

PRECISION DETERMINATION OF LATTICE CONSTANTS OF SINGLE CRYSTALS USING THE CONVENTIONAL WEISSENBERG CAMERA*

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ABSTRACT

A rapid, routine method is described for determining lattice constants of medium precision from single crystals with the conventional Weissenberg camera. The method involves the determination of a film correction factor, as a function of the reflection angle θ , from the powder pattern of a standard calibration substance exposed on the zero-level Weissenberg film of the single crystal. Lattice constants are obtained by the Bradley and Jay graphical extrapolation method. The experimental results on quartz and colemanite indicate that a precision of about 2 to 4 parts in 10,000 may be easily attained, and that the method is probably inherently capable of giving more precise results.

INTRODUCTION

Lattice constants of high precision may be determined readily by x -ray powder diffraction methods for crystalline materials having at least tetragonal or hexagonal symmetry (see e.g. Buerger, 1942, Chap. 20; Klug and Alexander, 1954, Chap. 8; Peiser, Rooksby, and Wilson, 1955, Chap. 15). The techniques employed depend upon the existence of sharp, sufficiently intense, and unequivocally indexable lines in the region of θ near 90° . For crystals of symmetry lower than tetragonal or hexagonal these conditions do not obtain and recourse must be made to single-crystal methods.

The theory governing the determination of precise lattice constants from single crystals is the same as that used in the powder methods (see refs. above). Briefly, the strategy usually employed is to obtain accurate high θ -values, relatively free from film shrinkage and camera radius errors, and to eliminate other errors, mainly those caused by specimen absorption and camera eccentricity, by graphical or analytical extrapolation methods. Buerger (1937) has suggested the use of a Weissenberg "back-reflection" camera to minimize film shrinkage and camera radius errors. Farquhar and Lipson (1946) have published a similar back-reflection technique employing the oscillating crystal principle. Weisz, Cochran, and Cole (1948) have described a method using the conventional Weissenberg camera in which the θ -values are obtained accurately by measuring on the rotation axis circle of the instrument the angular settings of the crystal giving peak intensities.

The first two of these methods require special cameras, not available commercially, and in addition the method of Farquhar and Lipson is

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difficult to apply to the monoclinic and triclinic cases. The method of Weisz et al. which makes use of the conventional Weissenberg camera and is readily applied to the monoclinic and triclinic cases, is however, according to the authors, lengthy and tedious when photographic techniques are used to fix peak intensities.

The present investigation was aimed at developing a method which would yield lattice constants of moderate precision in a rapid and routine way, using only readily available equipment. It was found possible to do this in the way described below.

DESCRIPTION OF THE METHOD

Preparation and calibration of film

A zero-level Weissenberg pattern of the crystal under investigation is made in the usual way except that the translation motion stop of the instrument is set so that a clear space about 2 cm. in width at one edge of the film is maintained. The goniometer head carrying the crystal is then replaced by a head bearing a powder spindle of a substance used as a calibrating agent. The Weissenberg layer screen is replaced by a screen having a slit 1 cm. in width, and the powder pattern of the calibrating substance recorded on the clear space of the film. A typical composite Weissenberg and powder pattern is shown in Fig. 1. The powder pattern screen used was made up simply by adding a removable slotted brass cylinder to the rotation shield furnished with the Weissenberg camera, as illustrated in Fig. 2. It was found that the use of the regular Weissenberg screen for the powder pattern recording was not satisfactory because of the narrow width (0.25 cm.) of the resulting powder pattern which precludes its accurate measurement.

After photographic processing the washed film is allowed to air-dry in a draft-free room, reasonable care being exercised to keep the film free of strain during drying. After at least two weeks aging the film is measured. Measurements of the spots and lines are made (at one sitting) to the nearest 0.01 cm. using a measuring device somewhat similar to that shown by Buerger (1942, p. 446). A 4× hand lens is used as an aid in setting the hair-line.

