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The Evaluation of Centroid Lattice Parameter Data for Tungsten by the Likelihood Ratio Method*

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The likelihood ratio method (*LRM*) was used to determine $\hat{\hat{a}}_0$, the maximum likelihood estimate of a_0 for tungsten under the hypothesis of 'no remaining systematic errors' in the Bragg angle measurements. $\hat{\hat{a}}_0$ was determined using centroid Bragg angle and systematic error correction data for tungsten powder. These data were kindly supplied by Dr B. W. Delf of Prof. A. J. C. Wilson's laboratory. The data were further used to evaluate various characteristics of the *LRM* related to lattice parameter precision and accuracy.

Wave length accuracy is not included in the discussion since the *LRM* can be used only to evaluate the precision and accuracy of the Bragg angle measurements corrected for systematic errors other than wave length. This problem, however, can be essentially by-passed by stating the centroid wave length value, albeit fictitious, which is used in the Bragg equation to calculate a given lattice parameter value. This centroid wave length would have truncation limits equivalent to the angular truncation limits used in calculating the centroid values for the diffraction profiles.

The W_m test function of the *LRM* indicated that all six systematic error corrections used by Delf were necessary and sufficient to remove the systematic errors within the precision of measurement. The $\hat{e}_i$ test function indicated a slight discrepancy in the angular scale correction for the 110 reflection; however, this discrepancy was insufficient to affect the accuracy of $\hat{\hat{a}}_0$ based on the value of W_m obtained when using all six corrections. This analysis of the tungsten data indicates that the W_m and $\hat{e}_i$ test functions of the *LRM* are adequate in providing accurate lattice parameter estimates as well as in determining real or potential difficulties in systematic error correction procedures.

$\hat{\hat{a}}_0$ was compared to extrapolated a_0 values for Delf's uncorrected centroid data. With the use of a cot θ extrapolation because of the predominating zero error correction, the extrapolated a_0 value was found to differ significantly (about ten times the 95% confidence limits on $\hat{\hat{a}}_0$) from $\hat{\hat{a}}_0$.

Introduction

The likelihood ratio method (*LRM*) is a statistical method which indicates when an accurate lattice parameter value has been attained after the systematic errors have been removed from the data within the precision of the Bragg angle measurements (Beu, Musil & Whitney, 1962; hereafter designated reference I). The *LRM* was originally developed for crystals of cubic symmetry but has been extended to include tetragonal and hexagonal crystals (Beu, Musil & Whitney, 1963).

The *LRM* is not an extrapolation method nor does it assess the accuracy of the wave length value used in the Bragg equation. As long as the same wave length value (peak, centroid, or other suitable feature of the characteristic wave length distribution) is used by all concerned, the wave length and Bragg angle accuracy problems can be handled separately. In the case of centroid Bragg angle determinations, this further implies that the truncation limits (wave length range) used for the centroid wave length value in the Bragg equation are equivalent to the truncation limits used for calculating the centroid angles from the diffraction profile data.†

The *LRM* is based on evaluating the internal consistency of the Bragg angle measurements for a given sample and is concerned only with the precision and accuracy of these measurements corrected for

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† A difficulty arises here since centroid wave lengths and their truncation limits have not yet been published. Other problems, such as the effect of filters on the wave length distribution in the vicinity of the characteristic radiation of interest, which actually reaches the sample, also arise. Until such problems are solved and centroid wave length data become available, it is suggested that a fictitious centroid wave length value be used; *i.e.*, the weighted mean $K\alpha$ wave length, designated $\lambda_{g(WM)}$. $\lambda_{g(WM)}$ could then be defined as that centroid wave length which has truncation limits corresponding to the Bragg angle truncation limits. It would, of course, be necessary to choose self-consistent angular truncation limits of sufficient width so that truncation error is minimized and so that the same value of $\lambda_{g(WM)}$ would apply to each centroid Bragg angle value. In addition, it would be necessary to specify in detail the truncation procedure used in determining the limits. Following this procedure based on $\lambda_{g(WM)}$, two or more observers may compare lattice parameter data and ascribe differences to factors other than wave length, factors which are responsive to the *LRM*.

all systematic errors except wave length or wavelength-dependent factors such as the kX-to-Ångström conversion (Lonsdale, 1950) or that part of the refraction correction due to wave length change within the crystal (Wilson, 1940).

