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Natural X-Ray Line Widths: Correction for Finite Resolving Power

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The resolving power of the x-ray double spectrometer has been increased by a factor of 2 to 4 by employing etched quartz crystals. The shapes of the $K\alpha$ lines of Mo, Cu and Ti have been observed in anti-parallel positions and the correction for the finite resolving power of the crystals is shown to be practically negligible. Data on the Au $L\alpha$ line is also considered.

INTRODUCTION

It was early recognized that the high resolving power of the two crystal x-ray spectrometer offers an approach to the problem of determining the natural widths of x-ray lines.[1] The instrument operating in any anti-parallel position gives ionization curves whose shapes are determined by three factors: (1) the contributions of the diffraction patterns of the two crystals, (2) the geometrical divergence or lack of perfect collimation of the x-ray beam, and (3) the natural distribution of energy in the x-ray line itself. In attempting to obtain natural line shapes or widths, investigators have used crystals whose diffraction patterns are as narrow as possible, though still finite, and they have limited the divergence of the incident beam until its contribution is practically negligible.

For qualitative measurements of line widths, sufficiently high resolving power is obtained with crystals whose (1, −1) curve width[2] is less than, say of the order of 1/5, the width of the (1, +1) curve being studied. "Perfect" calcite[3] crystals have the ratio[4, 5] (1, −1)/(1, +1) widths of about 1/5 for $K\alpha$ lines,[6, 7] about 1/10 for $L\alpha$ lines,[8] and about 1/15 for $M\alpha$ lines.[9]

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[1] In addition to the references given in footnote 1 of Allison, Phys. Rev. **44**, 63 (1933), see Swartschild, Phys. Rev. **32**, 162 (1928); Williams, Phys. Rev. **37**, 1431 (1931); **45**, 71 (1934); Bearden, Phys Rev. **43**, 92 (1933); Parratt, Phys. Rev. **44**, 695 (1933); **45**, 364 (1934); Richtmyer and Barnes, Phys. Rev. **46**, 352 (1934); Richtmyer, Barnes and Ramberg, Phys. Rev., November 15, 1934; and Smith, Phys. Rev. **46**, 343 (1934).

[2] No method has been developed to measure the crystal diffraction patterns directly but the width of the (1, −1) curve is intimately dependent upon the pattern widths and in practice is taken as a measure of them. The (1, −1) curve however gives very little information about the shape (other than width) of the diffraction patterns. Assuming monochromatic radiation of $\lambda = 1.54$A, Allison (Phys. Rev. **44**, 63 (1933)) has calculated the shape of the (1, +1) curve of "perfect" calcite crystals on the basis of the Darwin-Ewald-Prins theory of crystalline reflection. The width of this curve is approximately the same as the width of the observed symmetrical (1, −1) curve for the same wave-length but its shape is asymmetrical due to the asymmetry of the single crystal diffraction patterns predicted by the theory (see references 4 and 5).

[3] The width of the characteristic crystal diffraction pattern (or of the (1, −1) curve) can be considered as composed of two factors: (1) the interference pattern due to the arrangement of the electrons and atoms relative to each other in a "perfect" lattice structure, and (2) the distortions of the pattern, increase in width, due to imperfections in the lattice, the so-called mosaic structure. "Perfect" calcite refers to specimens in which there is no evidence of mosaic structure where the Darwin-Ewald-Prins theory of crystalline reflection is used as the criterion.

[4] Allison, Phys. Rev. **41**, 1 (1932).

[5] Parratt, Phys. Rev. **41**, 561 (1932).

[6] Allison, Phys. Rev. **44**, 63 (1933).

[7] Parratt, Phys. Rev. **44**, 695 (1933).

[8] Williams, Phys. Rev. **45**, 71 (1934).

[9] The width of the (1, +1) curve of U $M\alpha_1$ (3.9A) measured with the calcite crystals previously studied

The author has recently reported[10] on the practicality, for x-ray spectrometers, of etched quartz crystals reflecting from the $(11\cdot 0)$ planes. The diffraction patterns of quartz, as indicated by the widths of the $(1, -1)$ curves, are considerably narrower than those of calcite, offering from 2 to 4 times the resolving power. With etched quartz the ratios of $(1, -1)/(1, +1)$ widths are approximately 1/11 and 1/30 for $K\alpha$ lines ($\lambda > 0.7$A) and for $L\alpha$ lines, respectively. The greater resolving power brings the observed $(1, +1)$ curves much nearer the goal of true line shapes for the K lines but the increased resolution is perhaps of no great practical importance for the wide L and M lines. With "perfect" calcite crystals the $(1, +1)$ width[6] of Cu $K\alpha_1$ (1.54A) is 0.58 x.u.; with quartz, 0.475 x.u. With calcite the width[8] of Au $L\alpha_1$ (1.27A) is 1.13 x.u.; with quartz, 1.08 x.u.

