was arc welded onto a molybdenum button by performing the operation in the reducing part of a Bunsen flame. The coppered portion was then silver soldered to the standard target.

#### METHODS OF TAKING DATA

Most of the curves were taken with crystal *A* stationary, while crystal *B* was rotated in small steps through the region under investigation. If the angular range moved through by *B* is large, errors may be introduced due to the fact that as *B* is turned the region on the crystal faces from which the maximum intensity is reflected changes. Also the region on the focal spot which gives the principal part of the observed intensity changes. These disadvantages have been previously discussed by DuMond and Hoyt.<sup>8</sup> The double spectrometer designed by the author is however of such general construction that it can be used in a way which avoids these difficulties. This will be referred to as the method of double rotation, as contrasted with the method of single rotation, in which *B* only is moved. Let

us suppose that crystal *A* is rotated through an angle  $\delta\theta$  measured from some angle  $\theta_0$  at which  $\lambda_0$  is reflected. Then a wave-length  $\lambda_0 + (d\lambda/d\theta)\delta\theta$  is reflected from the same portion of crystal *A* and comes from the same part of the target as did  $\lambda_0$  at the original position. If furthermore axis *B* is rotated through an angle  $2\delta\theta$  around axis *A*, it is now in the same position relative to the reflected beam from *A* as it was in the previous setting. And finally, if crystal *B* is rotated through  $\delta\theta$ , the new wave-length strikes the same part of its surface as did the wave-length  $\lambda_0$  in the original setting. These motions can be carried out without any change in the design of the instrument, since the worm gears driving axis *A* and axis *B* are linked together in a two to one ratio, and a slow motion wheel for revolving *A* in steps of seconds of arc can be locked into the driving mechanism. The double rotation method, then, consists in rotating *A* about its axis through the same angular range as *B* is rotated between readings about its own axis. Axis *B* then follows the beam reflected from crystal *A* automatically due to the previously mentioned gear ratio.

In the method of double rotation in the (1, 1) position, the dispersion, measured in terms of the angle through which *B* is rotated about its own axis, is one-half that in the method of single rotation. The resolving power, however, is the same for the two methods, since the monochromatic rocking curves would be half as wide with double as with single rotation.

The following Table VI shows the data taken on cobalt, in which both methods were used. The experiment in the first row was performed with crystal *A* stationary, and so placed that the central ray through the slits made a glancing

TABLE VI. *Single and double rotation of the Co K $\alpha$  doublet.*

Method	Crystal <i>A</i>	$\alpha_1$		$\alpha_2$	
		$\Delta\theta$	$\Delta\lambda$	$\Delta\theta$	$\Delta\lambda$
Single rotation	$(\alpha_1 + \alpha_2)/2$	59 sec.	0.83 X.U.	66 sec.	0.93 X.U.
Single rotation	$\alpha_1$	56	0.79		
Single rotation	$\alpha_2$			66	0.93
Double rotation	varied	29.5	0.83	34	0.95
Average full width $\alpha_1 = 0.82$ X.U.;				$\alpha_2 = 0.94$ X.U.	

<sup>8</sup> DuMond and Hoyt, Phys. Rev. **36**, 1702 (1930).

angle of  $17^\circ 09' 31''$ , which is half way between the Bragg angles for  $\text{Co } K\alpha_1$  and  $\text{Co } K\alpha_2$ . Crystal  $B$  was then rotated through the entire range necessary to reflect  $\alpha_1$  and  $\alpha_2$ . The experiments in the second and third rows were performed in the usual manner, setting crystal  $A$  in a position to reflect the line in question, and then moving  $B$  over the range required to cover the line. The data in the fourth row were taken over both  $\alpha_1$  and  $\alpha_2$  by moving the entire spectrometer in the way described above. The results show that curves taken by the single rotation method were not seriously affected by the possibility of running off the focal spot, or changing the reflecting area of the crystal faces.

#### THE OVERLAPPING FACTOR

The two lines  $K\alpha_1$  and  $K\alpha_2$  were not completely separated in the elements Fe, Co, Ni, Cu, Zn. This cannot be attributed to an insufficient resolving power of the spectrometer, for the resolving power of the crystals used in this work has been shown to be about 11,000 in this region,<sup>3</sup> whereas the ratio  $\lambda/d\lambda$  for the  $K\alpha$  doublet of Ni, for instance, is about 430. This overlapping makes corrections to the observed ordinates (other than that due to the base-line of the general and scattered radiation) necessary if the complex is to be completely separated out into two lines. Special assumptions are necessary if the component lines are asymmetrical about their maximum ordinate, as is the case with many of these lines.

