HODGMAN, C. D. (1959*a*). *Handbook of Chemistry and Physics*. 40th ed., p. 218. Cleveland: Chemical Rubber Publishing Co.
HODGMAN, C. D. (1959*b*). *Handbook of Chemistry and Physics*. 40th ed., p. 216. Cleveland: Chemical Rubber Publishing Co.
LADELL, J., PARRISH, W. & TAYLOR, A. (1959). *Acta Cryst.* **12**, 253.
MOOD, A. M. (1950*a*). *Introduction to the Theory of Statistics*, p. 257. New York: McGraw-Hill.
MOOD, A. M. p1950*b*). *Introduction to the Theory of Statistics*, p. 259. New York: McGraw-Hill.
MUELLER, M. H., HEATON, L. & MILLER, K. T. (1960). *Acta Cryst.* **13**, 828.
MUELLER, M. H. & HEATON, L. (1961). *Determination of Lattice Parameters with the Aid of a Computer*. USAEC Report ANL-6176.
PARRISH, W. (1960). *Acta Cryst.* **13**, 838.
PIKE, E. R. & WILSON, A. J. C. (1959). *Brit. J. Appl. Phys.* **10**, 57.
STRAUMANIS, M. E. & IEVINS, A. (1940). *The Precision Determination of Lattice Constants by the Asymmetric Method.* [Originally published in German by Julius Springer, Berlin, and translated by K. E. Beu (April 15, 1959) as USAEC Report GAT-T-643.]
STRAUMANIS, M. E. (1960). *Acta Crys'.* **13**, 818.
VOGEL, R. E. & KEMPTER, C. P. (1959). *A Mathematical Technique for the Precision Determination of Lattice Constants*. USAEC Report LA-2317.

Acta Cryst. (1962). **15**, 1301

Precise and Accurate Lattice Parameters by Film Powder Methods.* II. An Exact Eccentricity Correction for Cylindrical Film Cameras†

BY K. E. BEU AND D. L. SCOTT

Physical Measurements Department, Development Laboratory, Goodyear Atomic Corporation, Portsmouth, Ohio, U.S.A.

(*Received* 24 *October* 1961)

An exact analytical method is presented which permits correcting cylindrical diffraction film measurements for sample eccentricity. This method is based on measuring the camera radius in three directions and using these measurements to calculate the eccentricity vector (P, σ), the true camera radius R, and the eccentricity corrections $\Delta\varphi$ or $\Delta\theta$. Radius measurements can be made and P can be calculated to about $\pm 0{\cdot}001$ mm. using standard high quality dial indicators, micrometers, and gage blocks. For eccentricities normally tolerated in precision cameras (about 0·01 mm. in cameras 50 to 150 mm. in diameter), the exact corrections may differ significantly from those obtained using the approximate method of Bradley & Jay, depending on the orientation of the eccentricity vector. Exact eccentricity curves are given for a camera especially built for the accurate determination of lattice parameters.

1. Introduction

Bradley & Jay (1932) developed an approximate method for making eccentricity corrections on films from cylindrical powder cameras by assuming that: (1) the component of eccentricity perpendicular to the primary X-ray beam is negligible, and (2) the primary beam consists only of parallel rays. With improvements in powder camera construction and measuring techniques (Straumanis & Ievins, 1940, 1940*a*) so that diffraction angles could be measured on film with higher precision (about $\pm 0{\cdot}001\ ^{\circ}\varphi$)‡ it seems worthwhile to re-evaluate existing correction procedures. It will be shown that the assumptions of Bradley & Jay restrict the accuracy of their correction procedure when using the $\pm 0{\cdot}001^{\circ}$ criterion. Averbukh & Tolkachev (1957) eliminate the perpendicular component assumption but still base their derivation on the parallel beam assumption. Straumanis (1940*b*) bypasses both assumptions experimentally, but his method cannot be used to calculate eccentricity corrections as a function of diffraction angle. Thus, an exact eccentricity correction procedure as a function of diffraction angle seems desirable.

It is a purpose of this paper to present a rigorous derivation of the eccentricity correction which includes both perpendicular and parallel components of eccentricity and which is based on the usual experimental condition of a collimated but divergent primary X-ray beam. The results are presented as correction curves of $\Delta\varphi$ versus φ or $\Delta\theta$ versus θ even though diffraction measurements are usually made in terms of 2θ or 4φ. $\Delta\theta$ or $\Delta\varphi$ corrections can be made directly on calculated θ or φ values after

* This work was performed under Contract AT-(33-2)-1 with the U.S. Atomic Energy Commission.

