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# Precise and Accurate Lattice Parameters by Film Powder Methods. I. The Likelihood Ratio Method*

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A statistical method called the Likelihood Ratio Method (*LRM*) has been developed which permits determining lattice parameters accurately within the precision of the Bragg angle measurements if these measurements have been individually corrected for systematic errors. The *LRM* incorporates a test (the *LRT*) which indicates when the systematic errors have been removed from the X-ray data in a valid statistical manner. The *LRM* is applicable to all diffractometer or film methods which can be corrected for systematic errors.

An application of the *LRM* is given involving analysis of the lattice parameter data on zone refined silicon, published by W. L. Bond. Of the three systematic error corrections used by Bond, only the application of the refraction correction satisfied the *LRT*. Using this correction, the maximum likelihood estimate of $a_0$ under the hypothesis of 'no remaining systematic errors,' designated $\hat{a}_0$, was calculated to be $5{\cdot}430736 \pm 0{\cdot}000014$ Å (95% confidence limits) at 25 °C. and based on a Cu $K\alpha_1$ wavelength of 1·540510 Å. The value $\hat{a}_0$ for this sample of silicon is accurate within the stated precision (one part in 390,000). This implies that, if another individual measured the lattice parameter of this sample with the stated precision using the same wavelength value and a diffraction technique which permits correcting the individual measurements for systematic error in a valid statistical manner, his average value would agree with the above value within one part in 390,000 at the 95% confidence level.

## 1. Introduction

In recent years, lattice parameter data using X-ray techniques have been reported with precisions exceeding one part in 50,000 (Straumanis & Ievins, 1940; Straumanis, 1960; Vogel & Kempter, 1959; Mueller, Heaton & Miller, 1960; Mueller & Heaton, 1961; Bond, 1960). In view of the high precisions claimed for a wide variety of techniques, it is disconcerting to observe the poor agreement obtained by various observers on samples distributed in connection with the International Union of Crystallography (IUCr) Project on Lattice Parameters (Parrish, 1960). In several respects this project was conducive to obtaining good agreement; i.e., the same sample was subsampled and distributed to participating laboratories, and it was agreed to use the same X-ray wavelength values, refraction corrections, expansion coefficients, etc. In spite of these favorable circumstances, the agreement turned out to be relatively poor compared to the reported precisions. This clearly indicates that systematic errors in the measurements of the various laboratories have not been eliminated from the lattice parameter calculations. Thus, while the precision may have been good, the accuracy was relatively poor.

A major limitation of any lattice parameter technique described in the literature is the lack of a suitable statistical yardstick for assessing the accuracy of the calculated lattice parameter values. For example, a least-squares extrapolation with or without weighting, in spite of its statistical implications, does not provide data for assessing the accuracy of the lattice parameter thus determined. This makes it difficult or impossible to determine whether or not the systematic errors have been truly removed within the precision of measurement.†

It is the purpose of this paper to describe a statistical method, called the Likelihood Ratio Method, which indicates when an accurate value of the lattice parameter has been attained after the systematic errors have been removed within the precision of measurement; to give an example of one case in

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† It is assumed that only precisions of at least $\pm 0{\cdot}005\%$ or one part in 20,000 are of interest here. Wavelength accuracy is not included in this discussion. As long as the same wavelength value (peak, center of gravity, or other suitable feature of the characteristic wavelength distribution) is used by all concerned, the wavelength and lattice parameter accuracy problems can be handled separately.

which this has been accomplished; and to discuss the significance of these findings. This method was first presented in preliminary form by title (Beu, Musil & Whitney, 1959) at the IUCr Lattice Parameter Conference held in Stockholm, Sweden, on June 10 and 11, 1959.

This paper represents part of a project to evaluate the maximum practical precision and accuracy attainable in lattice parameter determinations using a cylindrical film powder diffraction method. This project does not involve the asymmetrical diffractometer approach (Pike & Wilson, 1959; Ladell, Parrish & Taylor, 1959), nor does it involve extrapolation methods (Bradley & Jay, 1932; Cohen, 1935) with their inherent limitations. It does not deal with the wavelength accuracy problem which, except for the centroid method (Pike & Wilson, 1959), can be handled separately from the parameter problem.

The approach used is a modification of the Straumanis method (Straumanis & Ievins, 1940) and involves measuring diffraction line positions on film to a precision of about $\pm 0{\cdot}001°$ $\varphi$, correcting each measurement for geometrical systematic errors, and calculating the lattice parameter from the corrected data by means of a rigorous statistical method called the Likelihood Ratio Method (*LRM*). The *LRM* provides an accurate estimate of the lattice parameter $\hat{a}_0$, its variance $s^2_{a_0}$, and a test (the Likelihood Ratio Test) which indicates whether or not the systematic errors have been eliminated from the measurements in a valid statistical manner. Examples of the application of the *LRM* are given.

## 2. Definitions and assumptions

A. *Definitions*

$e_i$ is the unknown systematic error at $\theta_i$ in degrees $\theta$.

$\theta_i$ is the true but unknown value of the Bragg angle $\theta$, in degrees $\theta$ [approximate values of $\theta_i$ are also used in determining $W(a_0)$, see Section 3, B].

$\psi_{i\alpha}$ is the $\alpha$th measurement of the $i$th diffraction angle, corrected for known systematic errors, in degrees $\theta$.

$\psi_i$ is the average of $n_i$ measurements of $\psi_{i\alpha}$. $\psi_i=(1/n_i)\sum_\alpha \psi_{i\alpha}$.

$\sigma_i^2$ is the variance of the $\psi_{i\alpha}$ (see Assumptions).

$s_i^2$ is the experimentally determined variance of $\psi_{i\alpha}$. $s_i^2=(1/n_i)\sum_\alpha (\psi_{i\alpha}-\psi_i)^2$.

$k_i$ $=n\lambda\sqrt{(h^2+k^2+l^2)}/2$ (for cubic materials) where $n$, $\lambda$, $h$, $k$, and $l$ have their usual crystallographic meanings.

$a_0$ is the true lattice parameter of a cubic material in Å [approximate values of $a_0$ are also used in determining $W(a_0)$].

$H$ is the hypothesis of 'no remaining systematic errors'; $e_i=0$ for all $i$.

$W(a_0)$ is a function used to determine $a_0$ and to test $H$.

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

$w_\varepsilon$ is the critical value of the test statistic, $W_m$.

$\varepsilon$ is the significance level of the test.