A calibration curve for a given film is then prepared by plotting the ratio $k(\theta) = (\theta_{\text{theoretical}})/(\theta_{\text{measured}})$ vs. θ_{measured} for the calibrating substance. A typical calibration curve is shown in Fig. 3. The film constant $k(\theta)$ is then multiplied into the measured θ -values for the crystal to give corrected θ -values, from which d -spacings are calculated. This method of correction essentially eliminates errors due to film shrinkage (linear or nonlinear), as well as any continuous departure from radial symmetry in the camera. This will be true, of course, only if the measurements made on

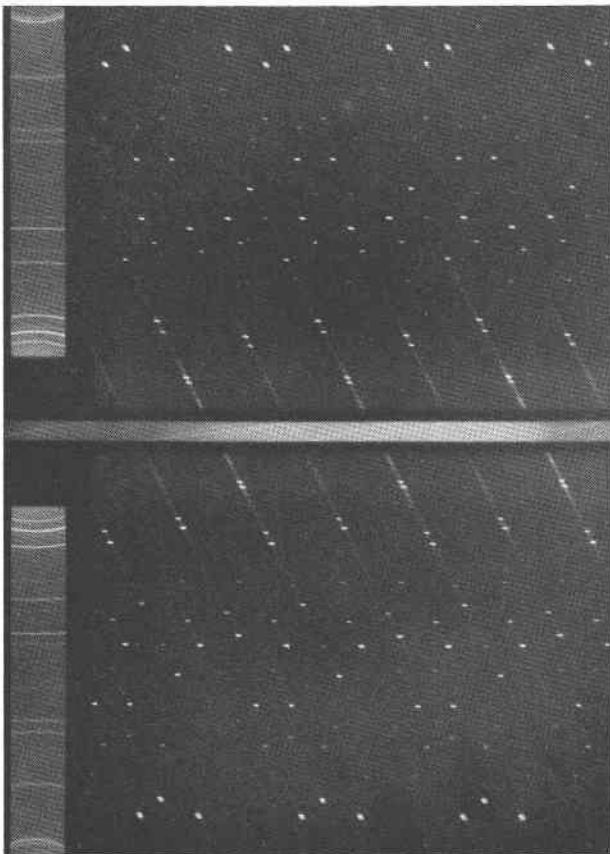


FIG. 1. Composite Weissenberg pattern of quartz around [001] and calibration powder pattern of silver.

the calibrating powder pattern at the edge of the film hold along the rest of the film. This question was examined by measuring powder patterns exposed at various places along the width of the film, and it was found that within a sufficient degree of approximation the calibration made at one edge of the film did hold for the rest of the film. Nevertheless, whenever possible the spots measured on the Weissenberg part of the film were taken close to the calibration pattern.

Calibration standards

Both quartz and silver were used as calibrating standards. The quartz was from a crystal fragment of clear material from Hot Springs, Arkansas, used in a powder spindle about 0.18 mm. in diameter. The silver was

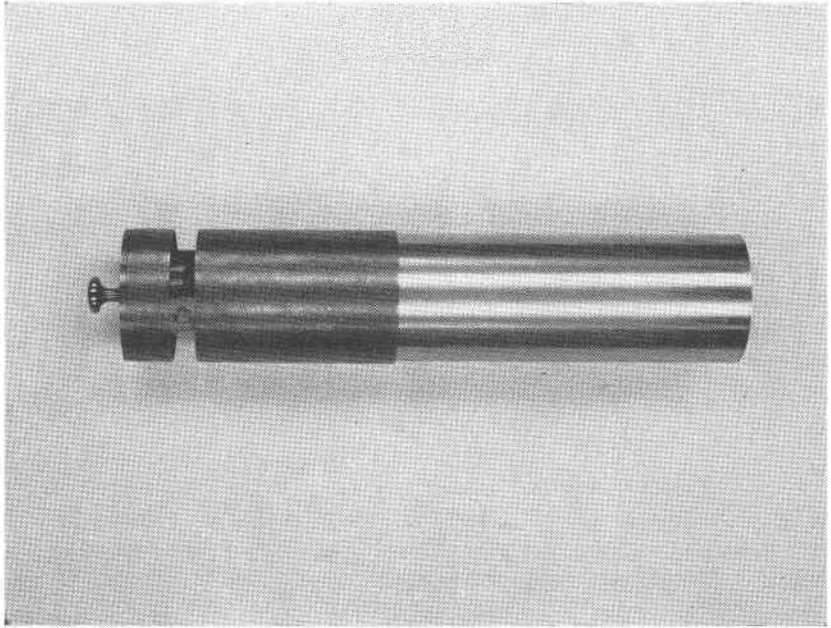


FIG. 2. Photograph showing rotation shield with removable slotted brass cylinder for recording powder pattern.