† Paper I, Beu, Musil & Whitney (1962).

‡ φ is defined according to the Bragg equation in the form: $n\lambda = 2d \cos \varphi$.

they have been corrected for other systematic errors and before d or lattice parameter values are calculated from the Bragg equation.

This eccentricity correction procedure was devised in connection with the likelihood ratio method (*LRM*) for the precise and accurate determination of lattice parameters (Beu *et al.*, 1961, 1962*a*). The *LRM* requires corrections for individual systematic errors at each diffraction angle of interest.

2. Discussion

A. A new approach to the eccentricity problem

This new approach is based on making accurate measurements of the camera radius in three directions* using dial indicators, micrometers, and gage blocks which are accurate to 0·0001 in. or better. These data are used with the analytical procedure described below to calculate the eccentricity vector (P, σ), the true camera radius R, and the corrections $\Delta\varphi$ or $\Delta\theta$. For cameras in which the film is mounted internally to the film cylinder, (P, σ) and R are calculated from radius measurements obtained using a dial indicator fastened to the sample spindle with the indicating probe contacting the film cylinder. The procedure is slightly more complicated for cameras in which the film is external to the film cylinder. Details on these and other points are available in a comprehensive report on this topic (Beu & Scott, 1962*b*).

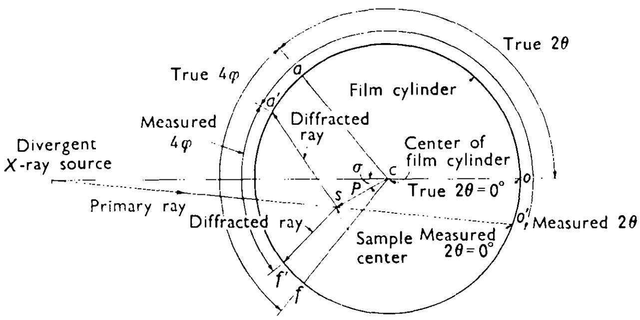

Fig. 1. True and measured 2θ and 4φ angles for eccentricity vector P in the general position and for a diverging beam of X-rays.

Fig. 1 illustrates the relationships of the corrected (true) and measured angles for (P, σ) in the general position and for a divergent beam of X-rays. Even though this procedure is derived for a point source, the calculated corrections apply without restriction to an extended source, the corrections being purely additive with respect to any criterion chosen to represent the diffraction line position.

* Before measuring the camera radii, the roundness of the film cylinder should be checked with a hole gage reading to 0·0001 in. If the out-of-roundness is more than $\pm 0{\cdot}00005$ in. the film cylinder should be rebored to obtain a camera of the highest practical precision.

This procedure requires the measuring tools to be accurate, the film to be truly in contact with the film cylinder (Straumanis & Ievins, 1940*c*), and the film thickness to be uniform. These requirements are readily met to $\pm 0{\cdot}00005$ in. ($\pm 0{\cdot}0013$ mm.) and this satisfies the $\pm 0{\cdot}001$ °φ criterion for cameras 50 to 150 mm. in diameter. Derivations of expressions for P, σ, R, $\Delta\varphi$, and $\Delta\theta$ are presented below.

B. Equations for calculating exact eccentricity corrections

1. *Equations for the eccentricity vector* (P, σ) *and the true camera radius* R.—The three measured radius vectors are designated (r_1, γ), (r_2, ∂), and (r_3, ε).* Then:

$$r_1^2+P^2-2Pr_1\cos(\gamma-\sigma) = R^2 \qquad (1)$$

$$r_2^2+P^2-2Pr_2\cos(\partial-\sigma) = R^2 \qquad (2)$$

$$r_3^2+P^2-2Pr_3\cos(\varepsilon-\sigma) = R^2. \qquad (3)$$

Solving these equations for P, σ, and R yields:

$$P=(r_1^2-r_2^2)/2[r_1\cos(\gamma-\sigma)-r_2\cos(\partial-\sigma)] \qquad (4)$$