Briefly, the *LRM* is based on the concept that a function (e_i) related to the systematic error remaining in a Bragg angle measurement (ψ_i) is related to the true, but unknown, value of the Bragg angle (θ_i) by the equation:

$$e_i = \psi_i - \theta_i \, .$$

The hypothesis (H) is then made that there are 'no remaining systematic errors' in the ψ_i after the ψ_i have been corrected for systematic errors; *e.g.*, H: $e_i = 0$. Based on this hypothesis, a likelihood ratio function (W_m) is derived* which can be shown to be distributed like chi-square† according to a theorem in statistics (Mood, 1950*a*). The extent of systematic error removal from the ψ_i is determined by comparing W_m with w_ε, a critical value of the chi-square distribution. If $W_m \geq w_\varepsilon$, the hypothesis is rejected; on the other hand, if $W_m < w_\varepsilon$, the hypothesis is accepted, at the ε significance level, that there are 'no remaining systematic errors' in the corrected ψ_i values. In this case $\hat{\hat{a}}_0$, the maximum likelihood estimate of a_0 under the hypothesis, has been determined (see, for example, Mood (1950*b*) for a discussion of maximum likelihood estimation). $\hat{\hat{a}}_0$ corresponds to the value of W_m obtained in a plot of a_0 *versus* $W(a_0)$ as will be illustrated in the example to be given in this paper. For further details see reference I.

In addition to providing the estimate $\hat{\hat{a}}_0$, the *LRM* can be used to determine the validity of a given systematic error correction procedure in terms of the W_m and $\hat{e}_i$ (maximum likelihood estimate of e_i) test functions. W_m provides a measure of the over-all effect of a given systematic error correction on all the measured Bragg angles while $\hat{e}_i$ indicates if a given correction to a given Bragg angle measurement is valid. Only if W_m and $\hat{e}_i$ decrease after applying a given correction can it be said that that correction is significant and useful.

Using the *LRM*, $\hat{\hat{a}}_0$ was calculated (reference I) from the Bragg angle of Bond (1960), for a silicon single crystal, and was shown to be precise and accurate to one part in 390,000 [$\hat{\hat{a}}_0 = 5{\cdot}430736 \pm 0{\cdot}000014$ Å (95% confidence limits for 12 measurements on three diffraction peaks) at 25 °C and based on a Cu $K\alpha_1$ wave length of 1·540510 Å]. Bond's data were obtained with a symmetrical diffractometer (measurements made on both sides of zero and 180° 2θ). The *LRM* demonstrated that only one of the three calculated corrections used by Bond was significant

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* W_m is the minimum value of $W(a_0)$.

where:

$$W(a_0) = \sum_i n_i \ln \left[1 + \frac{(\psi_i - \theta_i)^2}{s_i^2} \right]$$

n_i represents the number of measurements of the ith Bragg angle;

s_i is the standard deviation estimate of ψ_i.

$$s_i^2 = \frac{1}{n_i} \sum_\alpha (\psi_{i\alpha} - \psi_i)^2 .$$

(Note that n_i is used instead of $(n_i - 1)$ in calculating s_i^2. This is a consequence of maximum likelihood estimation.)

$\psi_{i\alpha}$ is the αth measurement of the ith angle.

† Chi-square is a distribution used for testing hypotheses.