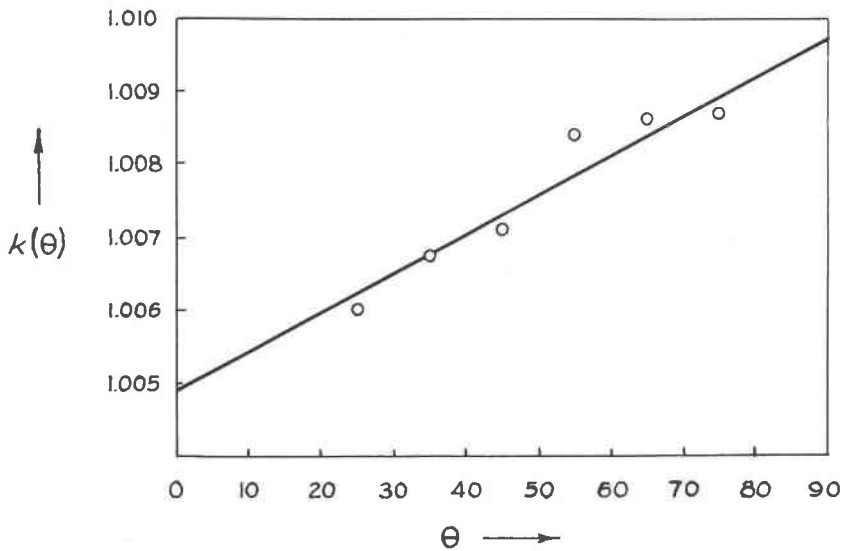


FIG. 3. Typical plot of $k(\theta)$ vs θ for calibration of Weissenberg pattern. $k(\theta)$ values averaged for 10° intervals and plotted at midpoint of interval.

Eimer and Amend, C. P. "precipitated powder," annealed in air at about 350 °C. for approximately 18 hours. The silver as taken from the bottle does not give sharp lines. The silver powder spindle used was 0.07 mm. in diameter. A spectrographic analysis of the silver, made by Richard S. Harner (then of the U. S. Geological Survey), yielded the following results:

0.0X% Cu, Si, Mg with estimated Cu < 0.05%
0.00X Al, Fe, Ca
0.000X Ni, Be, Cr

Thus, the silver is of sufficiently high purity so that the accurately measured lattice constant (Table 1), given in Straumanis and Ievins (1940, p. 100) may be assumed to apply.

With experience, it became apparent that silver was superior to quartz as a calibrating agent for the task at hand, mostly because its pattern is simpler and the lines in the back-reflection region are stronger and sharper. Obviously there are other standards that could be used. A discussion of the criteria that standards should meet, together with a list of standards and tables of their reflection angles (including those for quartz), has been given by Parrish (1953). The precise reflection angles for silver, however, have not appeared in the literature. These are given in Table 1.

The lattice constants of quartz were taken as follows: $a = 4.9131 \text{ \AA}$ and $c = 5.4046 \text{ \AA}$ (18° C.). These values in Angstrom units were obtained from those given in kX units by Wilson and Lipson (1941), by multiplying the kX values by 1.00202. The values of the lattice constant of silver and the wave lengths used to calculate reflection angles for it are given in Table 1.

Calculation of the single-crystal lattice constants

From the d -spacings, obtained from the corrected θ -values as explained above, the apparent values of the lattice constant of interest are calculated, these plotted against $\sin^2\theta$, and the linearly extrapolated value at $\sin^2\theta = 1$ taken as the true lattice constant, following the method of Bradley and Jay (1932).