In order to obtain some semiquantitative measure of the separation of the two peaks, a number called the "overlapping factor" has been introduced. Let  $I_1$  be the ordinate representing the maximum intensity observed on the  $\alpha_1$  peak, and  $I_{\min}$  the minimum ordinate between  $\alpha_1$  and  $\alpha_2$ . Then the overlapping factor  $f$  is

$$f = (I_{\min}/I_1)R_{1,2} \quad (3)$$

where  $R_{1,2}$  is the ratio of the intensity of  $\alpha_1$  to  $\alpha_2$  which has been taken simply as 2, disregarding the question as to whether this represents the ratio of the areas or maximum

ordinates of the two lines.<sup>9</sup> In this form the expression is readily extended other resolutions, for instance  $L\alpha_1$  and  $L\alpha_2$  where  $R_{1,2}$  is 10. According to the definition of  $f$ , an overlapping factor of unity means no minimum between the two lines, a factor of zero meaning complete separation.

#### CORRECTIONS TO THE OBSERVED WIDTHS

The largest overlapping factor observed in these experiments was 0.15 in the Fe  $K\alpha$  doublet. In this case the  $\alpha_1$ -line is certainly asymmetrical, being steeper on the short than on the long wave-length side. This asymmetry makes corrections for overlapping difficult, but any reasonable method seems to lead to corrections which are less than the experimental variations between different runs on the widths. The full widths at half maximum listed in Table VII are uncorrected for overlapping. Other overlapping factors were 27Co, 0.12; 28Ni, 0.10; 29Cu, 0.08; 30Zn, 0.02. At germanium and for the higher elements, no overlapping could be detected.

The effect of the finite resolving power of the crystals, or, in other words, the width of the (1, 1) rocking curve which would be obtained with truly monochromatic radiation must also be considered. The width of this (1, 1) curve depends, as has been shown, on that of the (1, -1) curve and the vertical divergence of the beam, which enters to the second power only. In Table II it has been shown that a sixfold variation in  $\phi_m^2$  made no significant difference in the observed width of Cu  $K\alpha_1$ . It has therefore been assumed in all the experiments that the geometric contribution to the observed widths was negligible. In the curve of Co  $K\alpha_1\alpha_2$  shown as Fig. 3, the width of the (1, -1) curve which would have been observed by the method of double rotation is indicated. This was taken from the data of Allison<sup>3</sup> taken previously on this same set of crystals. The ratio of the (1, -1) width to the angular width of Co  $K\alpha_1$  observed is 19 percent. This ratio ranged from 17 percent in 26Fe to 23 percent for 47Ag. In some previous work on line widths by this method, the (1, 1) observed line widths have been corrected for the (1, -1) widths by assuming that

<sup>9</sup> Spencer, Phys. Rev. 38, 630 (1931) has expressed the separation of Mo  $K\beta_1$  and Mo  $K\beta_2$  by giving the ratio of the minimum ordinate to the maximum of  $\beta_1$ .

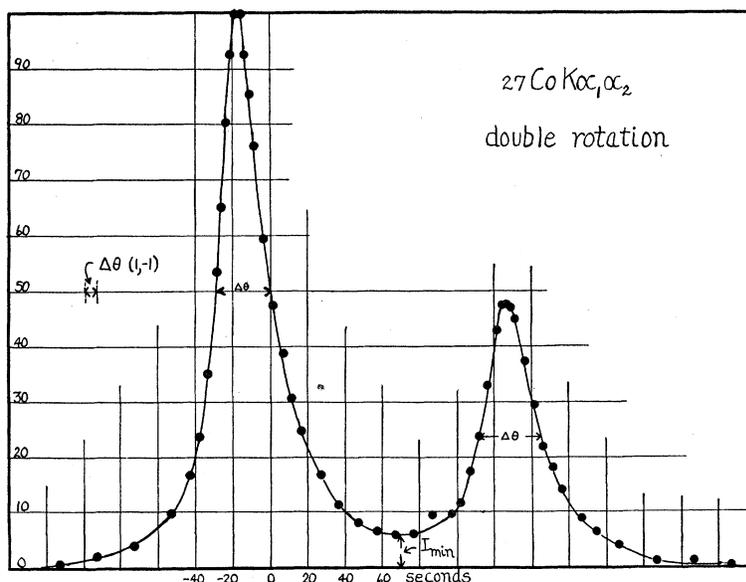


FIG. 3. The curve shown in this figure was obtained in the run mentioned in row 4 of Table VI. The full width at half maximum would be  $5.7''$  in the  $(1, -1)$  position with double rotation, which is 19 percent of the observed width of  $\text{Co } K\alpha_1$ .