Table 1. *Delf's centroid data for tungsten corrected to* 18 °C

hkl	110	211	310	321
Average 2θ (measured)	39·5012	72·4716	99·9392	130·6092
Average $\theta = \psi_i$ (uncorrected)	19·7506	36·2358	49·9696	65·3046
n_i (number of measurements)	7	7	9	8
s_i^2 $(\theta°)^2$	$60{\cdot}9 \times 10^{-8}$	$29{\cdot}9 \times 10^{-8}$	$75{\cdot}8 \times 10^{-8}$	602×10^{-8}
s_i $(\theta°)$	0·0008	0·0006	0·0009	0·0025
Truncation limits* (angular range, $\theta°$)	0·80	0·94	1·48	2·42

Corrections (°2θ)

	Correction code number					
hkl	1	2	3	4	5	6
110	+0·7675	+0·0053	+0·0080	+0·0160	0	−0·0015
211	+0·7675	+0·0045	+0·0039	+0·0050	0	+0·0039
310	+0·7675	+0·0036	+0·0391	0	0	−0·0003
321	+0·7675	+0·0023	+0·0212	−0·0074	−0·0050	−0·0020

Code No.	Type of correction
1	Zero
2	Specimen-surface displacement
3	Flat specimen
4	Vertical divergence
5	Dispersion, Lorentz and polarization
6	Angular scale

(The transparency error was taken as zero for all lines)

* Truncation method described by Delf (1963).

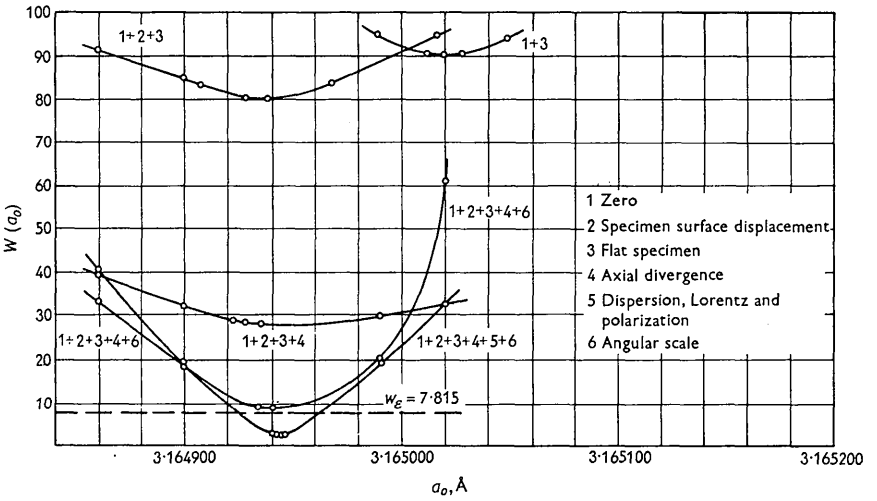

Fig. 1. $W(a_0)$ *versus* a_0 for Delf's data on tungsten (various combinations of systematic error corrections).

and this correction (refraction) was sufficient to reduce W_m below w_ε, thereby permitting the determination of $\hat{\hat{a}}_0$.

This article presents a further evaluation of the *LRM* based on centroid Bragg angle data for tungsten which were kindly supplied by Dr B. W. Delf. The centroid method used by Delf was developed largely in Prof. A. J. C. Wilson's laboratory (Wilson, 1950; Pike, 1957; Pike & Wilson, 1959; Pike & Hughes, 1959; Delf, 1961, 1963). A summary of Delf's original data and systematic error corrections is given in Table 1. The measured 2θ and θ (or ψ_i) angles are given to four decimal places based on s_i, the standard deviation estimates for these measurements. s_i varied from 0·0006° to 0·0024° θ for the four diffraction lines of tungsten measured by Delf. The data in Table 1 furnish the basis for the *LRM* evaluation to follow.