$\hat{a}_0$, $\hat{e}_i$, $\hat{\sigma}_i^2$, $\hat{\theta}_i$ are maximum likelihood estimates of these parameters under the Assumptions (see below). Single carets are used to indicate these estimates. Otherwise these parameters are defined exactly as given above.

$\hat{\hat{a}}_0$, $\hat{\hat{\sigma}}_i^2$, $\hat{\hat{\theta}}_i$ are maximum likelihood estimates of these parameters under the hypothesis $H$. Double carets are used to indicate these estimates under $H$.

B. *Assumptions*

1. $\psi_{i\alpha}$ is a normal random variable.
2. The $\psi_{i\alpha}$ are independent for:
   $i = 1, \ldots, m$ (the number of diffraction angles measured).
   $\alpha = 1, \ldots, n_i$ (the number of measurements at the $i$th diffraction angle).
   $\sum_i n_i = N$ (the total number of measurements).
3. The mean or expected value of $\psi_{i\alpha}$ is given by:
   $$E(\psi_{i\alpha})=\theta_i+e_i$$
   where $\theta_i$ satisfies the Bragg equation: $a_0\sin\theta_i=k_i$.
4. $\sum_i e_i=0$.
5. The variance of the $\psi_{i\alpha}$, denoted by $\sigma^2_{\psi_{i\alpha}}$, depends only on the angle, i.e.:
   $$\sigma^2_{\psi_{i\alpha}}=\sigma_i^2.$$

## 3. The likelihood ratio method (*LRM*)

A. *Philosophy*

This statistical approach to the accurate determination of lattice parameters is called the Likelihood Ratio Method (abbreviated *LRM*) since the crux of the method depends on the application of a statistical test called the Likelihood Ratio Test (*LRT*) (Mood, 1950). The *LRM* is based on the principle that a lattice parameter for a given crystalline sample is the same regardless of the (*hkl*) reflection from which it is calculated. By measuring the angular positions of at least three reflections and correcting the measured Bragg angles for all known systematic errors,* the lattice parameter values calculated from the corrected data should agree among themselves. If they do, this indicates that the systematic errors have indeed been removed from the corrected data within the precision of measurement. The *LRT* indicates in a valid statis-

* It is not the purpose of this report to describe how the systematic errors may be removed from the individual measurements. This has already been indicated for diffraction peak measurements using counter (Bond, 1960) and film (Beu, Musil & Whitney, 1959) techniques and for centroid measurements (Pike & Wilson, 1959).

tical manner whether or not this has been accomplished.

The *LRM* utilizes corrected diffraction data of high precision and provides an accurate estimate of the lattice parameter and its standard deviation after it has been shown that the systematic errors have been removed from the data, according to the *LRT*. The *LRM* is developed here for the cubic case which has only one lattice parameter, $a_0$. It can, however, be extended to cases involving additional parameters.

### B. *LRM procedure*

The Bragg angle for each (*hkl*) reflection of interest is measured $n_i$ times, and $\psi_i$ and $s_i^2$ are calculated The maximum likelihood estimates (Mood, 1950*a*) of the parameters under the assumptions, $\hat{a}_0$, $\hat{\sigma}_i$, $\hat{e}_i$, and $\hat{\theta}_i$ are then calculated using the following relationships [a derivation of the equations used in the *LRM* is given in Appendix I and in a comprehensive report (Beu, Musil & Whitney, 1961)]:

$$\begin{aligned} \hat{a}_0 \sin \hat{\theta}_i &= k_i \\ \hat{\sigma}_i^2 &= s_i^2 \\ \hat{e}_i &= \psi_i - \hat{\theta}_i \\ \sum_i \hat{e}_i &= 0 \,. \end{aligned}$$

In practice, $\hat{a}_0$, is determined by estimating $a_0$, calculating the $\theta_i$, summing the $e_i$ values, and plotting $\sum_i e_i$ versus $a_0$ for several $a_0$ estimates.* $\hat{a}_0$ is that value of $a_0$ corresponding to $\sum_i e_i = 0$ (see Figs. 1 and 3). $\hat{e}_i$ may then be calculated using the equations:

* A suggested method for the first estimate is to calculate $a_0$ from the corrected values of $\psi_i$ for each diffraction line and to use the average of these values of $a_0$. The values of $\theta_i$ are then calculated from this average $a_0$.

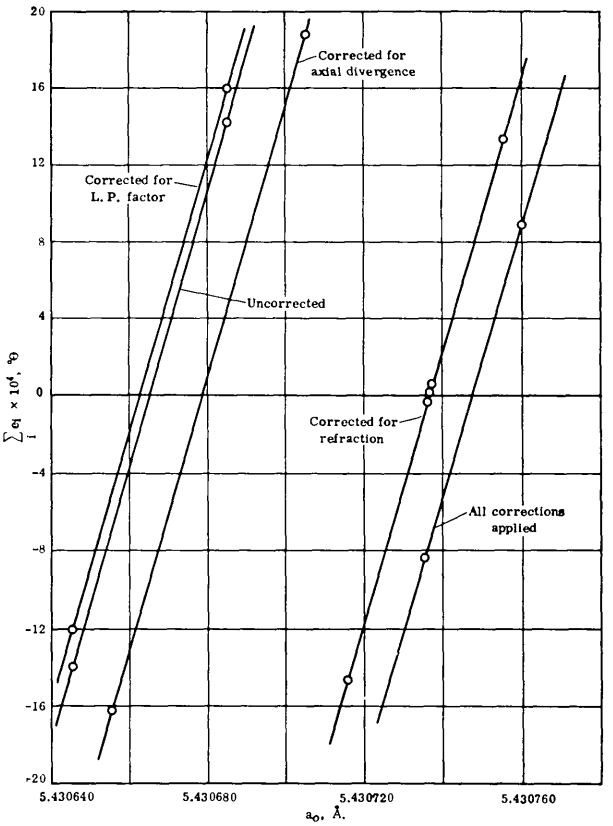


Fig. 1. $\sum_i e_i$ versus $a_0$ for Bond's data on zone refined silicon.

