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## A Modification of the Cohen Procedure for Computing Precision Lattice Constants from Powder Data\*

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The Cohen scheme for weighting the measurements upon the lines of powder patterns is shown to be inappropriate, and a modified weighting is proposed. Examples are given to illustrate the improvement in precision resulting from the modified method.

Cohen's method (Cohen, 1935, 1936 *a, b, c*) of analytical extrapolation, to eliminate the effect of the systematic errors inherent in all present types of precision cameras, is now firmly established as probably the most generally useful technique available for the precision determination of lattice constants.† One of its chief advantages lies in the fact that the basic analytical extrapolation can be extended to a least-squares treatment to reduce the effect of random errors in the initial data, and to estimate the precision of the calculated parameters from the criterion of external consistency (Jette & Foote, 1935).

Cohen has given formulae for this least-squares treatment. In his derivations, however, he has weighted the original measurements according to a system which the present discussion will show to be not generally appropriate. Consequently, his formulae are found to lead to lattice constants that differ somewhat from the most probable, and frequently to an underestimation of their precision, as compared with a corrected treatment. Since the estimation of the error of a precision measurement is fully as important as the measurement itself, this defect of Cohen's procedure has considerable significance, as will be illustrated by several examples, even though the changes in the calculated lattice constants themselves in general are not large.

\* The basic elements of this modified computation were developed several years ago in an equivalent form, though one somewhat less convenient than that presented below, while the author was employed at the Magnesium Laboratories, The Dow Chemical Company, Midland, Michigan.

† A comprehensive survey and bibliography of the subjects of systematic errors in X-ray cameras and the precision measurement of lattice constants has been given by Buerger (1942, chap. 20), while contributions of more recent date have been made by Warren (1943), Thomas (1948), Ekstein & Siegel (1949), and Straumanis (1949).

### Cohen's analytical extrapolation and least-squares treatment

To treat the systematic errors, Cohen (1935, 1936 *a*) proposed modifying the Bragg relationship to

$$\frac{n\lambda}{2d} = \sin(\theta + \Delta\theta) = \cos \frac{1}{2}(\phi + \Delta\phi). \quad (1)^*$$

Here  $\phi$  is the diffraction angle which is measured experimentally, and  $\Delta\phi$  is the small angle, due to the net effect of all the systematic errors, which must be added to  $\phi$  to make their sum  $\phi + \Delta\phi$  fulfill the Bragg relation. Then, by squaring, expanding the right-hand term by Taylor's theorem, and neglecting all powers of the small angle  $\Delta\phi$  except the first, Cohen obtained

$$\frac{n^2\lambda^2}{4d^2} = \cos^2 \frac{1}{2}\phi - \frac{1}{2}\Delta\phi \sin \phi \quad (2)$$

as the general modified form of the Bragg relationship applicable to experimentally measured diffraction angles.

Next Cohen expressed  $\Delta\phi$  in the analytical form appropriate to the camera used. For back-reflection Debye-Scherrer cameras he preferred  $\Delta\phi = K_1\phi$  (correcting an earlier suggestion of  $\Delta\phi = K_1 \sin \phi$ ) as being the best approximation, and Warren (1943) has confirmed this conclusion for the range  $\phi \leq 60^\circ$ . Similarly, for back-reflection symmetrical focusing cameras he found  $\Delta\phi = K_2\phi$  for  $\phi \leq 60^\circ$ . While the functional form of  $\Delta\phi$  for the third important type of precision camera,

\* Since only back-reflection methods (where the incident X-ray beam enters the camera through a hole in the film) are sensitive enough to lay claim to precision and at the same time possess a geometry to which the analytical extrapolation is easily adaptable, it is convenient to write all formulae in terms of the 'back-reflection angle'  $\phi$  (where  $\phi = 180^\circ - 2\theta$ ) rather than in terms of the usual Bragg angle  $\theta$ .

namely, the Sachs-type flat-film back-reflection camera, has not been discussed previously, the appropriate form can be shown to be  $\Delta\phi = K_3 \sin\phi \cos\phi$  (see Appendix II). In all the above relations  $K_i^*$  is a constant for any particular film, but may vary with successive films, so that the numerical value of the constant for a particular film is always unknown initially. With careful precision technique experience has shown that  $K$  is always less than  $\pm 0.02$  and usually less than  $\pm 0.005$ , so that  $\Delta\phi$  is always small enough to justify the approximations made in developing equation (2).