It is the purpose of the present experiments to measure the widths of several $K\alpha$ lines using the high resolving power of the quartz crystals. These widths, when compared with the widths of the same lines measured with calcite crystals, lead to a relation between the observed $(1, +1)$ and $(1, -1)$ widths that indicates the correction for the finite resolving power of the crystals in obtaining the *true* line width.

Apparatus and Measurements

The double spectrometer and general set-up have been previously described.[11]

All the curves herein reported were recorded by rotating the second crystal only. This procedure has been shown experimentally by Allison to give the same line shape and width for Co $K\alpha_1$ as obtained when both crystals were rotated simultaneously.[6] With the assurance of a broad focal spot the main objection to single rotation is the non-uniform reflectivity of various regions of the crystal surfaces, known to be present with many calcite cleavage surfaces. Richtmyer and Barnes[12] have found that this irregularity is eliminated by grinding and etching the calcite surfaces, and probably the ground and etched quartz surfaces have uniform reflectivity also. No tests on this point could be conveniently carried out.

A Siegbahn type molecular pump[13] was used on the x-ray tube part of the time but the vacuum so obtained was not as good as that produced with mercury condensation pumps. The inconstancy of voltage (above 25 kv) and the more rapid rate of deposition of tungsten on the target (for $\lambda \geqq 1.5$A) prohibited the use of this pump for accurate ionization measurements.

In recording all the data with quartz crystals a Seeman slit at crystal A was used, and all the data with calcite were taken with the conventional two slits.[11] The maximum horizontal divergence of any ray with respect to the central ray was 0.008 radians for the curves recorded with calcite, and approximately 0.005 radians for the curves with quartz. The maximum vertical divergence, ϕ_m, with respect to the central ray, and the x-ray tube voltage and current are included in the accompanying Tables

Table I. *Measurements on Cu $K\alpha_1$ with etched quartz crystals $(11\cdot 0)$ planes.*

Position	ϕ_m (radians)	Voltage (kv)	Current (m.a.)	Full width at half max. int. (secs.)	(x.u.)	Degree of asymmetry
(1, −1)	0.015	15	20	4.0	0.045	1
	0.01	"	"	3.5	0.039	"
	0.007	"	"	3.4	0.038	"
	0.0048	"	"	3.4	0.038	"
(2, −2)	0.01	25	20	2.25	0.01	1
	0.007	"	"	2.2	0.01	"
	0.0048	"	"	2.2	0.01	"
(1, +1)	0.015	25	30	50	0.566	1.3
	0.01	"	"	43	0.486	1.25
	0.007	"	"	42	0.475	1.2
	"	15	45	42	0.475	1.2
	0.0048	25	30	42	0.475	1.2
(1, +2)	0.01	29	35	80	0.525	1.3
	0.0048	"	"	71	0.47	1.2
(2, +1)	0.01	29	35	82	0.54	1.3
	0.0048	"	"	71	0.47	1.2
(2, +2)	0.01	30	40	119	0.55	1.35
	0.0048	"	"	95	0.44	1.2

(reference 5) is 440 seconds of arc. (This measurement has not been reported before).

[10] Parratt, Rev. Sci. Inst. 5, Dec. (1934). Bozorth and Haworth, Phys. Rev. 45, 821 (1934), found very narrow $(1, -1)$ curves at $\lambda = 0.71$A (Mo $K\alpha$) with etched quartz crystals and very kindly supplied the author with a pair of similarly treated crystals. These crystals, whose reflectivity has been studied for $0.5 < \lambda < 4.6$A, are the quartz crystals used in the present experiments.

[11] Parratt, Phys. Rev. 41, 553 (1932); Rev. Sci. Inst. 5, Dec. (1934).

[12] Richtmyer and Barnes, Rev. Sci. Inst. 5, 351 (1934).