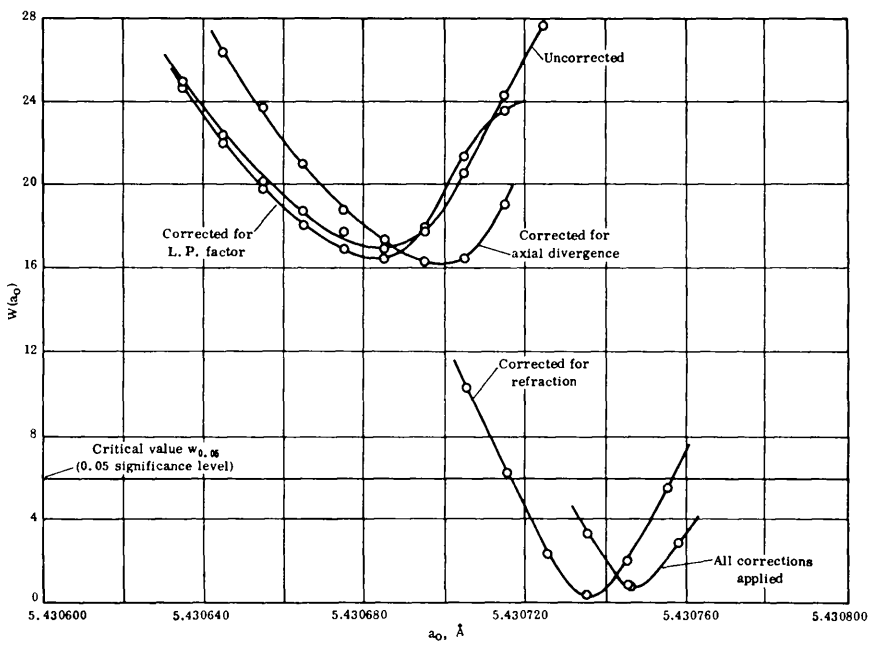


Fig. 2. $W(a_0)$ versus $a_0$ for Bond's data on zone refined silicon.

$$\hat{a}_0 \sin \hat{\theta}_i = k_i \quad \text{and} \quad \hat{e}_i = \psi_i - \hat{\theta}_i \, .$$

The $\hat{e}_i$ need be determined only if subsequent calculations indicate the presence of systematic errors beyond the precision of measurement.

The hypothesis is then made that there are 'no remaining systematic errors' in the corrected $\psi_{i\alpha}$ measurements:

$$H\colon \; e_1 = e_2 = e_3 = \ldots = e_m = 0 \, .$$

The maximum likelihood estimates under the hypothesis, $\hat{\hat{a}}_0$ and $\hat{\hat{\sigma}}_i^2$, are determined as follows:

A function $W(a_0)$ is given by the equation:

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

where $\theta_i$ is defined by $a_0 \sin \theta_i = k_i$.

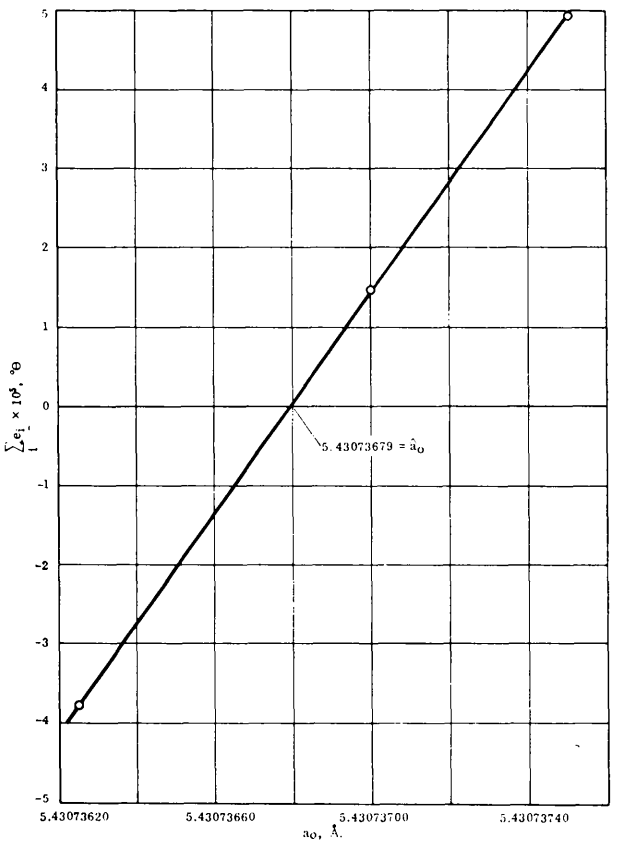


Fig. 3. $\sum_i e_i$ versus $a_0$ for Bond's data corrected for refraction only (expanded scale).

A graph of $W(a_0)$ versus $a_0$ in the vicinity of $\hat{a}_0$ is examined for a minimum value of $W(a_0)$. The value of $a_0$ corresponding to this minimum is $\hat{\hat{a}}_0$ and the minimum value of $W(a_0)$ is designated $W(\hat{\hat{a}}_0)$ or $W_m$ (see Figs. 2 and 4 for typical graphs). The maximum likelihood estimate $\hat{\hat{\theta}}_i$ may then be determined from the equation:

$$\hat{\hat{a}}_0 \sin \hat{\hat{\theta}}_i = k_i \, .$$

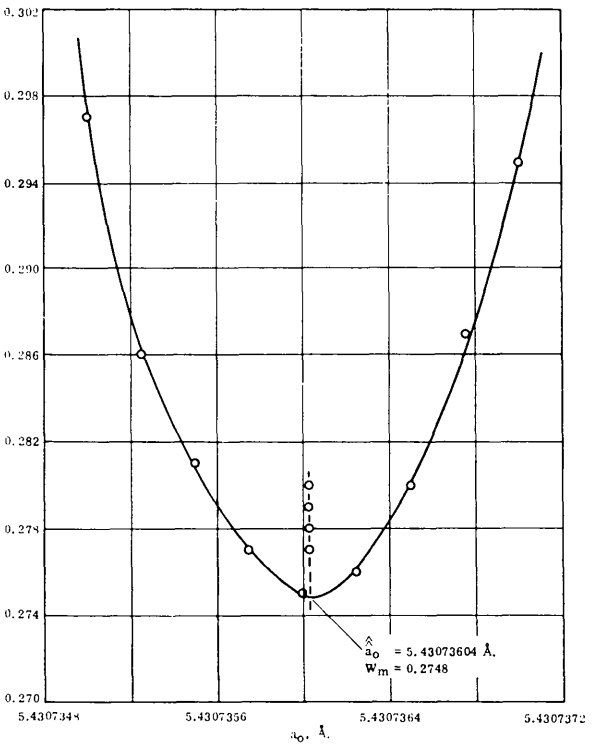


Fig. 4. $W(a_0)$ versus $a_0$ for Bond's data corrected for refraction only (expanded scale).