LRM evaluation of Delf's centroid data

Evaluation of data in terms of W_m

W_m was determined for Delf's uncorrected data and for his data corrected for various systematic error combinations as shown in Table 2. W_m values were determined from $W(a_0)$ *versus* a_0 curves similar to those given in Fig. 1 for some of the error correction combinations listed in Table 2. W_m was reduced from 252 for no corrections to 239 ± 1 for corrections No. 2 to 6 taken one at a time and to 109 for correction No. 1 (see Table 1 for coding of error corrections). Each correction reduced W_m, which indicates that all six corrections were significant and useful. Correction No. 1 was apparently the most significant correction since it reduced W_m more than any of the other five corrections. This may have been expected since No. 1 was the largest of the six corrections; however, it was also a constant correction to each measured centroid value. This demonstrates that the *LRM* is sensitive to Bragg angle corrections of constant, as well as variable, magnitude.

W_m continued to decrease (Table 2) as corrections were added one at a time. (Corrections for centroid data may be combined simply by adding the numerical values algebraically (Pike & Wilson, 1959).) This verifies the observation already made that each correction was significant and useful. After all six corrections had been applied, W_m was reduced to 2·503, a value less than w_ε for the experimental conditions used. [$w_\varepsilon = 7{\cdot}815$ at the 0·05 significance level (corresponding to 95% confidence limits) and for three degrees of freedom (corresponding to the four measured diffraction profiles). w_ε was obtained from a table of chi-square distribution (Hodgman, 1959).] The fact that W_m was less than w_ε (1) verifies that all six corrections were not only useful but necessary and sufficient in removing the systematic errors from the data within the precision of measurement and (2) indicates that the assumption of a zero transparency error correction is probably valid (a reasonable assumption because of the extremely high absorption of Cu $K\alpha$ radiation in tungsten).

Table 2. *Values of* W_m *for various systematic error corrections to measured* ψ_i *values*

Corrections*	W_m
None	252
2, 3, 4, 5, or 6	239 ± 1
1	109
1+3	90·3
1+2+3	80·0
1+2+3+4	28·2
1+2+3+4+5	20·5
1+2+3+4+6	8·95
—	$7{\cdot}815 = w_\varepsilon$
1+2+3+4+5+6	2·503

* See Table 1 for correction code.

Table 3. *Effect of No. 5 (dispersion, Lorentz and polarization) correction on* W_m

	Tungsten reflections				
Correction used	110	211	310	321	W_m
ψ_i corrected for 1+2+3+4+6, $\theta°$	20·1483	36·6282	50·3746	65·6954	8·95
No. 5 correction, $\theta°$	0·0000	0·0000	0·0000	−0·0025	—
ψ_i corrected for 1+2+3+4+6+5, $\theta°$	20·1483	36·6282	50·3746	65·6929	2·503

$\hat{\hat{a}}_0$ corresponding to $W_m=2{\cdot}503$ was found to be $3{\cdot}164944 \pm 0{\cdot}000018$ Å (95% confidence limits based on 31 measurements on four diffraction profiles)* for IUCr tungsten powder at 18 °C, uncorrected for refraction,† and using a fictitious centroid wave length, namely the weighted mean Cu $K\alpha$, $\lambda_{g(WM)}=1{\cdot}541760$ Å, with a wave length range of 0·018 Å (the method of truncation is described by Pike & Wilson (1959)‡). This value of $\hat{\hat{a}}_0$ is precise and accurate to about one part in 180,000 based on the stated qualifications.§

The sensitivity of the *LRM* to small but necessary corrections is indicated by observing the decrease in W_m when the No. 5 correction (dispersion, Lorentz and polarization) is applied last (Table 3). The No. 5 correction is very small (zero for three reflections and $-0{\cdot}0025° \theta$ for the fourth). By applying all corrections except the No. 5, $W_m=8{\cdot}95$ (larger than w_ε); on the other hand, including the No. 5 correction reduced W_m to 2·503 (smaller than w_ε). Thus, the No. 5 correction is necessary to reduce W_m below w_ε even though it seems to be relatively insignificant, numerically.