$$\sigma=\tan^{-1} \times \left[\frac{(r_3^2-r_2^2)r_1\cos\gamma+(r_1^2-r_3^2)r_2\cos\partial+(r_2^2-r_1^2)r_3\cos\varepsilon}{(r_2^2-r_3^2)r_1\sin\gamma+(r_3^2-r_1^2)r_2\sin\partial+(r_1^2-r_2^2)r_3\sin\varepsilon}\right] \qquad (5)$$

$$R=(r_1^2+P^2-2r_1P\cos(\gamma-\sigma))^{\frac{1}{2}}. \qquad (6)$$

2. *Equations for* $\Delta\theta$ *and* $\Delta\varphi$ *using* (P, σ) *and* R.—Referring to Fig. 2:

$$\Delta 2\theta = 2\theta_{\text{true (corrected)}} - 2\theta_{\text{measured}} = 2\theta_t - 2\theta_m \qquad (7)$$

$$2\theta_t = \sigma+\alpha+\beta\,. \qquad (8)$$

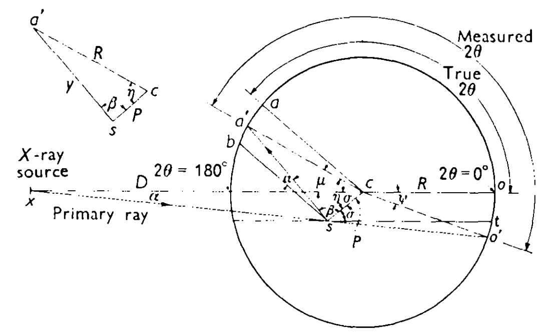

Fig. 2. Geometry for calculating true (corrected) 2θ angles for P in the general position and for a diverging beam of X-rays.

Angle $2\theta_t$ is equal to angle *aco*. Line *ac* is parallel to line *bs*, and line *co* is parallel to line *st*. Therefore angle *aco* is equal to angle *bst*, and angle *bst* is equal to $\sigma+\alpha+\beta$.

$$\alpha=\tan^{-1}[P\sin\sigma/(D-P\cos\sigma)] \qquad (9)$$

* For convenience, the radius vectors are measured counterclockwise with respect to $2\theta=0°$ while σ is measured counterclockwise with respect to $2\theta=180°$.

$$\beta=\cos^{-1}\left[\frac{P-R\cos\left(\sigma+180-2\theta_m+\dfrac{180\left[(R+D)\dfrac{P\sin\sigma}{D-P\cos\sigma}\right]}{\pi R}\right)}{\left(R^2+P^2-2RP\cos\left(\sigma+180-2\theta_m+\dfrac{180\left[(R+D)\dfrac{P\sin\sigma}{D-P\cos\sigma}\right]}{\pi R}\right)\right)^{\frac{1}{2}}}\right]=\cos^{-1}M\,. \quad (10)$$

Then:

$$\Delta 2\theta=\sigma+\tan^{-1}[P\sin\sigma/(D-P\cos\sigma)]+\cos^{-1}M\,. \quad (11)$$

β is evaluated as follows:

Since arc oo' is extremely small, we may assume arc oo' is equal to chord oo' and that xoo' is a right triangle with $(R+D)$ the hypotenuse.* Then chord oo' is equal to $(R+D)\tan\alpha$ and

$$\psi=180(R+D)\tan\alpha/\pi R$$
$$=180(R+D)[P\sin\sigma/(D-P\cos\sigma)]/\pi R \quad (10a)$$

$$\mu=180-(2\theta_m-\psi) \quad (10b)$$

$$\eta=\sigma+\mu=\sigma+180-2\theta_m$$
$$+[180(R+D)(P\sin\sigma/(D-P\cos\sigma))/\pi R] \quad (10c)$$

Solving the triangle in the inset of Fig. 2 yields:

$$y=(R^2+P^2-2RP\cos\eta)^{\frac{1}{2}} \quad (10d)$$

$$\beta=\cos^{-1}[(y^2+P^2-R^2)/2yP]$$
$$=\cos^{-1}[(P-R\cos\eta)/(R^2+P^2-2RP\cos\eta)^{\frac{1}{2}}]\,. \quad (10e)$$

Finally, substituting for η from equation (10c) into (10e), we obtain the equation for β in terms of P, σ, R, and D (equation (10)). $\Delta 2\theta$ is then given by equation (11). Finally, $\Delta\theta=\Delta 2\theta/2$.