Using the values of $\hat{\hat{\theta}}_i$ just determined, $\hat{\hat{\sigma}}_i^2$ is calculated from:

$$\hat{\hat{\sigma}}_i^2 = s_i^2 + (\psi_i - \hat{\hat{\theta}}_i)^2 .$$

An estimate of the standard deviation of $\hat{\hat{a}}_0$, denoted by $s_{a_0}$, may then be calculated using the equation:

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

The values of $\hat{\hat{a}}_0$ and $s_{a_0}$ just calculated have significance only after it has been shown statistically that $a_0$ has no remaining systematic errors. This is accomplished by using the likelihood ratio test (*LRT*) (Mood, 1950*a*). $W(a_0)$ is derived using the likelihood ratio, and $W_m$, the minimum value of this function in the vicinity of $a_0$, is used as the statistic to test $H$. As a consequence of a theorem relating to the likelihood ratio (Mood, 1950*b*), $W_m$ can be shown to be distributed approximately like chi-square ($\chi^2$) with $(m-1)$ degrees of freedom where $m$ is the number of diffraction lines measured. To test $H$, $W_m$ is compared to a critical value, $w_\varepsilon$, where $w_\varepsilon$ and $\varepsilon$ are defined as follows:

$$\int_{w_\varepsilon}^{\infty} \chi^2 \text{ distribution},^* \; (m-1) \text{ d.f.} = \varepsilon \, .$$

* The $\chi^2$ distribution is given by the equation:

$$F(u) = \int_0^u [x^{(n-2)/2} e^{-x/2} / 2^{n/2} [(n-2)/2]!] dx \, .$$

$\varepsilon$ is the significance level of the test chosen by the investigator (a commonly used value for $\varepsilon$ is 0·05). After having chosen $\varepsilon$ and having looked up $w_\varepsilon$ in the table, (Hodgman, 1959*a*), the comparison is made with $W_m$.

If $W_m \geq w_\varepsilon$, the hypothesis is rejected and we may conclude with $100(1-\varepsilon)$ percent confidence that systematic errors remain in the corrected measurements and calculations. In this case it is necessary to re-evaluate and improve the techniques used for removing systematic errors. If $W_m < w_\varepsilon$, the hypothesis is not rejected; it is accepted at the $\varepsilon$ significance level that there are 'no remaining systematic errors' in the calculated values of $\hat{\bar{a}}_0$ and $s_{\bar{a}_0}$.

C. *Features of the LRM*

1. The most important feature of the *LRM* is that it provides a valid statistical criterion for determining the accuracy of a lattice parameter calculation based on the premise of internal self-consistency of the data; i.e., a lattice parameter value for a given sample is the same within the precision of measurement regardless of which (*hkl*) reflection is used to calculate this parameter.

2. All systematic error factors which are related directly to $\theta$ will be included in the *LRM* evaluation of accuracy. Even those factors which require a constant correction in $\theta$ for each diffraction angle will be included in this evaluation. The zero setting error is a factor of this type and is of special importance in diffractometer work. The major factor which does not enter directly into the *LRM* evaluation is the X-ray wavelength and, as has been pointed out in the Introduction, wavelength accuracy can be handled separately from $\theta$ accuracy.

3. A comparison of $W_m$ calculated after making each systematic error correction, with the critical value $w_\varepsilon$ obtained from the chi-square distribution, will indicate if the correction is valid. If $W_m$ remains about the same or increases, then the correction is either insignificant or improper. The correction is useful only if $W_m$ decreases. Finally, after all corrections are made, if $W_m$ is still greater than $w_\varepsilon$, then either one or more corrections are of the wrong magnitude or there are additional unknown systematic errors. Only if $W_m < w_\varepsilon$ can it be claimed that all systematic errors have been removed within the precision of measurement at the chosen significance level.

4. If $W_m < w_\varepsilon$, this implies further that dispersion and the asymmetry of the characteristic wavelength distribution have a negligible effect at the $\varepsilon$ significance level on the calculated value of the lattice parameter. This does not, however, indicate whether the characteristic (peak, center of gravity, etc.) used to calculate the lattice parameter is an accurate value. It only indicates when $W_m < w_\varepsilon$, the wavelength distribution and its resolution, or lack of resolution, into the $\alpha_1$–$\alpha_2$ doublet for example, does not have a significant effect on the accuracy of the calculated lattice parameter value based on the self-consistency criterion.

5. After correcting the $\psi_i$ values for systematic errors, one at a time, the magnitude of the $\hat{e}_i$ values may be observed for $\sum_i e_i = 0$. If the $\hat{e}_i$ values have not decreased significantly for a given systematic error correction, then the technique for making that correction is suspect and should be re-examined. Thus, the *LRM* is useful in pinpointing the sources of systematic error and in evaluating the techniques used in correcting for systematic errors. These points will be illustrated in the next section.

## 4. Application of the *LRM*

A. *Bond's data on zone refined silicon*

In order to demonstrate the utility of the *LRM*, lattice parameter data of very high precision and potentially great accuracy were chosen. These data were obtained by Bond (1960) on a single crystal of zone refined silicon using a special diffractometer which could be used to make measurements symmetrically about $2\theta = 0°$ and 180°.

Bond's method of measuring diffraction angles (crystal position rather than counter angle) results in the elimination of eccentricity, absorption, asymmetrical source profile, and zero errors from the raw data. The measured diffraction angles, however, still require correction, according to Bond, for axial divergence, Lorentz and polarization (*LP*) factor, and refraction. Table 1 in Bond's paper lists the measured diffraction angle values together with the separate corrections to these values. Bond measured the peak positions of the (111), (333), and (444) reflections of silicon using the centerline method (Beu, 1957).*

A summary of Bond's data together with *LRM* results on his data are given in Table 1. An abbreviated *LRM* calculation using Bond's data corrected for refraction is given in Appendix II. To facilitate interpretation of Table 1, degrees $\theta$ from Bond's Table 1 were converted from min. and sec. to decimals. An X-ray wavelength for Cu $K\alpha_1$ = 1·54051 Å was used as recommended in the IUCr project (Parrish, 1960) instead of the Siegbahn wavelength of 1·540501 Å (1·537395 kX.U.) used by Bond. Lattice parameter and wavelength values were converted from kX. units to Å using the kX.-to-Å ratio

* We have found the centerline method to give the most reproducible measure of the peak position, especially for sharp peaks where small intensity variations near the peak make it difficult to determine the true peak position precisely (to about 0·001° $\theta$) by inspection, parabola fitting, or other methods.