Evaluation of data in terms of $\hat{e}_i$

$\hat{e}_i$'s are maximum likelihood estimates of e_i for which $\sum_i e_i=0$ to the desired number of decimal places. In practice, two estimates of a_0 are chosen in solving for two θ_i's using the Bragg equation in the form: $a_0 \sin\theta_i=K_i$. (K_i is used here instead of k_i as used in reference I to avoid confusion with the Miller index k.) These θ_i's are used to calculate e_i's and $\sum_i e_i$ based on the equation $e_i=\psi_i-\theta_i$. Only two estimates of a_0 are required such that the corresponding values of $\sum_i e_i$ are positive and negative. $\hat{a}_0$ corresponding to $\sum_i e_i=0$ is then obtained by interpolation since a_0 estimates vary linearly with $\sum_i e_i$. After $\hat{a}_0$ is determined, $\hat{e}_i$'s and $\hat{\theta}_i$'s are calculated by the equations: $\hat{a}_0 \sin\hat{\theta}_i=K_i$ and $\hat{e}_i=\psi_i-\hat{\theta}_i$.

In general, it was observed that the $\hat{e}_i$'s for the individual diffraction lines decreased in absolute value after application of each systematic error correction, as would be expected if the corrections were valid. There was one small, but clear-cut, exception to this observation in that $\hat{e}_i$ for the 110 reflection increased slightly after application of the No. 6 correction (angular scale).* This effect was observed (Table 4) whether No. 6 was applied at an early stage of correction (Group A: 1+3 corrections) or at the last stage (Group B: 1+2+3+4+5 corrections). $\hat{e}_i$'s for the (110) reflection increased in absolute value from 0·0094 to 0·0101° θ and from 0·0003 to 0·0004° θ for Groups A and B, respectively, after applying No. 6.

* The 95% confidence limits (95% L.E.) are calculated based on s_{a_0}, an estimate of the standard deviation of $\hat{\hat{a}}_0$; 95% L.E. $=\pm 1{\cdot}96 s_{a_0}$. (See page 1153 for the equation for s_{a_0}.)

† The refraction correction for powders is primarily due to the wave length change within the crystallites (Wilson, 1940) and, in this case, is applied as a correction to $\hat{\hat{a}}_0$ after $\hat{\hat{a}}_0$ has been determined using the *LRM*.

‡ This procedure has been modified slightly by Delf (Delf, 1963) and is described in detail by Beu (1964).

§ *Note added in proof.* — $\hat{\hat{a}}_0$ calculated at 25 °C and corrected for refraction is $3{\cdot}16519 \pm 0{\cdot}000018$ Å (95% confidence limits). This is to be compared with $\bar{a}=3{\cdot}165190$ Å given by Delf for the same data but calculated in a different manner (Delf, 1963). Both $\hat{\hat{a}}_0$ and $\bar{a}$ agree within the stated confidence limits.

* Dr Delf had some reservations about the angular scale correction for the diffractometer he used; however, the *LRM* demonstrated that these corrections were essentially of the proper magnitude.

Table 4. *Effect of No. 6 (angular scale) correction on* $\hat{e}_i$

	Before applying No. 6		After applying No. 6		
Group	Corrections	$\hat{e}_i$ ($\theta°$)	Corrections	$\hat{e}_i$ ($\theta°$)	*hkl*
A	1+3	−0·0094	1+3+6	−0·0101	110
		−0·0046		−0·0026	211
		+0·0015		+0·0014	310
		+0·0124		+0·0114	321
B	1+2+3+4+5	+0·0003	1+2+3+4+5+6	−0·0004	110
		−0·0018		+0·0001	211
		+0·0001		−0·0001	310
		+0·0014		+0·0004	321

On the other hand, all of the $\hat{e}_i$'s for the other three reflections decreased in absolute value or remained the same after applying No. 6 to either Group *A* or *B*.