[13] This pump, constructed in Siegbahn's laboratory, is identical with the one pictured on page 103 of Seigbahn's *Specktroskopie der Röntgenstrahlen*, second edition.

TABLE II. *Measurements on Cu $K\alpha_1$ with relatively "poor" calcite crystals.*

Position	ϕ_m (radians)	Voltage (kv)	Current (m.a.)	Full width at half max. int. (secs.)	(x.u.)	Degree of asymmetry
			Crystals A_1B_1			
(1, −1)	0.015	16	10	13	0.185	1
(2, −2)	"	16	20	5.7	0.036	1.1(?)
(1, +1)	"	20	15	52	0.74	1.3
(1, +2)	"	20	25	74	0.65	1.4
(2, +1)	"	20	25	78	0.68	1.4
(2, +2)	"	25	30	104	0.66	1.4
			Crystals A_2B_2			
(1, −1)	0.015	16	10	15	0.214	1
(1, +1)	"	20	15	59	0.84	1.4

TABLE III. *Measurements on Cu $K\alpha_2$ with various crystals.*

Position	ϕ_m (radians)	Voltage (kv)	Current (m.a.)	Full width at half max. int. (secs.)	(x.u.)	Degree of asymmetry
			Etched quartz crystals			
(1, −1)	0.007	15	20	3.4	0.038	1
(1, +1)	0.007	25	30	58.5	0.66	1.2
			Calcite crystals A_1B_1			
(1, −1)	0.015	16	10	13	0.185	1
(1, +1)	0.015	20	15	62	0.88	1.2
			Calcite crystals A_2B_2			
(1, −1)	0.015	16	10	15	0.214	1
(1, +1)	0.015	20	15	69	0.98	1.2

TABLE IV. *Measurements on the $K\alpha$ doublet of Mo and Ti with etched quartz crystals.*

Line	Position	ϕ_m (radians)	Voltage (kv)	Current (m.a.)	Full width at half max. int. (secs.)	(x.u.)	Degree of asymmetry
Mo $K\alpha$	(1, −1)	0.005	30	30	2.5	0.029	1
α_1	(1, +1)	"	"	"	22.5	0.265	1
α_2	(1, +1)	"	"	"	23.8	0.281	1
Ti $K\alpha$	(1, −1)	0.007	10	15	7.6	0.075	1
α_1	(1, +1)	"	25	25	92	0.905	1.12
α_2	(1, +1)	"	"	"	120	1.18	1.06

I–IV. The vertical stops, one near the x-ray tube and the other at the window of the ion chamber, were 42 cm apart.

The $K\alpha$ doublet lines of Mo, Cu and Ti were chosen as representative of a wide range of wave-lengths and line widths. With another pair of similar etched quartz crystals, the width of the $L\alpha_1$ line of Au was measured by Richtmyer, Barnes and Ramberg[14] in this laboratory. The high voltage equipment used by the author was not capable of exciting wave-lengths shorter than Mo $K\alpha$ with sufficient intensity to measure; however, the resolving power of quartz relative to that of calcite decreases rapidly for shorter wave-lengths and little could be gained by measuring, say, the W $K\alpha_1$ line with quartz.

In Tables I–IV are presented the measurements of the full widths and degrees of asymmetry[6, 7] of the observed curves taken in various positions of the spectrometer and with various values of vertical divergence. The data are averages of at least two independent trials in each case.

The $K\alpha$ doublet lines of Cu are, with quartz crystals, completely separated; that is, the "overlapping factor" (defined[6] as twice the ratio of the minimum intensity between the doublet to the maximum intensity of the α_1 line) is zero. Using "perfect" calcite crystals these factors were found to be 0.08 and 0.34 for Cu[6] and Ti[7], respectively. The data on the Ti $K\alpha$ doublet refer to the component lines obtained by correcting[15] the observed contour for overlapping.

As mentioned in the previous report[10] on quartz crystals, the second order reflection is relatively more intense than is the case with calcite crystals. The possibility of the observed curves being altered by second order reflection of the continuous radiation of half the wave-length was checked in the (1, +1) position with Cu $K\alpha_1$ by running at 15 kv and at 25 kv as indicated in Table I. The excitation potential of Cu $K\alpha_1$ is 8.9 kv. No difference in shape or width was detected.