Various other extrapolation functions have been proposed for use in the graphical extrapolation method (Nelson and Riley, 1945). The possibility of the use of other appropriate functions was considered briefly during this work, but these were not investigated systematically, mainly due to the fact that the use of the $\sin^2\theta$ plot gave such excellent results.

The values of the wavelengths used in calculating d -spacings of the single crystals studied were taken from Bragg (1947), and are:

CuK: $\lambda\beta_1=1.39217 \text{ \AA}$ $\lambda\alpha_1=1.54050$ $\lambda\alpha_2=1.54434$ $\lambda\alpha=1.5418$

RESULTS

Measurements on quartz

As a check of the method the lattice constant a of a single, clear, natural crystal of quartz (locality unknown) was measured using the $hkl0$ reflections, and using silver as the calibration standard. The value $a=4.9130\pm 0.0005 \text{ \AA}$ (approx. 23° C.) was obtained, in good agreement with the values 4.9131 \AA (18° C.) of Wilson and Lipson (1941) and 4.9125 \AA (18° C.) of Keith (1955). These latter values were obtained by

TABLE I. PRECISE REFLECTION ANGLES FOR SILVER*

Ag, face-centered cubic, $a=4.07784 \text{ kX}$ (25° C.)			
CuK: $\lambda\beta_1=1.38935 \text{ kX}$			
$\lambda\alpha_1=1.537395$			
$\lambda\alpha_2=1.541232$			
$\lambda\alpha=1.53867$			
$\lambda\alpha=(2\lambda\alpha_1+\lambda\alpha_2)/3$			
hkl	θ°	hkl	θ°
111	17.161 β	400	42.965 β_1
	19.057 α_1		48.941 α_1
	19.100 α_2		49.106 α_2
	19.073 α		48.996 α
200	19.920 β	331	47.950 β_1
	22.149 α_1		55.254 α_1
	22.207 α_2		55.461 α_2
	22.168 α		55.323 α
220	28.806 β	420	49.628 β_1
	32.221 α_1		57.462 α_1
	32.311 α_2		57.687 α_2
	32.251 α		57.537 α
311	34.403 β	422	56.572 β_1
	38.698 α_1		67.443 α_1
	38.813 α_2		67.790 α_2
	38.736 α		67.558 α
222	36.166 β	511, 333	62.275 β_1
	40.769 α_1		78.381 α_1
	40.893 α_2		79.099 α_2
	40.810 α		
		440	74.509 β_1

* Lattice constant of silver and wave-length values from Straumanis and Ievins (1940, p. 100).

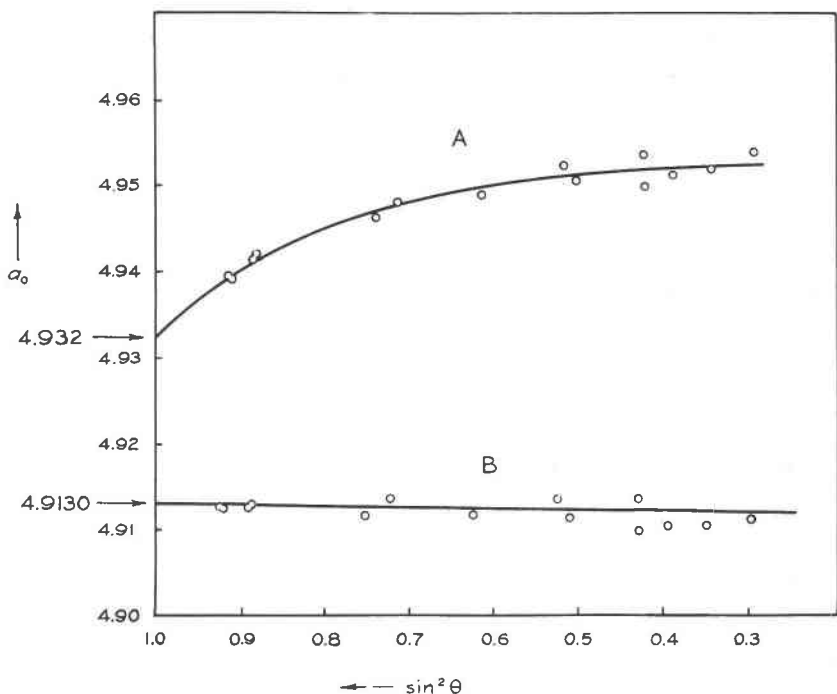


FIG. 4. Determination of a for quartz.