Table 1. *LRM data calculated from Bond's data on zone refined silicon*
($\lambda = 1{\cdot}54051$ Å)

| Exper. no. | Type of correction | (*hkl*) | Uncorrected $\psi_i$ (°$\theta$) | Correction (°$\theta$) | Corrected $\psi_i$ (°$\theta$) | $\hat{e}_i$ (°$\theta$) | $W_m$ | $a_0$ (Å) | Standard deviation (Å) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | None | (111) | 14·22263 | — | — | +0·00153 | | | |
| | | (333) | 47·47598 | — | — | +0·00009 | | | |
| | | (444) | 79·31213 | — | — | −0·00162 | | | |
| | | | | | | | 16·96 | 5·430685 | |
| 2 | *LP* | (111) | Same as (1) | +0·00000 | 14·22263 | +0·00152 | | | |
| | | (333) | Same as (1) | +0·00000 | 47·47598 | +0·00006 | | | |
| | | (444) | Same as (1) | +0·00017 | 79·31230 | −0·00160 | | | |
| | | | | | | | 16·41 | 5·430685 | |
| 3 | Axial | (111) | Same as (1) | −0·00004 | 14·22259 | +0·00153 | | | |
| | divergence | (333) | Same as (1) | −0·00020 | 47·47578 | +0·00001 | | | |
| | | (444) | Same as (1) | −0·00070 | 79·31143 | −0·00158 | | | |
| | | | | | | | 16·20 | 5·430700 | |
| 4 | Refraction | (111) | Same as (1) | −0·00180 | 14·22083 | −0·00007 | | | |
| | | (333) | Same as (1) | −0·00090 | 47·47508 | −0·00001 | | | |
| | | (444) | Same as (1) | −0·00230 | 79·30983 | +0·00001 | | | |
| | | | | | | | 0·275 | 5·430736 ($\hat{\hat{a}}_0$) | ±0·000007 ($s_{a_0}$) |
| 5 | *LP* + axial | (111) | Same as (1) | −0·00184 | 14·22079 | −0·00010 | | | |
| | divergence + | (333) | Same as (1) | −0·00110 | 47·47488 | −0·00007 | | | |
| | refraction | (444) | Same as (1) | −0·00283 | 79·30930 | +0·00016 | | | |
| | | | | | | | 0·65 | 5·430747 | ±0·000007 |

of 1·00202.* The uncorrected $\psi_i$ values of Table 1 correspond to the mean $\theta$ values given by Bond. The axial divergence and refraction corrections were converted from kX. units to degrees $\theta$.

B. *Analysis of Bond's data*

We are now ready to observe the statistical significance of the systematic error removal from these data using Bond's corrections. This is done by comparing the value of $W_m$ at each level of removal with the critical value of the chi-square distribution, $w_{0.05}$. The critical value of $w_{0.05}$ is 5·99 as can be determined by inspecting a chi-square distribution table (Hodgman, 1959*a*) at the 0·05 significance level and two degrees of freedom (for three diffraction lines).

The hypothesis of 'no remaining systematic errors' is rejected if $W_m \geq 5{\cdot}99$ and is not rejected if $W_m < 5{\cdot}99$. On this basis we can see that the hypothesis would be rejected ($W_m > 16$) for experiments No. 1, 2, and 3 listed in Table 1. It would be expected that the hypothesis would be rejected for No. 1 since $W_m$ in this case was determined for the uncorrected data. It is perhaps a little surprising that the $W_m$ values for the *LP* (No. 2) and axial divergence (No. 3) corrections do not change significantly compared to $W_m$ for the uncorrected data. This implies that the *LP* and axial divergence corrections do not reduce the systematic errors significantly.

Next, we observe that $W_m = 0{\cdot}275$ when using the refraction correction. Since this is less than 5·99, this implies that the refraction correction alone has removed the systematic errors from the data within the precision of measurement and $\hat{\hat{a}}_0$, the maximum likelihood estimate of $a_0$ under the hypothesis $H$, is that value of $\hat{\hat{a}}_0$ corresponding to $W_m = 0{\cdot}275$ (Fig. 2). The value of $\hat{\hat{a}}_0$ is 5·430736 Å (at 25 °C.) and this is an accurate value of $a_0$ for this sample of silicon within the precision of measurement.

After $\hat{\hat{a}}_0$ was determined, the estimate of the standard deviation of $\hat{\hat{a}}_0$, $s_{a_0}$, was calculated to be 0·000007 Å. It is interesting to note that $s_{a_0}$ is comparable to the precision with which high angle diffraction lines can be measured even though both high and low angle lines are used in the *LRM* calculation.

The fact that the refraction correction alone results in a value of $a_0$ accurate within the precision of measurement may be further demonstrated by examining the $\sum_i e_i$ versus $a_0$ and $W(a_0)$ versus $a_0$ curves in more detail. It will be recalled that $\hat{a}_0$, the estimate under the assumptions, is determined when $\sum_i e_i = 0$ and that $\hat{\hat{a}}_0$, the estimate under the hypothesis, is determined at the minimum value of $W(a_0)$. If $\hat{a}_0$ differs from $\hat{\hat{a}}_0$ by less than the precision of measurement, then this provides further verification that the hypothesis of 'no remaining systematic errors' has been satisfied.

Fig. 3 is a greatly enlarged plot of $\sum_i e_i$ versus $a_0$ in the vicinity of $\sum_i e_i = 0$. The value of $\hat{a}_0$, by direct interpolation,* is 5·43073679 Å. Fig. 4 is a greatly enlarged plot of $W(a_0)$ versus $a_0$ in the region of minimum $W(a_0)$. Using the centerline method (Beu, 1957), $W_m$ is 0·2748 and $\hat{\hat{a}}_0$ corresponding to this minimum* is 5·43073604 Å. The difference between

* Since the wavelength accuracy problem is being handled separately from the *LRM*, the fact that $\lambda$ (1·54051 Å) and the conversion factor (1·00202) are given only to five decimals is no limitation on reporting lattice parameter accuracy and precision to six decimals, as will be done in the next section.

* Appendix II gives the calculations for these values of $\hat{a}_0$ and $\hat{\hat{a}}_0$, as well as for $W(a_0)$ and $s_{a_0}$.