Finally, after all the measurements had been made, the (2, −2) curve of Cu $K\alpha$ was repeated in order to make sure the crystals had not changed or got out of adjustment. The width was the same and the curve was symmetrical, as it was three months before. Various tests of the reflectivity of calcite have shown that calcite, if carefully handled, does not change over a period of time, and it is to be expected that quartz, a much harder and more stable crystal, would not change.

[14] Richtmyer, Barnes and Ramberg, reference 1.

[15] This correction, since the lines are asymmetrical and of different degrees of asymmetry, is necessarily approximate (see reference 7).

True[16] Line Width

With the influence of the geometrical divergence reduced to a negligible amount, one can determine the true line shape *if* a correction for the finite resolving power of the crystals can be made. Smith has recently worked out a method[17] of obtaining the true line shape by correcting for the crystals but this method involves an analytic expression for the observed curve in each of the (1, +1), (1, +2), (2, +1) and (2, +2) positions. More expedient would be a correction for the width at half maximum intensity of the single (1, +1) curve (the crystals having been previously calibrated in the (1, −1) positions) by some sort of subtraction formula. Several different subtraction formulae have been proposed.

First, on the assumption[18] that the true and (1, −1) shapes are both adequately represented by the Gaussian error function

$$I = ae^{-c\theta^2} \tag{1a}$$

the (1, +1) curve must also be an error curve and the correction follows that

$$W_\tau^2 = W_0^2 - W_c^2, \tag{1b}$$

where W_τ refers to the true width, W_0 and W_c the widths of the observed (1, +1) and (1, −1) curves, respectively, all at half maximum intensity. Subsequent work has shown that neither the (1, +1) nor the (1, −1) curve is of the Gaussian form.

Second, on the assumption that the true and (1, −1) curves are of the classical dispersion shape[19]

$$I = a[1 + (\theta/b)^2]^{\frac{1}{2}} \tag{2a}$$

the (1, +1) curve must be of the same shape and the correction is

$$W_\tau = W_0 - W_c. \tag{2b}$$

With the W $K\alpha_1$ line, the (1, +1) and (1, −1) curves observed with calcite are both represented surprisingly accurately by the classical shape, Eq. (2a). For such lines this correction formula seems adequate but with quartz the (1, −1) shapes are different[10] and invalidate the correction. Also for longer wave-lengths the (1, −1) curves of calcite do not fit[10] this classical shape. For $\lambda > 1.4$A the (1, +1) curves of K lines become asymmetrical. Asymmetry of the (1, +1) curves of $L\alpha_1$ and $M\alpha_1$ lines is also observed at silver and uranium, respectively.

Third, the empirical correction,

$$W_\tau = W_0 - \tfrac{1}{2} W_c, \tag{3}$$

which is sort of "in between" the above two corrections, seems to satisfy for the Mo $K\alpha_1$ line in first, second, and third order reflections and is being applied by Richtmyer, Barnes and Ramberg[14] to the (1, +1) measurements of the Au $L\alpha$ lines.

Another approach to the problem of correcting for the crystals is sketched in Fig. 1, in which the widths of the (1, −1) curves are plotted against the widths of the (1, +1) curves. Each point, for a given line, represents data taken with a separate pair of crystals. Calcite and quartz data are plotted on the same graph so the widths have been converted from angular measure to x.u., taking account of the different dispersions. The intercept on the ordinate axis of the extrapolated curve is the (1, +1) width which might be observed were the (1, −1) width zero. Zero (1, −1) width implies that the crystal diffraction patterns have zero width, or that the spectrometer has infinite resolving power. This intercept is then to be interpreted as the true line width.

The variety of points of Cu $K\alpha_1$ in the figure indicates clearly that the correction formula is not linear, as are Eqs. (2b) and (3) except to a first approximation for small (1, −1)/(1, +1) widths ratios. The figure shows also that this approximation is perhaps justified in the cases of Au $L\alpha_1$, Mo $K\alpha_1$ and probably W $K\alpha_1$, especially with the higher orders of reflection,[19] if in each

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[16] The theory of line shapes (Weisskopf and Wigner, Zeits. f. Physik **63**, 54 (1930)) indicates a convenience in distinguishing between "true" and "natural" line widths. The terminology adopted by Richtmyer, Barnes and Ramberg is as follows: "True" refers to the line as it emerges from the target or as it is incident upon the spectrometer. "Natural" refers to that part of the "true" line produced by what amounts to classical radiation damping: characteristic of the atom alone rather than of the atom and its environment as they exist in the target. In the present report, as in all previous experimental reports on line widths, by the term "natural" is meant "true."