Curve *A* plot of apparent values of a derived from *uncorrected* θ -values. $a=4.932 \pm 0.001$ Å.

Curve *B* plot of apparent values of a derived from *corrected* θ -values. $a=4.9130 \pm 0.0005$ Å.

Calibrating standard, silver.

the more precise powder method and as quoted have been rounded-off to five significant figures.

The results obtained for quartz are shown plotted in two ways in Fig. 4. It is seen from this that when the apparent lattice constants derived from uncorrected θ -values are used the extrapolation is not linear, but has in fact the form predicted from the analysis of the error function (Buerger, 1942, p. 419).

A comparison of the values for a obtained in several ways from these same data is as follows:

(a) Linear extrapolation using corrected θ -values

$$a=4.9130 \pm 0.0005 \text{ \AA.}$$

(b) Average value of a using four largest corrected θ -values

$$a=4.9126 \pm 0.0001 \text{ \AA.}$$

(c) Nonlinear extrapolation using uncorrected θ -values

$$a=4.932 \pm 0.001 \text{ \AA.}$$

(d) Average value of a using four largest uncorrected θ -values

$$a=4.941 \pm 0.001 \text{ \AA.}$$

The limits of error quoted are the estimated extrapolation errors for (a) and (c) and the average deviations for (b) and (d).

These results are enlightening. In the first place they show that the practice of calculating an average lattice constant from high θ -values without any correction can lead to quite wrong results, even though the deviation of the individual results from the mean is small. In this case the value of a is off by 0.028 Å, i.e. 0.6%. If the apparent lattice constants derived from smaller θ -values are included in the average the result will be in greater error. It is also seen that, in general, the extrapolation plot using uncorrected θ -values leads to unreliable results. On the other hand, the average obtained from the large corrected θ -values is fairly close to the true lattice constant. The latter result emphasizes the need for at least determining the average effective camera radius for each camera used.

The function $k(\theta)$

It is of interest to inquire as to how $k(\theta)$ varies from film to film for the same camera. In this investigation it was found that $k(\theta)$ is usually a linear function of θ but not always. In fact for the film from which the results for quartz, as cited above, were obtained, the plot of $k(\theta)$ was not linear (Fig. 5). From this it is seen that $k(\theta) = 1.014_5$ at $\theta = 75^\circ$. For the corresponding θ -value in the plot of Fig. 3, $k(\theta) = 1.008_9$. The film from which the $k(\theta)$ plot of Fig. 5 was derived was measured two years after it had been prepared, whereas the other $k(\theta)$ plot was obtained from measurements made two weeks after the film was made, both films having been made in the same camera. It seems likely that the additional correction is due to additional shrinkage over the longer period of time. In both cases the corrections are rather large. Since one would expect a shrinkage correction of not more than about 0.4% for a relatively young film, it follows that the remainder of the correction is due to error in the effective film radius.

Measurements on colemanite

Lattice constant determinations were also made for the monoclinic crystal, colemanite (results previously reported by Christ, 1953). The final values obtained are listed in Table 2. The values of d_{100} , d_{010} , and d_{001} were obtained by graphical extrapolation from measurements of the reflection angles for $h00$, $0k0$, and $00l$, respectively. The plot for d_{010} ($=b$) shown in Fig. 6 is fairly typical of those obtained for d_{100} and d_{001} . Each of these plots had an indicated extrapolation error of ± 0.0005 Å. The value of the angle β was obtained by using the relationship:

$$\cos \beta = \frac{d_{001}d_{100}}{2hl} \left(\frac{h^2}{d_{100}^2} + \frac{l^2}{d_{001}^2} - \frac{1}{d_{h0l}^2} \right).$$