$\hat{a}_0$ and $\hat{\hat{a}}_0$ is 0·00000075 Å. This difference is about one-tenth as large as $s_{a_0}$, thereby confirming the fact that the value of $\hat{\hat{a}}_0$ is indeed accurate within the precision of measurement.

Values of the silicon lattice parameters and their deviations calculated by Bond and by us using the *LRM* are summarized as follows: $\hat{\hat{a}}_0 = 5{\cdot}430736 \pm 0{\cdot}000014$ Å at 25 °C. This is an accurate estimate of $a_0$ and its deviation at the commonly used 95 percent confidence level. This value of $\hat{\hat{a}}_0$ is based on the X-ray wavelength of 1·54051 Å for Cu $K\alpha_1$, as recommended for the IUCr project† (Parrish, 1960). The 95 percent confidence limits of $\pm 0{\cdot}000014$ Å are based on four sets of measurements of the (111), (333), and (444) reflections (a total of twelve measurements made by Bond). It is interesting to note that Bond's method of calculating an $a_0$ value for each of three (*hkl*) reflections results in a poorer precision (one part in 290,000), calculated at the 95 percent confidence limits, than when using the *LRM* on exactly the same data (one part in 390,000). The value of $a_0 = 5{\cdot}430747$ Å using the *LRM* with all of Bond's corrections differs from $\hat{\hat{a}}_0$ by 0·000011 Å and Bond's weighted value of $a_0 = 5{\cdot}430752$ Å (converted from kX. units) differs by 0·000016 Å. Neither of these values is significantly different from $\hat{\hat{a}}_0$ at the 0·05 significance level as determined by $t$ and $F$ tests (Hodgman, 1959*b*). Hence all of these lattice parameter values are accurate within precision limits based on $s_{a_0}$. Nevertheless, the value of $\hat{\hat{a}}_0$ is to be preferred since it is the maximum likelihood estimate of $a_0$ under the hypothesis.

## APPENDIX I

### Statistical analysis and derivation of equations used in the *LRM*

A. *Analysis*

Using the assumptions stated in Section 2, B of this paper, the lattice parameter, its accuracy and precision are estimated in terms of a hypothesis of 'no remaining systematic errors' in the corrected Bragg angle measurements, $\psi_{i\alpha}$. The hypothesis is tested using the likelihood ratio $\lambda_{LR}$. The likelihood ratio (Mood, 1950*a*) as applied to this problem is defined in terms of its logarithm:

$$\ln \lambda_{LR} = L(\hat{\hat{a}}_0, \hat{\hat{\sigma}}_i) - L(\hat{a}_0, \hat{\sigma}_i, \hat{e}_i)$$

where $L(\hat{\hat{a}}_0, \hat{\hat{\sigma}}_i)$ is the logarithm of the maximum value of the sample density function ($\psi_{i\alpha}$ are the sample values) consistent with the hypothesis and assumptions, and $L(\hat{a}_0, \hat{\sigma}_i, \hat{e}_i)$ is the logarithm of the maximum value of the sample density function consistent with the assumptions.

Large values of $\lambda_{LR}$ (or its logarithm) are regarded as evidence that the hypothesis is true while small values indicate the hypothesis to be false, i.e., that systematic errors still remain in the data. The distinction between what is taken to be true or false is statistically determined at the $\varepsilon$ significance level by evaluating $W_m$, a function of $\lambda_{LR}$, which is distributed approximately like chi-square ($\chi^2$). By comparing $W_m$ with a critical value $w_\varepsilon$ obtained from a table of chi-square values, the hypothesis is rejected if $W_m \geq w_\varepsilon$. On the other hand the hypothesis is not rejected, i.e., it is accepted at the $\varepsilon$ significance level, if $W_m < w_\varepsilon$. In this case $\hat{\hat{a}}_0$, a value of $a_0$ accurate within the precision of measurement, has been determined. Having determined $\hat{\hat{a}}_0$, its standard deviation may then be calculated. The equations supporting this procedure are now derived.

B. *Estimates under the assumptions*

The sample density function of the $\psi_{i\alpha}$ is

$$\prod_{i\alpha} (1/\sqrt{(2\pi)}\sigma_i) \exp -[(1/2\sigma_i^2)(\psi_{i\alpha} - \theta_i - e_i)^2]$$

and its logarithm is:

$$L(a_0, \sigma_i, e_i) = -N \ln \sqrt{(2\pi)} - \sum_i n_i \ln \sigma_i - (1/2) \sum_i (1/\sigma_i^2) \sum_\alpha (\psi_{i\alpha} - \theta_i - e_i)^2 . \quad (1)$$

The maximum likelihood estimates of the parameters, $a_0$; $\sigma_1, \ldots, \sigma_m$; $e_1, \ldots, e_m$ are functions of the $\psi_{i\alpha}$ and are denoted by $\hat{a}_0$; $\hat{\sigma}_1, \ldots, \hat{\sigma}_m$; $\hat{e}_1, \ldots, \hat{e}_m$.

These estimates maximize the sample density function or, equivalently, its logarithm. Since a side condition is involved, i.e., $\sum_i e_i = 0$, the maximum likelihood estimates must satisfy the $(2m+2)$ equations:

$$\partial(L + \lambda_M \sum_i e_i)/\partial a_0 = 0, \quad \partial(L + \lambda_M \sum_i e_i)/\partial \sigma_i = 0,$$
$$\partial(L + \lambda_M \sum_i e_i/\partial e_i = 0, \quad \sum_i e_i = 0 .$$

Note: The Lagrange multiplier $\lambda_M$ is used only in connection with the relation $\sum_i e_i = 0$ to facilitate differentiating the above equations. The relation $a_0 \sin \theta_i = k_i$ is used to eliminate the $\theta_i$ from the problem of determining the maximum likelihood estimates.

Carrying out the indicated derivatives and setting the partial derivatives equal to zero to obtain equations for maximum likelihood estimates yields:

$$\partial(L + \lambda_M \sum_i e_i)/\partial a_0 = -(1/a_0) \sum_i (\tan \theta_i/\sigma_i^2) \sum_\alpha (\psi_{i\alpha} - \theta_i - e_i) = 0$$

$$\partial(L + \lambda_M \sum_i e_i/\partial e_i = -(1/\sigma_i^2) \sum_\alpha (\psi_{i\alpha} - \theta_i - e_i) + \lambda_M = 0$$

$$\partial(L + \lambda_M \sum_i e_i)/\partial \sigma_i = -(n_i/\sigma_i) + (1/\sigma_i^3) \sum_\alpha (\psi_{i\alpha} - \theta_i - e_i)^2 = 0$$

$$\sum_i e_i = 0 .$$

† If the wavelength of 1·540501 Å (1·537395 kXU.) is used (Bond, 1960) then $\hat{\hat{a}}_0 = 5{\cdot}430704$ Å.