[17] Smith, Phys. Rev. **46**, 343 (1934).

[18] Ehrenberg and Mark, Zeits. f. Physik **42**, 807 (1927). Swartschild, Phys. Rev. **32**, 162 (1928).

[19] Hoyt, Phys. Rev. **40**, 477 (1930); Barnes and Palmer, Phys. Rev. **43**, 1050 (1933).

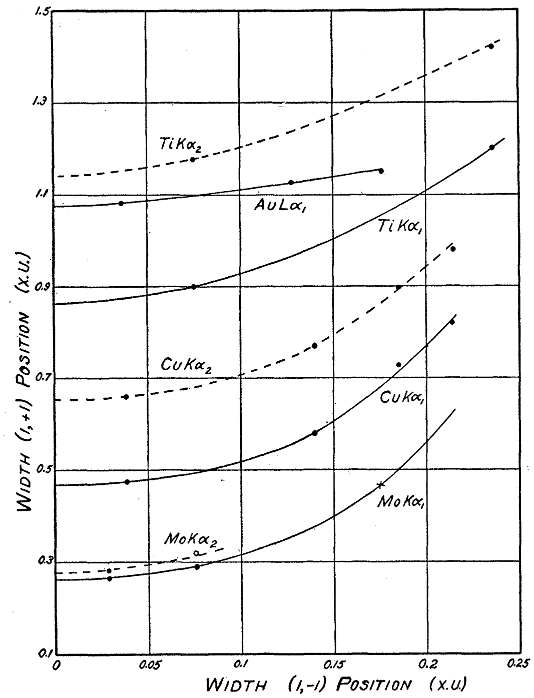

FIG. 1. A plot of the full widths of the rocking curves recorded in the (1, +1) and (1, −1) positions with quartz and with various calcite crystals. The value of the extrapolated (1, +1) width for zero (1, −1) width (that is, for infinite resolving power) may be interpreted as the *true* width of the x-ray line. The data for Mo $K\alpha_{1,2}$ and Cu $K\alpha_{1,2}$ with "perfect" calcite crystals are taken from reference 6, for Ti $K\alpha_{1,2}$ from reference 7. The point marked by a cross on the Mo $K\alpha_1$ curve is taken from reference 21. The three Au $L\alpha_1$ points were measured by the investigators indicated in Table V.

case "perfect" calcite crystals are employed. Further, it seems reasonable that the slope of the correction curve as it intercepts the axis of (1, +1) widths should decrease to zero as the resolving power increases to infinity. Consequently the equation of the curves of Fig. 1 has been assumed to be of the form

$$W_r = W_0 - f(W_c) = W_0 - kW_c^x \quad (4)$$

with the same notation as above. A determination of the constants k and x and the resulting W_r gives[20]

$$W_r = W_0 - 30W_c^{2.86} = 0.265 \text{ x.u.} \quad \text{for Mo } K\alpha_1 \quad \lambda = 0.71\text{A}, \quad (5)$$

$$W_r = W_0 - 30W_c^{2.86} = 0.47 \text{ x.u.} \quad \text{for Cu } K\alpha_1 \quad \lambda = 1.54\text{A}, \quad (6)$$

$$W_r = W_0 - 6W_c^2 = 0.865 \text{ x.u.} \quad \text{for Ti } K\alpha_1 \quad \lambda = 2.74\text{A}. \quad (7)$$

Several investigators have reported[1] two crystal measurements on the Cu $K\alpha$ and Mo $K\alpha$ lines but in most cases either the crystals are not reliable, giving various (1, −1) and (2, −2) widths with correspondingly large experimental errors, or the requisite limitation of the vertical divergence is not satisfied. Spencer reports[21] that the crystals he used in measuring the Mo $K\alpha_1$ width gave (1, −1) curves at λ = 0.71A of widths "from 12 seconds upwards," sometimes having a "double peak." Nevertheless, in need of some point with relatively poor crystals (low resolving power) Fig. 1 includes his measurements.

The three points for Au $L\alpha_1$ (1.27A) are given in Table V.