The No. 6 correction for the 110 reflection thus seems to be slightly incorrect, but not sufficiently so as to affect W_m adversely since W_m decreased when No. 6 was applied to all the measured lines. The data in Table 4 illustrate the utility of the $\hat{e}_i$ function in pinpointing potential (and, presumably, real) difficulties when making systematic error corrections to individual diffraction lines.

As a final note about the $\hat{e}_i$'s, it is of interest to compare corresponding $\hat{e}_i$ values between Groups *A* and *B*. The large decrease in $\hat{e}_i$ for a given diffraction line after many corrections are applied becomes immediately apparent.

Comparison of $\hat{a}_0$, $\hat{\hat{a}}_0$, s_{a_0}, *and* Δa_0

$\hat{a}_0$ and $\hat{\hat{a}}_0$ have been previously defined. The difference between these estimates of a_0 is related to the systematic error remaining in the Bragg angle measurements. It is interesting to note that the difference between $\hat{a}_0$ and $\hat{\hat{a}}_0$ for the 'all correction' case is less than s_{a_0},† an estimate of the standard deviation of $\hat{\hat{a}}_0$, only when $W_m < w_\varepsilon$. In this case, the two estimates are:

$$\hat{\hat{a}}_0 = 3{\cdot}164944\,2 \text{ Å} \quad (W_m = 2{\cdot}503)$$
$$\hat{a}_0 = 3{\cdot}164943\,7 \text{ Å} \quad (\textstyle\sum_i \hat{e}_i = 0{\cdot}0000^\circ\ \theta)$$
$$\text{Difference} \quad 0{\cdot}000000\,5 \text{ Å}$$

and $s_{a_0} = 0{\cdot}000009$ Å. This explicitly illustrates that the systematic errors have been removed from the data within the precision of measurement when $W_m < w_\varepsilon$ since s_{a_0} is about twenty times as large as the difference between $\hat{a}_0$ and $\hat{\hat{a}}_0$.

The magnitude of s_{a_0} (based on n_i measurements of m diffraction lines for a total of N measurements where $N = \sum_{i=1}^{i=m} n_i$) is comparable to the precision obtainable by making N measurements at the highest Bragg angle alone based on the widely used equation for precision of a_0: $|\Delta a_0| = a_0 \cot\theta |\Delta\theta|$. s_{a_0}, however, has the added advantage of providing a standard deviation estimate of $\hat{\hat{a}}_0$, a quantity which has been tested for both precision and accuracy, while $|\Delta a_0|$ is only a measure of precision of an a_0 which is not necessarily an accurate value based on the internal consistency of the Bragg angle measurements.

For Delf's data, the highest angle measured was $130{\cdot}6^\circ\ 2\theta$ ($65{\cdot}3^\circ\ \theta$) and this angle was measured with a precision of $s_{(321)} = 0{\cdot}0025^\circ\ \theta$ per measurement. In this case $|\Delta a_0| = 0{\cdot}000063$ Å per measurement. Since Delf made a total of 31 measurements on four reflections, the precision per 31 measurements is $|\Delta a_0|/\sqrt{(31)} = 0{\cdot}000011$ Å and this is comparable to $s_{a_0} = 0{\cdot}000009$ Å.