the shapes of single crystal diffraction patterns and of spectral lines are given by the Gaussian error curve function. If these assumptions were correct, it can be shown that the observed curves, both in the  $(1, -1)$  and  $(1, 1)$  positions should also have the Gaussian error curve shape. The work of Williams<sup>10</sup> and of Hoyt<sup>11</sup> has shown that this is not the case for the observed line shapes, or for the  $(1, -1)$  curves either, the curves falling off more gradually than does this function. Furthermore Laue<sup>5</sup> has shown that it is impossible to obtain a unique solution for the shape of the single crystal diffraction pattern from the rocking curve in the  $(1, -1)$  position. These considerations make the status of the correction doubtful at the present time. Recently Barnes and Palmer<sup>12</sup> have suggested that the observed widths of  $W K\alpha_1$  in various orders may be best reduced to the true wave-length width by direct subtraction of the observed widths in the  $(n, -n)$  position from those in the  $(n, n)$ . Such a procedure does not, however, improve the data observed on the line width observed for  $\text{Mo } K\alpha_1$  in many orders by Allison and Williams,<sup>2</sup>

and there seems no good reason for applying it to the softer wave-lengths reported on here. The widths recorded in Table VII are those obtained directly from the experimental data, uncorrected for any of the effects mentioned above. They are in each case the full width at half maximum.

## RESULTS

In Table VII the wave-length, frequency, and voltage widths are calculated from the observed angular widths by the following relations:

$$\Delta\lambda = \lambda^{-1} \tan \theta \Delta\theta \quad (4)$$

$$\Delta\nu/R = 9.1126 \times 10^5 \lambda^{-2} \Delta\lambda \quad (5)$$

$$\Delta V = 1.2336 \times 10^7 \lambda^{-2} \Delta\lambda. \quad (6)$$

In the above expressions,  $V$  is in volts and  $\lambda$  in  $X$ -units. The results are shown graphically in Figs. 4 and 5. Perhaps the most striking feature of the results is the large difference in width between  $\alpha_1$  and  $\alpha_2$  for the elements  $^{26}\text{Fe}$  to  $^{32}\text{Ge}$  inclusive. With the possible exception of  $\text{Ge}$ , this difference is well beyond the experimental error, and, as has previously been pointed out, has been found in  $^{29}\text{Cu}$  by Spencer. The present experiments show that this behavior

<sup>10</sup> J. H. Williams, Phys. Rev. **37**, 1431 (1931).

<sup>11</sup> A. Hoyt, Phys. Rev. **40**, 477 (1932).

<sup>12</sup> Barnes and Palmer, Bull. Am. Phys. Soc. **8**, 15 (1933).

TABLE VII. Results. Full widths at half maximum.

Line	$\lambda$ (Siegbahn)	$\Delta\theta$	$\Delta\lambda$	$\Delta\nu/R$	$\Delta V$
26Fe $K\alpha_2$	1936.012 X.U.	76 sec.	1.06 X.U.	0.26	3.5 volts
26Fe $K\alpha_1$	1932.076	72	1.00	0.24	3.3
27Co $K\alpha_2$	1789.19	67	0.95	0.27	3.7
27Co $K\alpha_1$	1785.29	58	0.81	0.23	3.1
28Ni $K\alpha_2$	1685.35	58	0.82	0.26	3.6
28Ni $K\alpha_1$	1654.50	45	0.64	0.21	2.9
29Cu $K\alpha_2$	1541.232	54	0.77	0.30	4.0
29Cu $K\alpha_1$	1537.395	41	0.58	0.22	3.0
30Zn $K\alpha_2$	1436.03	41	0.58	0.26	3.5
30Zn $K\alpha_1$	1432.17	36	0.51	0.23	3.1
32Ge $K\alpha_2$	1255.21	32	0.46	0.27	3.7
32Ge $K\alpha_1$	1251.30	30	0.43	0.25	3.4
38Sr $K\alpha_2$	877.61	25	0.36	0.43	5.8
38Sr $K\alpha_1$	873.45	24	0.35	0.42	5.7
40Zr $K\alpha_2$	788.51	24	0.35	0.51	6.9
40Zr $K\alpha_1$	784.30	23	0.33	0.49	6.6
41Cb $K\alpha_2$	748.89	21	0.31	0.51	6.9
41Cb $K\alpha_1$	744.65	23	0.33	0.54	7.4
42Mo $K\alpha_2$	712.105		(0.32)*	(0.56)	(7.7)
42Mo $K\alpha_1$	707.831	20	0.29	0.53	7.2
44Ru $K\alpha_2$	646.06	20	0.29	0.63	8.6
44Ru $K\alpha_1$	641.74	20	0.29	0.64	8.7
45Rh $K\alpha_2$	616.37	20	0.29	0.70	9.4
45Rh $K\alpha_1$	612.02	20	0.29	0.70	9.5
46Pd $K\alpha_2$	588.63	20	0.29	0.76	10.3
46Pd $K\alpha_1$	584.27	19	0.28	0.75	10.1
47Ag $K\alpha_2$	562.67	20	0.29	0.83	11.3
47Ag $K\alpha_1$	588.28	19	0.28	0.82	11.1

\* The value for Mo  $K\alpha_2$  is taken from Allison and Williams,<sup>2</sup> although Spencer,<sup>1</sup> reports no difference between Mo  $K\alpha_1$  and Mo  $K\alpha_2$ .

is typical of other elements in this region of the periodic system.