$\Delta\varphi$ may be obtained by calculating $\Delta 2\theta$ twice, once each for the corresponding diffraction line segments on each side of $2\theta=180°$. Referring to Fig. 1, the net correction for eccentricity along the film cylinder is

$$[(\text{arc } oa-\text{arc } o'a')+(\text{arc } of-\text{arc } o'f')]=\Delta 4\varphi\,.$$

Finally, $\Delta\varphi=\Delta 4\varphi/4$.

C. *Comparison of exact and approximate methods for eccentricity correction*

The approximate method of Bradley & Jay (1932) is satisfactory if eccentricity corrections need not be determined to an accuracy better than $\Delta\varphi=0{\cdot}01°$, provided the magnitude of P is not greater than 0·01 mm. in a camera about 150 mm. in diameter or less. However, if corrections on the order of $\Delta\varphi=0{\cdot}001°$ are required and $P=0{\cdot}01$ mm. or larger, then the exact method is necessary to calculate accurate correction values. For example, if $P=0{\cdot}0005$ in. (0·0127 mm.), a value readily obtainable in precisely built cameras (Straumanis & Ievins, 1940b), and $\sigma=45°$, the difference between the approximate and the exact eccentricity corrections varies from $-0{\cdot}0014°$ to $+0{\cdot}0056\ °\varphi$ in the range of $\varphi=5°$ to $22{\cdot}5°$. On the other hand, if $\sigma=0°$ or $90°$ the difference between the approximate and exact methods is negligible according to the 0·001° criterion (see Table 1). It is clear, however, that unless σ can be kept in the vicinity of 0° or 90°, the use of the approximate method can lead to errors significantly greater than 0·001 $°\varphi$ for $P=0{\cdot}01$ mm. It seems preferable to have $\sigma=90°$ since the eccentricity error in this case is negligible using either the exact or the approximate method.

Table 1. *$\Delta\varphi$ versus φ eccentricity calculations based on an eccentricity vector $P=0{\cdot}0005$ in. (0·0127 mm.) and various eccentricity angles, σ*

(Camera diameter = 57·3 mm.)

		$\Delta\varphi$ correction required, $°\varphi$		
$°\varphi$	Eccentricity angle, σ	Exact method (A)*	Approximate method (B)*	Difference (A)–(B)
45	0°	+0·0126	+0·0126	0·0000
22·5	0	+0·0089	+0·0089	0·0000
5	0	+0·0018	+0·0021	−0·0003
45	45	+0·0116	+0·0089	+0·0027
22·5	45	+0·0121	+0·0065	+0·0056
5	45	+0·0002	+0·0016	−0·0014
45	90	0·000000	0·000000	0·0000
22·5	90	+0·000014	0·000000	0·0000
5	90	+0·000007	0·000000	0·0000

* (A): This report. (B): (Bradley & Jay, 1932).

D. *Eccentricity measurements on a precision* 57·3 mm. *camera*

A 57·3 mm. Philips camera was rebuilt as a precision camera (Beu & Musil, 1962c), the major rebuilding involving the replacement of the sample spindle with a 0·5 in. steel shaft which was lapped to a precision ground spindle hole. The film cylinder was also precision ground in the same operation as the spindle hole. Provisions for translation as well as rotation of the sample and spindle were also provided (Garlits & Bolt, 1961). The diameter and out-of-roundness of the camera were measured with a Federal hole gage accurate to 0·0001 in. No out-of-roundness was detected. The diameter was 2·26790 in. at the rear (sample spindle) plane of the camera, 2·26795 in.

* Using typical values for a precision 57·3 mm. camera, (i.e., $D=95$ mm., $R=28{\cdot}803$ mm., $P=0{\cdot}001$ mm., $\sigma=90°$) $\alpha=0{\cdot}000764°$ and $\psi=0{\cdot}003290°$. Thus, for these conditions, this assumption causes an error in ψ of only 0·000015°. This is well within the 0·001° criterion.

(57·6059 mm.) at the central plane, and 2·26800 in. at the front (cover plate) plane, indicating a taper of 0·0001 in. over the width (about 35 mm.) of the film cylinder. This slight taper has a negligible effect on accurate film measurements.