Comparison of extrapolated values of a_0 *with* $\hat{\hat{a}}_0$ *for tungsten*

It is of some interest to compare $\hat{\hat{a}}_0$ with a_0 values obtained by extrapolation methods. Since the largest systematic error is the zero correction, the appropriate extrapolation function is $\cot\theta$ (*International Tables for X-ray Crystallography*, 1959). Fig. 2 shows an extrapolation plot of a_0 *versus* $\cot\theta$ for Delf's uncorrected data. The data fit a straight line very closely and the extrapolated value of a_0 agrees remarkably well with $\hat{\hat{a}}_0$ in spite of the fact that the highest θ value used was only $65{\cdot}3^\circ$. On a larger graph than Fig. 2, it can be seen that the extrapolated a_0 value actually differs from $\hat{\hat{a}}_0$ by about ten times the 95% confidence limits of $\hat{\hat{a}}_0$, indicating that a_0 and $\hat{\hat{a}}_0$ are significantly different. Correcting the data for all systematic errors except zero error caused no significant change in the extrapolated value of a_0; *i.e.*, $\hat{\hat{a}}_0$ and a_0 still differ by about ten times the 95% confidence limits of $\hat{\hat{a}}_0$. This may indicate that the $\cot\theta$ function is not entirely adequate in removing the effects of zero error from these data by extrapolation or that the highest available angle ($65{\cdot}3^\circ\ \theta$) was not high enough for a satisfactory extrapolation.

If the data are corrected for all six systematic errors, the a_0 values fall within the 95% L.E. for $\hat{\hat{a}}_0$ regardless of the extrapolation function used. This is

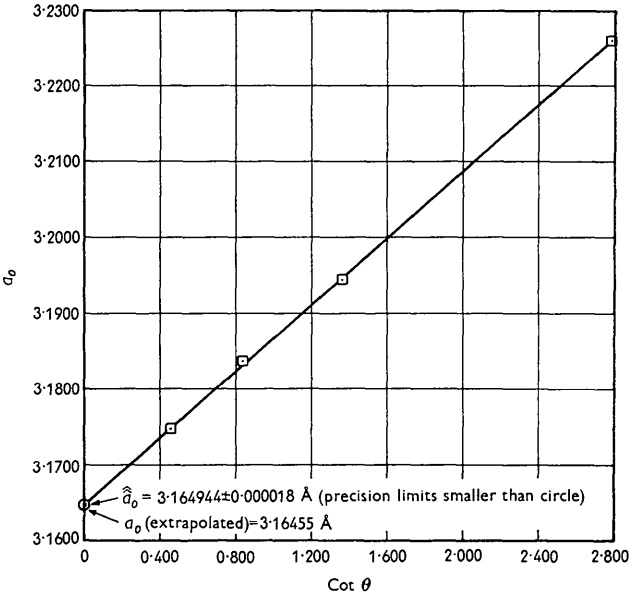

Fig. 2. Cot θ extrapolation plot for Delf's uncorrected data on tungsten.

† $s^2_{a_0} = \hat{\hat{a}}_0^2 / \sum_i (n_i/\hat{\hat{\sigma}}_i^2) \tan^2\hat{\hat{\theta}}_i$.

This equation is solved for s_{a_0} using: $\hat{\hat{a}}_0 \sin\hat{\hat{\theta}}_i = K_i$ where $K_i = n\lambda/(h^2+k^2+l^2)/2$ (for cubic materials) and $\hat{\hat{\sigma}}_i^2 = s_i^2 + (\psi_i - \hat{\hat{\theta}}_i)^2$.