Next, the generalized interplanar spacing  $d$  in (2) is rewritten in terms of the lattice constants and the Miller indices, giving an 'observation equation'. For example, choosing the cubic system and a back-reflection Debye camera, the specific observation equation becomes

$$\frac{n^2\lambda^2}{4a_0^2} (h^2 + k^2 + l^2) + K \cdot \frac{1}{2}\phi \cdot \sin\phi = \cos^2 \frac{1}{2}\phi. \quad (3)$$

Now, if two lines having  $\phi \leq 60^\circ$  are available on the film, then an equation (3) may be written for each of the two measured diffraction angles and solved simultaneously for the unknown lattice constant,  $a_0$ , and the systematic-errors constant,  $K$ , since all other quantities are determined from the indexing of the diffraction lines.

In computing  $a_0$  from such simultaneous equations the assumption is inherent that all the known quantities in the equations are exact, hence that the measured diffraction angles have been measured exactly.† However, owing to purely physical limitations upon the precision of measurements, there must always be small, random uncertainties in the measurements of the diffraction-ring diameters, and, consequently, uncertainties in any results computed from them. By measuring additional ring diameters—the more, the better—and employing a least-squares treatment of the data, the effect of these ever present uncertainties can theoretically be reduced, and the most probable value of the lattice constants can be determined.

Superficially, the technique of least-squares treatment is well known, but the basic principle will bear reiteration. Repeated similar measurements upon a quantity—the same diameter, for example—constitute a population; the individual readings deviate from the exact (but unknown) value in randomness by small uncertainties, and in general the mean of such a set of readings does also. Similar sets of measurements upon similar quantities—other diameters—likewise deviate individually from their respective exact values by similar small errors in a random fashion; and the same

is true of their respective means. No amount of repetition of measurements can ever determine such a quantity exactly, but from many repetitions a most probable value can be determined. The basic least-squares principle leading to the most probable value is to minimize the sum of the weighted squares of the residuals of the quantities *actually measured*, where a residual by definition is the difference between the observed value of a quantity and its calculated value.

Cohen suggested such a least-squares extension of his basic analytical extrapolation, and outlined the computation procedure as follows. He recast the specific observation equation, for example, (3), into the form

$$\alpha A + \delta D = \gamma, \quad (4)$$

employing the substitutions

$$\begin{aligned} \alpha &\equiv n^2(h^2 + k^2 + l^2), & \delta &\equiv \phi \sin\phi, \\ \gamma &\equiv \cos^2 \frac{1}{2}\phi, & A &\equiv \lambda^2/(4a_0^2) \quad \text{and} \quad D \equiv \frac{1}{2}K, \end{aligned}$$

and said that if  $N$  equations of the form of (4) were available from the measurement of  $N$  different lines on the film, then the 'normal equations' to be solved simultaneously for the most probable values of the unknown parameters  $A$  and  $D$  have the form

$$\left. \begin{aligned} A\sum\alpha_i^2 + D\sum\alpha_i\delta_i &= \sum\alpha_i\gamma_i, \\ A\sum\alpha_i\delta_i + D\sum\delta_i^2 &= \sum\delta_i\gamma_i. \end{aligned} \right\} \quad (5)$$

#### Weighting the original observations

In taking the normal equations (5) to represent the least-squares development of (4), two assumptions regarding the observation equation are necessarily implied (Deming, 1943; Worthing & Geffner, 1943). These assumptions are: (1) that only the  $\gamma_i$  quantities are subject to error, and (2) that the most probable values for the parameters are those that minimize the sum of the equally weighted squares of the residuals of  $\gamma$ .