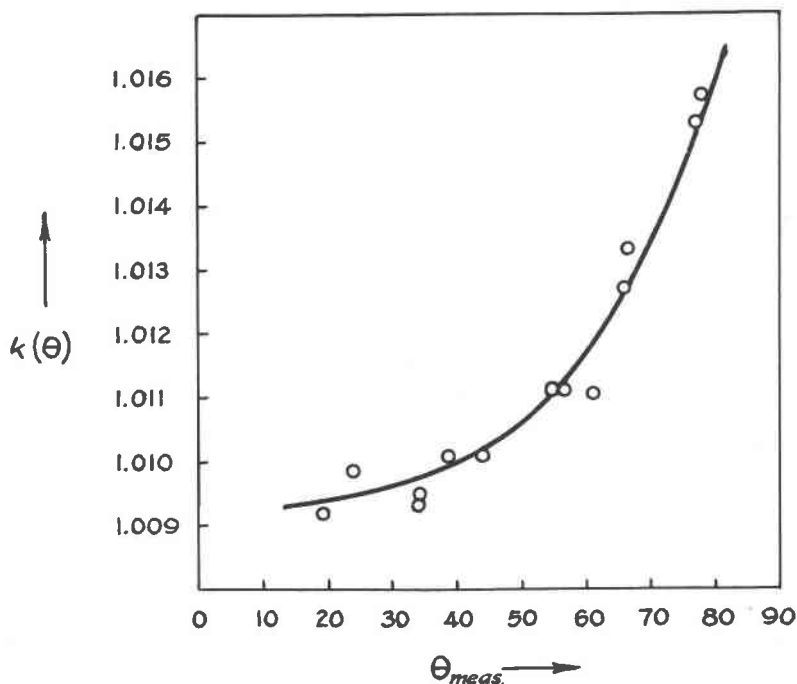


FIG. 5. Plot of $k(\theta)$ used in determination of a for quartz.

The known values of d_{001} and d_{100} and ten values of d_{h0l} from corrected θ measurements in the region of $\theta = 75$ to 80° were used to calculate an average β . With this method the probable error for β is $\pm 5'$, leading to the probable errors shown for a and c in Table 2. This method for determining β is relatively inaccurate. Interaxial angles as well as interplanar spacings may be determined precisely by the graphical extra-

TABLE 2. LATTICE CONSTANT MEASUREMENTS FOR COLEMANITE
 $\text{CaB}_2\text{O}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$, monoclinic, $P2_1/a$

Constant	Present Method	Precession Method
d_{100}	8.2100 ± 0.0005	
d_{010}	11.2637 ± 0.0005	
d_{001}	5.7300 ± 0.0005	
a	8.743 ± 0.004	8.73 ± 0.01
b	11.264 ± 0.002	11.25 ± 0.02
c	6.102 ± 0.003	6.10 ± 0.015
β	$110^\circ 7' \pm 5'$	$110^\circ 10' \pm 5'$

Linear measurements in Ångstrom units. Wavelengths used, CuK: $\lambda_{\beta_1} = 1.39217$, $\lambda_{\alpha_1} = 1.54050$, $\lambda_{\alpha_2} = 1.54434$, $\lambda_{\alpha} = 1.5418$ Å.

polation method. However, for the precision sought for the lattice constants of colemanite an error of $\pm 5'$ in β was tolerable and no further work was done on this.