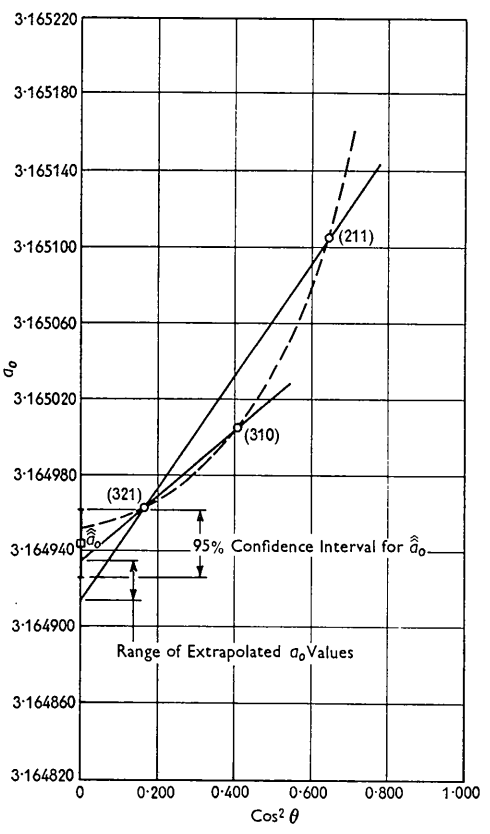

Fig. 3. $\cos^2\theta$ extrapolation plot for Delf's data corrected for all systematic errors except specimen-surface displacement.

not surprising since, if systematic errors are properly eliminated, the data should fall on a straight, horizontal line within the precision of measurement.

Wilson (1950) has pointed out that Bragg angle data corrected for all systematic errors except sample surface displacement from the diffractometer axis of rotation (S–S displacement error) can be used in a $\cos^2\theta$ or $\cos\theta\cot\theta$ extrapolation to eliminate the effect of S–S displacement error. To test this, a $\cos^2\theta$ extrapolation was made (Fig. 3) with Delf's data corrected for all except S–S displacement error. In order to be able to see the 95% L.E. of $\hat{\hat{a}}_0$ on this graph, it was necessary to omit the last point ($\cos^2\theta = 0{\cdot}886$). The other three points fall on a smooth curve (dotted line) which intersects the ordinate axis within the 95% L.E. range of $\hat{\hat{a}}_0$. With the 321 value as a pivot point and the 310 and 211 values to fix the slopes of two extrapolation lines, extrapolated a_0 values were found to fall in the range of 3·164915 to 3·164935 Å with the higher value falling within the 95% L.E. This indicates that the $\cos^2\theta$ extrapolation to eliminate S–S displacement error is valid if used with caution. On the basis of available data, it seems that a smooth curve drawn through the experimental points is also satisfactory.

Thanks are due to Prof. D. R. Whitney for many helpful discussions and to Frank J. Musil, Phyllis Fustanio, William Butler, Mrs Mary Greer, Donald Scott, and Verlin Webb who carried out the numerous calculations involved.

References

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

Beu, K. E., Musil, F. J. & Whitney, D. R. (1963). *Acta Cryst.* **16**, 1241.

Beu, K. E. *The Precise and Accurate Determination of Lattice Parameters by X-ray Diffraction Methods.* (1964). E. F. Kaelble, ed. *Handbook of X-rays.* New York: To be published by McGraw-Hill.

Bond, W. L. (1960). *Acta Cryst.* **13**, 814.

Delf, B. W. (1961). *Brit. J. Appl. Phys.* **12**, 421.

Delf, B. W. (1963). *Brit. J. Appl. Phys.* **14**, 345.

Hodgman, C. D. (1959). *Handbook of Chemistry and Physics.* 40th ed., p. 218–9. Cleveland: Chemical Rubber Publishing Co.

Lonsdale, K. (1950). *Acta Cryst.* **3**, 400.

International Tables for X-ray Crystallography (1959). Vol. II. p. 221. Birmingham: Kynoch Press.

Mood, A. M. (1950*a*). *Introduction to the Theory of Statistics.* p. 259. New York: McGraw-Hill.

Mood, A. M. (1950*b*). *Introduction to the Theory of Statistics,* Chap. 8. New York: McGraw-Hill.

Pike, E. R. (1957). *J. Sci. Instrum.* **34**, 355.

Pike, E. R. & Wilson, A. J. C. (1959). *Brit. J. Appl. Phys.* **10**, 57.

Pike, E. R. & Hughes, J. W. (1959). *J. Sci. Instrum.* **36**, 212.

Wilson, A. J. C. (1940). *Proc. Camb. Phil. Soc.* **36**, 485.

Wilson, A. J. C. (1950). *J. Sci. Instrum.* **27**, 321.