The first assumption is an approximation. The ring-diameter measurements are clearly the fundamental quantities subject to random uncertainties, and therefore rigor demands that in a direct solution both  $\delta$  and  $\gamma$  should be considered subject to error, since both are functions of these diameter measurements. However, it will be shown later that ignoring the uncertainties in  $\delta$  is equivalent in its effect on the computation to an alternate approximation that can be fully justified.

The second assumption, however, appears to violate the basic least-squares principle of minimizing the sum of the weighted squares of the residuals of the quantities *actually measured*. In justifying this assumption Cohen has reasoned that the ring diameters are not similar quantities—that the diameter measurements do not constitute a single population—because the diffraction lines are broadened as  $\phi$  approaches zero, owing to such causes as inhomogeneities in the structure and temperature variation in the specimen during the exposure. Consequently, line centers for lines having small  $\phi$  angles

\* This constant, commonly called the 'drift constant', is here denoted by  $K$  instead of  $D$  (Cohen) to avoid later confusion with the camera diameter  $D$ .

† The fact that the measured angles contain systematic errors can be considered irrelevant to the following argument, for such errors were already accounted for by modifying (1) to the generalized observation equation (2), written in terms of the diffraction angles actually recorded on the film.

were believed to be less well determined than the centers for lines of larger back-reflection angle. He has, therefore, proposed that the ring-diameter measurements should be weighted inversely with the square of this broadening, and has deduced that the net effect of such weighting was to make the derived observations on  $\gamma$  approximate a population. Hence, he concluded that the sum of the equally weighted squares of the residuals of  $\gamma$  should be minimized, as he has done in his procedure.

Cohen's argument is unconvincing, however, since the conditions of inhomogeneities in the structure and temperature fluctuation in the specimen during the exposure, upon which his argument is based, are themselves incompatible with accepted precision technique. It is desirable, therefore, to re-examine the subject of the weighting of line measurements for patterns where excessive line broadness due to these causes is absent.

Several years ago the present writer noted, for patterns with the line broadening due to inhomogeneities in the structure prevented by careful preliminary specimen preparation, and with the temperature variation during exposure reduced to less than  $\pm 0.3^\circ \text{C}$ ., that the line positions of *all* lines could be measured visually to essentially equivalent precision.

Recently, confirmation of this conclusion has been indicated in the results of Ekstein & Siegel (1949) regarding the accuracy of line-position measurements from diffraction patterns. They found visual measurement to be superior to microphotometer measurement over the usual range of line widths. Furthermore, their data suggest that experienced observers are able to estimate the centers of all diffraction lines, within the normal range of line widths, to exactly equivalent absolute accuracy (see their Table 1).

These observations indicate that there is no justification for Cohen's arbitrary weights with patterns taken under accepted standards of precision technique, where the limiting factor in line broadness is the spectral width of the line itself (Ekstein & Siegel, 1949). Instead, the weights of the diffraction-line measurements should, in general, be considered equal and independent of  $\phi$ . To be sure, all lines of a particular pattern cannot necessarily be measured with equal certainty. Frequently very weak lines cause difficulty, and occasionally exceptionally intense lines prove troublesome, but these effects bear no relation to line width or diffraction angle, and, when encountered, the measurements from such lines must simply be weighted less, in as objective a manner as possible.

### The modified normal equations

It now becomes necessary to find new formulae which satisfy the principle of minimizing the sum of the weighted squares of the residuals of the ring-diameter measurements. Still employing as an example the cubic system and a back-reflection Debye camera, the former

observation equation (3), rewritten in terms of the ring diameters,  $s_i$ , and the camera diameter,  $D$ , becomes

$$\frac{1}{a_0^2} \frac{\lambda^2}{4} n^2(h^2 + k^2 + l^2) + K_0 \frac{s}{2D} \sin \frac{s}{D} = \cos^2 \frac{s}{2D}. \quad (3a)$$

This new observation equation is non-linear in terms of the ring diameters, and the more common techniques of least-squares computation are not adequate for the task of deriving appropriate normal equations. Fortunately, however, Deming (1943) has recently generalized the Gauss solution of the non-linear least-squares problem to include the case where parameters are present. Adequate details and proofs of his method have been presented elsewhere, hence no review need be attempted here. Instead, Deming's systematized procedure will merely be accepted and applied to the present case.\*

Basically, Deming's method consists of linearizing the observation equations by rewriting them as Taylor series in terms of parameter residuals, employing approximate values of the unknown parameters, and then neglecting all powers of these residuals higher than the first. All derivatives in the expansion are likewise evaluated with the approximate parameters. Therefore, in choosing the approximations to be used for the parameters, care must be exercised that the approximations are reasonably good, or else the neglected terms may not be truly negligible.