Using the definitions for $\psi_i$ and $s_i^2$, these equations may be rewritten:

$$-(1/a_0)\sum_i (n_i \tan \theta_i/\sigma_i)(\psi_i-\theta_i-e_i)=0 \quad (2)$$

$$(n_i/\sigma_i^2)(\psi_i-\theta_i-e_i)+\lambda_M=0 \quad (3)$$

$$-(n_i/\sigma_i)+(n_i/\sigma_i^3)[s_i^2+(\psi_i-\theta_i-e_i)^2]=0 \quad (4)$$

$$\sum_i e_i=0\,. \quad (5)$$

Combining equations (2) and (3) gives

$$(\lambda_M/a_0)\sum_i \tan\theta_i=0$$

which implies $\lambda_M=0$ since $1/a_0\neq 0$ and $\tan\theta\neq 0$.

Equations (2), (3), and (4) then reduce to

$$\sigma_i^2=s_i^2$$
$$e_i=\psi_i-\theta_i\,.$$

The maximum likelihood estimates, $\hat{a}_0$, $\hat{\sigma}_i$, $\hat{e}_i$, and $\hat{\theta}_i$ then satisfy the equations:

$$\hat{a}_0 \sin\hat{\theta}_i=k_i \quad (6)$$

$$\hat{\sigma}_i^2=s_i^2 \quad (7)$$

$$\hat{e}_i=\psi_i-\hat{\theta}_i \quad (8)$$

$$\sum_i \hat{e}_i=0\,. \quad (9)$$

Explicit values for $\hat{a}_0$ and $\hat{e}_i$ can be obtained by successive approximations using equations (6) to (9) as indicated in Section 3, B of this paper. By substituting in equation (1), the maximum of the logarithm of the sample density function under the assumptions then is

$$L(\hat{a}_0, \hat{\sigma}_i, \hat{e}_i)=-N\ln\sqrt{(2\pi)}-\sum_i n_i \ln s_i - N/2\,. \quad (10)$$

Since $L(\hat{a}_0, \sigma_i, \hat{e}_i)$ is the number desired and it does not depend on the values of $\hat{a}_0$ and $\hat{e}_i$, it will be unnecessary in many cases to compute these two estimates.

C. *Estimates under the assumptions and hypothesis*

The sample density function of the $\psi_{ix}$ under the hypothesis is

$$\prod_{ix}(1/\sqrt{(2\pi)}\sigma_i)\exp -[(1/2\sigma_i^2)(\psi_{ix}-\theta_i)^2]$$

and its logarithm is

$$\begin{aligned}&L(a_0, \sigma_i)\\ &=-N\ln\sqrt{(2\pi)}-\sum_i n_i\ln\sigma_i-(1/2)\sum_i(1/\sigma_i^2)\sum_x(\psi_{ix}-\theta_i)^2\\ &=-N\ln\sqrt{(2\pi)}-(1/2)\sum_i n_i\ln\sigma_i^2-(1/2)\sum_i(n_i/\sigma_i^2)\\ &\qquad\times[s_i^2+(\psi_i-\theta_i)^2]\,. \quad (11)\end{aligned}$$

Differentiating with respect to $\sigma_i$ only and setting the partial derivative equal to zero yields:

$$\partial L(a_0, \sigma_i)/\partial\sigma_i=-n_i/\sigma_i+(n_i/\sigma_i^3)[s_i^2+(\psi_i-\theta_i)^2]=0$$

which reduces to

$$\sigma_i^2=s_i^2+(\psi_i-\theta_i)^2.$$

The maximum likelihood estimates $\hat{\hat{a}}_0$, $\hat{\hat{\sigma}}_i^2$, and $\hat{\hat{\theta}}_i$ then satisfy the equations:

$$\hat{\hat{a}}_0 \sin\hat{\hat{\theta}}_i=k_i \quad (12)$$

$$\hat{\hat{\sigma}}_i^2=s_i^2+(\psi_i-\hat{\hat{\theta}}_i)^2. \quad (13)$$

By substituting in equation (11):

$$\begin{aligned}&L(a_0, \hat{\hat{\sigma}}_i)\\ &=-N\ln\sqrt{(2\pi)}-(1/2)\sum_i n_i\ln[s_i^2+(\psi_i-\hat{\hat{\theta}}_i)^2]-N/2\,.\end{aligned} \quad (14)$$

Note: Another equation that the estimates must satisfy may be obtained from $\partial L/\partial a_0=0$; however, this equation is not so amenable to numerical calculation.

The value of $\hat{\hat{a}}_0$ can now be obtained by finding that value of $a_0$ which maximizes $L(a_0, \hat{\hat{\sigma}}_i)$ or, equivalently, which minimizes:

$$\begin{aligned}W(a_0)&=-2\ln\lambda_{LR}\\ &=-2[L(a_0, \hat{\hat{\sigma}}_i)-L(\hat{a}_0, \hat{\sigma}_i, \hat{e}_i)]\\ &=\sum_i n_i\ln[s_i^2+(\psi_i-\theta_i)^2]-\sum_i n_i\ln s_i^2\\ &=\sum_i n_i\ln\left[1+\frac{(\psi_i-\theta_i)^2}{s_i^2}\right]\end{aligned} \quad (15)$$

subject to: $a_0\sin\theta_i=k_i$.

By plotting $W(a_0)$ versus $a_0$, $W_m$, the minimum of $W(a_0)$, and $\hat{\hat{a}}_0$ can be found by inspection (see Figs. 2 and 4). Once $\hat{\hat{a}}_0$ is found, $\hat{\hat{\theta}}_i$ and $\hat{\hat{\sigma}}_i^2$ can be calculated from equations (12) and (13).