The eccentricity of the sample spindle was checked by fastening a dial gage to the spindle with the probe contacting the film cylinder. No variations in dial gage readings were observed when the spindle was rotated, indicating the spindle and the cylinder to be concentric within $\pm 0{\cdot}00005$ in. Assuming the magnitude of P to have its maximum value of 0·00005 in. and for P to have an undesirable orientation (i.e., $\sigma=45°$), $\Delta\theta$ varies from $-0{\cdot}0020°$ to $-0{\cdot}0021°$ in the range of θ from 45° to 85° (Fig. 3), while $\Delta\varphi$ varies from $+0{\cdot}0011°$ to $+0{\cdot}0002°$ in the same range, namely, φ from 45° to 5°. It should be remembered that these values for $\Delta\theta$ and $\Delta\varphi$ are based on the assumption of unfavorable conditions for (P, σ) and that the actual eccentricity may be less than indicated.

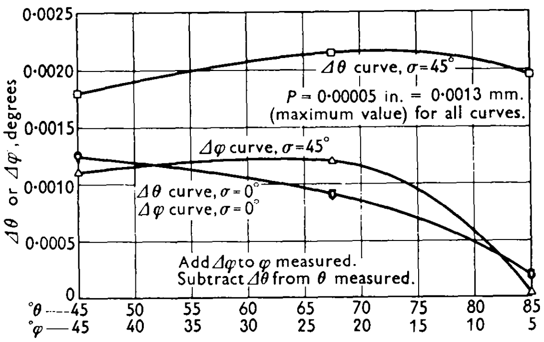

Fig. 3. $\Delta\theta$ versus θ and $\Delta\varphi$ versus φ using exact eccentricity corrections for a precision 57·3 mm. powder camera.

Ordinarily, for lattice parameter work using this precision camera, φ angles are measured for φ less than 45°. The eccentricity corrections for these conditions, again assuming unfavorable values for P and σ, are not greater than $+0{\cdot}0015\ °\varphi$ in this range. However, these data illustrate that, unless extreme care is taken in building and checking the tolerances of a cylindrical camera, the eccentricity error may easily become significant and require correction according to the 0·001° criterion. It should be noted that correction curves such as those illustrated in Fig. 3 are valid as long as nothing is done to change the sample spindle centering.

Thanks are due K. L. Ritchie and F. J. Musil for helpful discussions and to R. R. Garlits for rebuilding the camera and making the required measurements.

References

Averbukh, E. D. & Tolkachev, S. S. (1957). *Uchenye Zapiski Leningrad, Gosudarst. Univ. im. A. A. Zhdanova* No. 211, *ser. Khim. Nauk.* No. 15, 223. [Translated by V. Lagunoff as USAEC Report GAT-Z-5025 (July 21, 1961)].

Beu, K. E., Musil, F. J. & Whitney, D. R. (1962). *Acta Cryst.* **15**, 1292.

Beu, K. E., Musil, F. J. & Whitney, D. R. (1962*a*). *The Precise and Accurate Determination of Lattice Parameters Using Film Powder Diffraction Methods: The Likelihood Ratio Method.* USAEC Report GAT-392. (In preparation.)

Beu, K. E. & Scott, D. L. (1962*b*). *The Precise and Accurate Determination of Lattice Parameters Using Film Powder Diffraction Methods: The Eccentricity Correction.* USAEC Report GAT-392. (In preparation.)

Beu, K. E. & Musil, F. J. (1962*c*). *The Precise and Accurate Determination of Lattice Parameters Using Film Powder Diffraction Methods: A Precision* 57·3 mm. *Camera.* USAEC Report GAT-392. (In preparation.)

Bradley, A. J. & Jay, A. H. (1932). *Proc. Phys. Soc.* (*London*), **44**, 569.

Garlits, R. R. & Bolt, C. C. (1961). *Norelco Rep.* **8**, 37.

Straumanis, M. E. & Ievins, A. (1940). *Die Praezisionbestimmung von Gitterkonstanten nach der Asymmetrischen Methode.* Berlin: Springer.

Straumanis, M. E. & Ievins, A. (1940*a*). *The Precision Determination of Lattice Constants by the Asymmetric Method.* [Originally published in German by Julius Springer, Berlin, and translated in part by K. E. Beu (April 15, 1959) as USAEC Report GAT-T-643].

Straumanis, M. E. & Ievins, A. (1940*b*). *The Precision Determination of Lattice Constants by the Asymmetric Method*, p. 19.

Straumanis, M. E. & Ievins, A. (1940*c*). *The Precision Determination of Lattice Constants by the Asymmetric Method*, p. 49.