The first step in his systematic procedure is to transpose all terms of the observation formula to one side of the equation, the resulting function being denoted  $F$ . Later treatment will be simplified, however, if this function is recast into the form

$$F = A_0\alpha + K_0\delta - \gamma \quad (6)$$

by means of the substitutions

$$\begin{aligned} A_0 &\equiv 1/a_0^2, \\ \alpha &\equiv \frac{1}{2}\lambda^2 n^2(h^2 + k^2 + l^2), \\ \delta &\equiv \frac{s}{D} \sin \frac{s}{D}, \\ \gamma &\equiv 1 + \cos \frac{s}{D} = 2 \cos^2 \frac{s}{2D}. \end{aligned}$$

The next step is to obtain satisfactory approximations for the parameters  $A_0$  and  $K_0$ . The approximation  $A_a$  for the  $A_0$  parameter might be secured, for instance, by calculation from one of the diffraction-line measurements, momentarily ignoring systematic errors. For the 'drift constant',  $K_0$ , it will become apparent later that zero will always be a sufficiently good approximation. We now define the parameter residuals:

$$\Delta A = A_a - A_0 \quad \text{and} \quad \Delta K = 0 - K_0. \quad (7)$$

\* For greater detail, as well as numerous short-cuts and aids to actual computation and to estimation of the precision indices, reference to Deming's complete treatise (Deming, 1943) can be heartily recommended.

It is next necessary to compute values of  $F_0$  at every observed point, where  $F_0$  is defined as the numerical value of the function  $F$  at each observed point, evaluated furthermore with the approximate parameters. Hence

$$F_0 = A_0 \alpha - \gamma. \quad (8)$$

Derivatives of the function  $F$  with respect to each of the desired parameters, and likewise with respect to each quantity subject to random error, are also required. Each derivative is evaluated at every observed point,  $s_i$ , again employing the approximate parameters:

$$\frac{\partial F}{\partial A} \equiv F_A = \alpha, \quad (9)$$

$$\frac{\partial F}{\partial K} \equiv F_K = \delta, \quad (10)$$

$$\frac{\partial F}{\partial s} \equiv F_s = K \frac{\partial \delta}{\partial s} - \frac{\partial \gamma}{\partial s} = \frac{1}{D} \sin \frac{s}{D} \left[ 1 + K \left( 1 + \frac{s}{D} \cot \frac{s}{D} \right) \right]. \quad (11)$$

Finally, we need the  $L$  coefficients (Deming's notation) given in the general case by

$$L = \frac{1}{w_x} \left( \frac{\partial F}{\partial x} \right)^2 + \frac{1}{w_y} \left( \frac{\partial F}{\partial y} \right)^2 + \dots,$$

where  $x, y, \dots$  are the observed quantities subject to error, and  $w_x, w_y, \dots$  are the respective weights of these quantities. In the present case:

$$L = \frac{1}{w_s} F_s^2 = \frac{1}{w_s} \left[ 1 + K \left( 1 + \frac{s}{D} \cot \frac{s}{D} \right) \right]^2 \left[ \frac{1}{D^2} \sin^2 \frac{s}{D} \right]. \quad (12)$$

Here, the factors in brackets may be looked upon as modifying the observation weight  $w_s$ . Since  $K$  is always less than  $\pm 0.02$ , the first factor is approximately constant (within 1%) over the entire useful range of  $\phi$ . Multiplication of all weights by a constant is pointless, however, since weights are fundamentally only relative quantities. Furthermore, the initial assignment of weights is necessarily too arbitrary, even under the most objective procedure, to justify correction for the small departure of the factor from constancy, and this entire factor may consequently be neglected. Similarly the constant  $1/D^2$  may be dropped, so that the  $L$  coefficients become

$$L \simeq \frac{1}{w_s} \sin^2 \frac{s}{D}. \quad (12a)$$

It may be noted that the above approximation is equivalent, in its subsequent effect upon the normal equations, to choosing zero as the initial approximation for  $K_0$  as already suggested, or alternatively to ignoring the errors in  $\delta$ .