D. *Determination of* $s_{a_0}^2$

Under the hypothesis, an estimate of the variance of $\hat{\hat{a}}_0$ is given by

$$\begin{aligned}1/s_{a_0}^2&=E\{[\partial L(a_0, \sigma_i)/\partial a_0]^2\}\\ &=E\{[-(1/a_0)\sum_i(n_i\tan\theta_i/\sigma_i^2)(\psi_i-\theta_i)]^2\}\\ &=(1/a_0^2)\sum_i(n_i^2\tan^2\theta_i/\sigma_i^4)E(\psi_i-\theta_i)^2\\ &=(1/a_0^2)\sum_i(n_i^2\tan^2\theta_i/\sigma_i^4).(\sigma_i^2/n_i)\\ &=(1/a_0^2)\sum_i(n_i\tan^2\theta_i/\sigma_i^2)\end{aligned}$$

and

$$s_{a_0}^2=\hat{\hat{a}}_0^2/\sum_i(n_i/\hat{\hat{\sigma}}_i^2)\tan^2\hat{\hat{\theta}}_i\,. \quad (16)$$

## APPENDIX II

### Example of *LRM* calculation using Bond's data corrected for refraction

1. Determination of $\hat{a}_0$ (data for Fig. 3):

| $(hkl)$ | (111) | (333) | (444) | $\sum_i e_i$ | Estimate of $a_0$ |
|---|---|---|---|---|---|
| $k_i$ | 1·3341209 | 4·0023621 | 5·3364830 | | |
| 1st estimate | | | | | 5·43073750 Å |
| $\psi_i$ | 14·2208250 | 47·4750750 | 79·3098250 | | |
| $\theta_i$ | 14·2209055 | 47·4750577 | 79·3097121 | | |
| $e_i$ | −0·0000805 | +0·0000173 | +0·0001129 | +0·0000497 | |
| 2nd estimate | | | | | 5·43073700 |
| $\psi_i$ | 14·2208250 | 47·4750750 | 79·3098250 | | |
| $\theta_i$ | 14·2209069 | 47·4750635 | 79·3097400 | | |
| $e_i$ | −0·0000819 | +0·0000115 | +0·0000850 | +0·0000146 | |
| 3rd estimate | | | | | 5·43073625 |
| $\psi_i$ | 14·2208250 | 47·4750750 | 79·3098250 | | |
| $\theta_i$ | 14·2209089 | 47·4750721 | 79·3097819 | | |
| $e_i$ | −0·0000839 | +0·0000029 | +0·0000431 | −0·0000379 | |

2. Determination of $\hat{\hat{a}}_0$ (partial data for Fig. 4):

| | $a_0$ | $\sin\theta$ | $\theta$ | $e_i=\psi_i-\theta_i$ | $e_i^2/s_i^2$ | $\log_{10}(1+(e_i^2/s_i^2))$ |
|---|---|---|---|---|---|---|
| (111) reflection | 5·43073575 | 0·2456611703 | 14·2209102 | −0·0000852 | 0·0713 | 0·029911 |
| $\psi_i$ = 14·2208250 | 5·43073600 | 0·2456611590 | 14·2209095 | −0·0000845 | 0·0702 | 0·029465 |
| $s_i^2 = 10{\cdot}1875\times10^{-8}$ | 5·43073625 | 0·2456611476 | 14·2209089 | −0·0000839 | 0·0690 | 0·028978 |
| (333) reflection | 5·43073575 | 0·7369834004 | 47·4750779 | −0·0000029 | 0·0001 | 0·000043 |
| $\psi_i$ = 47·4750750 | 5·43073600 | 0·7369833665 | 47·4750750 | 0·0000000 | 0·0000 | 0·000000 |
| $s_i^2 = 9{\cdot}1875\times10^{-8}$ | 5·43073625 | 0·7369833326 | 47·4750721 | +0·0000029 | 0·0001 | 0·000043 |
| (444) reflection | 5·43073575 | 0·9826445707 | 79·3098099 | +0·0000151 | 0·0003 | 0·000130 |
| $\psi_i$ = 79·3098250 | 5·43073600 | 0·9826445255 | 79·3097959 | +0·0000291 | 0·0010 | 0·000434 |
| $s_i^2 = 87{\cdot}1875\times10^{-8}$ | 5·43073625 | 0·9826444802 | 79·3097819 | +0·0000431 | 0·0022 | 0·000954 |

| $a_0$ | $\sum_i e_i$ | $\sum_i \log_{10}(1+(e_i^2/s_i^2))$ | $W(a_0)=\sum_i n_i \ln(1+(e_i^2/s_i^2))$ |
|---|---|---|---|
| 5·43073575 | −0·0000729 | 0·030084 | 0·277 |
| 5·43073600 | −0·0000554 | 0·029899 | 0·275 |
| 5·43073625 | −0·0000379 | 0·029975 | 0·276 |

$W_m$ is obtained by plotting $W(a_0)$ versus $a_0$. $W_m=0{\cdot}2748$ and $\hat{\hat{a}}_0=5{\cdot}43073604$ Å if *LRT* is satisfied.
$w_\varepsilon$ is equal to 5·991 at 0·05 significance level and 2 degrees of freedom. Hence $W_m$ is less than $w_\varepsilon$ and *LRT'* is satisfied.

3. Variance, standard deviation $s_{a_0}$, and 95% confidence interval for $a_0$:

| $(hkl)$ | $\hat{\hat{\theta}}_i$ (degrees) | $\hat{\hat{\sigma}}_i^2\times10^8$ (degrees) | $\hat{\hat{\sigma}}_i^2\times10^{11}$ (radians) |
|---|---|---|---|
| (111) | 14·2209094 | 10·902 | 3·3209 |
| (333) | 47·4750745 | 9·188 | 2·7988 |
| (444) | 79·3098245 | 83·271 | 25·3658 |

$$s_{a_0}^2 = \hat{\hat{a}}_0^2/\sum_i (n_i/\hat{\hat{\sigma}}_i^2)\tan^2\hat{\hat{\theta}}_i = (5{\cdot}430736)^2/(62{\cdot}015914\times10^{10})$$

$$s_{a_0} = 6{\cdot}9\times10^{-6} = 0{\cdot}000007 \text{ Å}$$

95% confidence interval for $a_0 = \pm1{\cdot}96\, s_{a_0} = \pm0{\cdot}000014$ Å

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

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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 ($P$, $\sigma$), 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 $\varphi$ or $\Delta\theta$ versus $\theta$ even though diffraction measurements are usually made in terms of $2\theta$ or $4\varphi$. $\Delta\theta$ or $\Delta\varphi$ corrections can be made directly on calculated $\theta$ or $\varphi$ values after

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

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