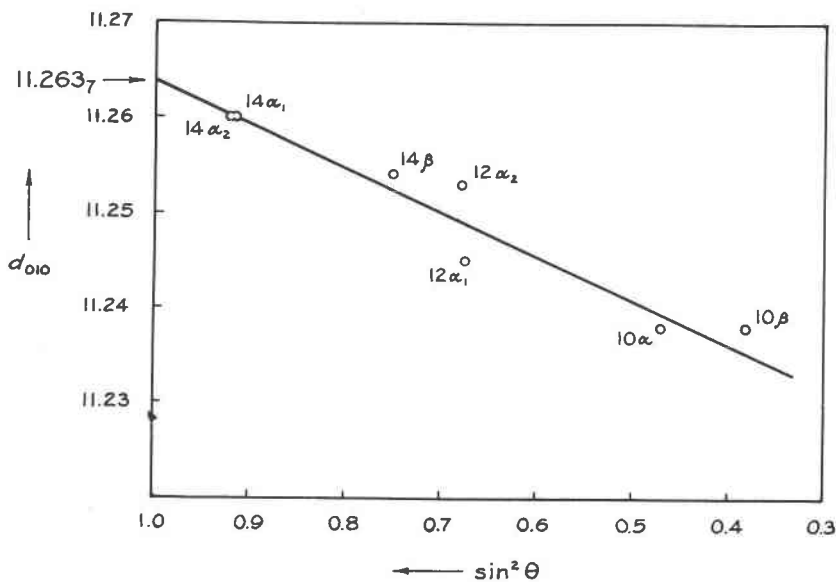


FIG. 6. Determination of d_{010} for colemanite. $d_{010} = 11.2637 \pm 0.0005$ Å. Calibrating standard, silver. Orders of the reflections $0k0$ indicated.

Many more points can be obtained on the plot for a given lattice spacing by using general zone reflections. For example, for the determination of d_{100} , measurements of the angles for the $hk0$ reflections instead of just the $h00$ reflections may be used. The relationships governing the use of general zone reflections and those used in the determination of interaxial angles are given by Weisz et al. (1948).

Some idea of the efficacy of the present method may be gained from the following example. Plots of the values of d_{100} (from $h00$ reflections only) were obtained from two different films which had significantly different $k(\theta)$'s. One film represented the $h0l$ zone and the other the $hk0$ zone. Nevertheless, the two plots gave exactly the same value of d_{100} , namely 8.2100 ± 0.0005 Å. The exact agreement is, of course, fortuitous, but it does indicate that the extrapolation error of ± 0.0005 Å assigned the several Bradley-Jay plots for colemanite is not too small.

The assignment of probable errors to the lattice constants listed in Table 2 was done in the following way. For the interplanar spacings the estimated extrapolation error is listed. The errors for a and c are fixed by

the relatively large error in β . For b the error is taken as four times the extrapolation error as only one determination of b was made. Measurements made on a calibrated, shrinkage-corrected precession film by an independent observer (Joan R. Clark, U. S. Geological Survey) are included in Table 2. These are of lower precision, and the comparison essentially furnishes a check on the precession method. Of particular interest, however, is the precession method measurement of β , as this is a direct measurement independent of the values of d_{100} and d_{001} . It is seen that the two measurements are in excellent agreement.

DISCUSSION

The method described is a rapid and routine method for obtaining lattice constants of moderate precision. It is apparent that in the present study no real attempt has been made to push the method to its utmost limits of precision. The Weissenberg camera used is a typical commercial instrument. The measuring device employed gives readings directly with vernier only to the nearest 0.01 cm., with the possibility of estimating whether the third figure is nearer to 0.000 or 0.005 cm. Similarly, unless a gross error was detected, readings of line or spot positions were usually made only once. The crystals used were of moderate size; for example, the quartz crystal measured had a projected width on the film of 0.3 mm. at $\theta = 70^\circ$. Obviously, for higher accuracy a more precise measuring device could be used, averages of several θ measurements used instead of a single one, and crystals of smaller size employed.

Despite the relatively unrefined techniques used the results obtained are good. It would be necessary to carry the investigation further to establish accurately the limits of precision, but from what has been done it seems likely that the method will yield lattice spacings precise to 2 to 4 parts in 10,000. The precision of the corresponding unit-cell constants depends upon the precision with which intervector angles can be determined in the monoclinic or triclinic cases. As was pointed out above, these angles can be determined with the same degree of precision as the lattice spacings using the relationships listed by Weisz et al. (1948). In the Bradley-Jay plots obtained by the present method the extrapolation is linear to fairly low values of $\sin^2\theta$. In view of the approximations inherent in the Bradley-Jay method these results are somewhat surprising, albeit very welcome.

It is perhaps not out of place here to point out that in many papers in the mineralogical literature lattice constants determined from rotation or Weissenberg patterns are given with an implied precision of 1 part in a 1000 or better. It is clear from the context of the same papers that, barring fortunate accidents, these results have a probable error of from 0.5

to 1.0%. It is suggested that when results of precision better than 0.5% are desired, at least an average film constant for the camera in use be obtained.

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