Unsymmetrical lines are also found in these elements, having been reported by various authors.<sup>13</sup> Larsson noted the asymmetrical nature of the Fe  $K\alpha_1$  line, in contrast to the symmetrical Mo  $K\alpha_1$ . Seljakow, Krasnikow and Stellejsky concluded that the Cu  $K\alpha_1$  line is symmetrical, which is not supported by the present results and those of Spencer. They however detected lack of symmetry in 28Ni, 27Co and 26Fe. Bearden and Shaw have also found lack of

<sup>13</sup> A. Larsson, Phil. Mag. **3**, 1136 (1927). Seljakow, Krasnikow and Stellejsky, Zeits. f. Physik **45**, 548 (1927). Spencer, Phys. Rev. **38**, 618 (1931). Bearden and Shaw, Bull. Am. Phys. Soc. **8**, 15 (1933).

symmetry in this region. In the present results, asymmetrical lines were noted in the  $K\alpha_1$  of 26Fe, 27Co, 28Ni, 29Cu, 30Zn, and 32Ge. An index of the asymmetry may be obtained by giving the ratio of the part of the full width at half maximum lying to the long wave-length side of the maximum ordinate to that part on the short wave-length side. This ratio was: Fe  $K\alpha_1$ , 1.8; Co  $K\alpha_1$ , 1.5; Ni  $K\alpha_1$ , 1.1; Cu  $K\alpha_1$ , 1.4; and considerably nearer unity for the elements up to Ge. It may be noted that the asymmetry in 28Ni is less than would be expected from its place in the order of atomic numbers. In all these cases the effect consists in a flaring out of the line to the longer wave-lengths.

It may be significant that these anomalies,

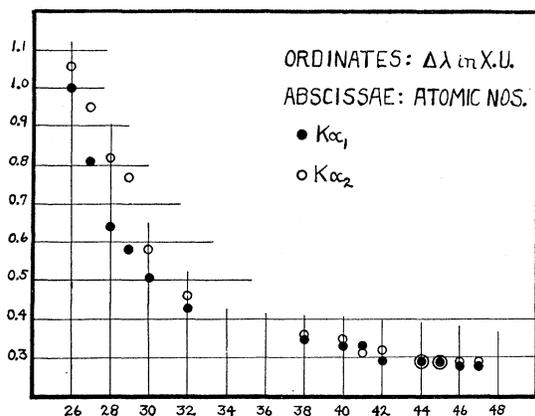


FIG. 4. The full wave-length width at half maximum of  $K\alpha_1$  and  $K\alpha_2$  as a function of atomic number. The difference in width of  $K\alpha_1$  and  $K\alpha_2$  for the lower atomic numbers greatly exceeds the experimental error (in most cases about 5 percent).

namely, the difference in width between  $\alpha_1$  and  $\alpha_2$ , and the lack of symmetry, occur in a region where the  $M_{IV}M_V$  shells are filling as shown by spectroscopic evidence obtained from atoms in the arc and spark. In the solid state, from which the x-ray spectra are obtained, these M shells are probably distorted considerably above  $29\text{Cu}$ , where the data from optical spectra indicates that the  $3d$  levels have obtained their 10 electrons.

The accuracy of the results has been estimated in a crude way from the variations in the

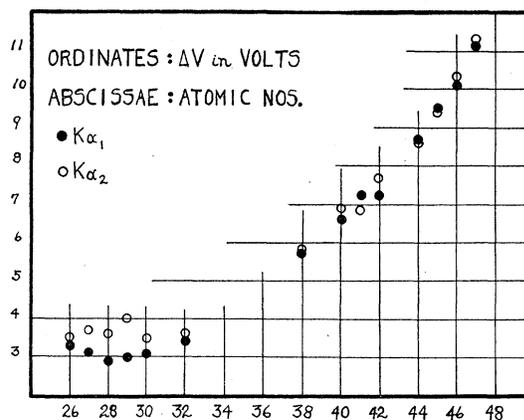


FIG. 5. The full width at half maximum in volts as a function of atomic number.

individual runs and the author's opinion of the steadiness of operation of the x-ray tube and electrometer during the taking of the points. The angular widths are estimated as correct to within  $\pm 5$  percent, except in the following cases. The data on  $26\text{Fe}$  seem upon examination to be less reliable than for the other elements and in this case the accuracy is judged to be  $\pm 10$  percent. Because of the many curves taken on copper, the result seems to be correct within  $\pm 3$  percent. The same may be said for the  $\text{Mo } K\alpha$  lines, in view of the many experiments of the author and others on their widths.