TABLE V. *Full widths, x.u., of Au $L\alpha_1$ for the (1, −1) and (1, +1) positions.*

	Quartz Richtmyer, Barnes and Ramberg[14]	Calcite Williams[8]	Calcite[22] Richtmyer, Barnes and Ramberg[14]
(1, −1)	0.035	0.127	0.176
(1, +1)	1.08	1.13	1.15

These points fall very nearly on a straight line. However, as the resolving power approaches infinity, the curve should intercept the (1, +1) axis with a slope approaching zero, and such a curve has been drawn in the figure. The value of W_r so obtained is 1.073. The difference between W_r and W_0 with quartz is well within the experimental error.

The values of k and x for Mo $K\alpha_1$ are sensitive to the position of the point marked by a cross in Fig. 1. The experimental error of this point is rather large and so the constants of Eq. (5) may not be correct. There is an insufficient number of points on the Ti $K\alpha_1$ curve to be certain of the constants in Eq. (7). The third Au $L\alpha_1$ point is somewhat indefinite[22]—the Au curve is probably more nearly parallel to the Ti curves

[20] The dimensions of Eq. (4) require the value of k to depend upon the units of the width terms. Eqs. (5), (6) and (7) are in x. units.

[21] Spencer, Phys. Rev. **38**, 630 (1931).

[22] As Richtmyer, Barnes and Ramberg point out, these measurements were taken with the spectrometer and crystals out of adjustment. The increase in width, which results from malalignment of the crystals, of the (1, −1) curve is much more sensitive than that of the (1, +1) curve, and the point in Fig. 1 representing these data is therefore somewhat indefinite.

than is shown in the figure. However, probably both k and x are functions of the (1, +1) and (1, −1) widths, or perhaps of the wave-length and the ratio of (1, +1)/(1, −1) widths. Possibly with more data these functions could be ascertained but considering the variations of (1, −1) shapes with both wave-length and crystals,[10] and that many (1, +1) shapes are asymmetrical, it seems unlikely that the complicated general correction formula would be worth while. Particularly is this so since the (1, +1) widths taken with quartz are so near the intercept values that the correction for most K and for all L and M lines would be close to or less than the experimental error.

The different degrees of asymmetry of Cu $K\alpha_{1,2}$ obtained with calcite and with quartz warrants comment. Allison reports[6] the asymmetry of this line, measured with calcite, as 1.4. One would expect that with higher resolution the observed asymmetry would be increased. The asymmetry of the (1, +1) curve of the crystals only, i.e., for strictly monochromatic radiation, would contribute slightly either positively or negatively to the true line asymmetry. The absorption of the x-rays in calcite causes the diffraction patterns to be asymmetrical[2] as determined from the Darwin-Ewald-Prins theory. The theory has not yet been applied to quartz crystals. Also the observed asymmetry may conceivably be increased by the geometrical divergence of the x-ray beam. Larger values of ϕ_m seem to be accompanied by greater degrees of asymmetry, Table I.

The asymmetries of the Ti $K\alpha$ lines as measured with quartz are also somewhat less than as measured with calcite.

The shapes of the (1, +1) curves of Mo $K\alpha_{1,2}$ are symmetrical as measured with either quartz or calcite and, within experimental error, agree with the classical line shape, Eq. (2a).

A plot of the vertical divergence, ϕ_m, against the observed line width shows that if the geometrical resolving power is greater than the physical resolving power,[23] i.e.,

$$4/\phi_m^2 > \lambda D/W_c \tag{8}$$

where D is the dispersion and W_c the width of the curve in the parallel position, no further decrease in the width of the curve in the anti-parallel position could be obtained. That the resolving power is limited by the geometry of the instrument when ϕ_m does not satisfy Eq. (8) is shown in the greater widths of the observed lines, Tables I and II.

The original intention in recording the rocking curves of Cu $K\alpha_1$ in the various positions of the quartz crystals was to provide data to determine the true line shape by the method of Smith.[17] It was found that the shapes of the (1, +1), (1, +2), (2, +1) and (2, +2) curves are the same. This may be taken as a reasonable indication that the contributions of the crystal diffraction patterns are negligible—that the common shape of these curves actually represents within experimental error the true line shape. However, an attempt to prove this point merely from the expressions given by Smith was unsuccessful, and, to make certain, the experimental curves are being studied further in accordance with this method. It is intended that these several rocking curves be repeated in the near future with "poorer" crystals for the purpose of more decisively checking Smith's analysis.

Acknowledgments

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[23] Allison, Phys. Rev. 38, 203 (1931).