In terms of the above functions, Deming's 'normal equations' become

$$\left. \begin{aligned} \Delta A \Sigma \frac{F_A F_A}{L} + \Delta K \Sigma \frac{F_A F_K}{L} &= \Sigma \frac{F_A F_0}{L}, \\ \Delta A \Sigma \frac{F_A F_K}{L} + \Delta K \Sigma \frac{F_K F_K}{L} &= \Sigma \frac{F_K F_0}{L}, \end{aligned} \right\} \quad (13)$$

or, specifically, for the present case

$$\left. \begin{aligned} \Delta A \Sigma \alpha^2 \frac{w_s}{\sin^2 \phi} + \Delta K \Sigma \alpha \delta \frac{w_s}{\sin^2 \phi} &= \Sigma \alpha F_0 \frac{w_s}{\sin^2 \phi}, \\ \Delta A \Sigma \alpha \delta \frac{w_s}{\sin^2 \phi} + \Delta K \Sigma \delta^2 \frac{w_s}{\sin^2 \phi} &= \Sigma \delta F_0 \frac{w_s}{\sin^2 \phi}. \end{aligned} \right\} \quad (13a)$$

Simultaneous solution then provides  $\Delta A$  and  $\Delta K$ , which in turn can be reduced to  $A_0$  and  $K_0$  by (7), and finally to  $a_0$ .

Modifications of the above derivation appropriate for other crystal systems and other cameras are summarized in Appendix I. The equations, useful in single-crystal work, for the refinement of  $d$  spacings are also given there.

### Comparison of the procedures

It is instructive to compare these modified normal equations with those obtained by the Cohen procedure of minimizing the sum of the residuals of  $\gamma$ . For the same case of the cubic system and back-reflection Debye camera, and employing the same substitutions used above, one obtains by the Cohen procedure:

$$\left. \begin{aligned} \Delta A \Sigma \alpha^2 w_\gamma + \Delta K \Sigma \alpha \delta w_\gamma &= \Sigma \alpha F_0 w_\gamma, \\ \Delta A \Sigma \alpha \delta w_\gamma + \Delta K \Sigma \delta^2 w_\gamma &= \Sigma \delta F_0 w_\gamma. \end{aligned} \right\} \quad (14)$$

The effect of correcting the Cohen assumption has been, therefore, to replace Cohen's weight of each observation,  $w_\gamma$ , (i.e. unity) with the weight  $w_s \operatorname{cosec}^2 \phi$ , where  $w_s$  also is generally unity except for abnormal lines. Similarly, with symmetrical focusing cameras, the effect of modifying the Cohen argument is to replace the weight  $w_\gamma$  with the weight  $w_s \operatorname{cosec}^2 \phi$ . The modified inherent weight for the flat-film back-reflection camera becomes  $w_s \operatorname{cosec}^2 \phi \sec^4 \phi$  instead of  $w_\gamma$ . A plot of these functions is given in Fig. 1. This plot shows that over a large portion of the useful range of  $\phi$  the modified weights do not depart by more than a factor of 10 from the equality assumed by Cohen. Such changes in weights have in general a minor effect upon the calculated least-squares parameters. However, the very large changes in weighting for observations where  $\phi$  is small increase the estimated precision calculated from the data by using the criterion of external consistency, and in a lesser degree they may alter the actual values calculated for the parameters.

To illustrate the differences that may be expected between the two procedures for the average sample, four successive patterns of the same sample of Horsehead Special zinc were taken in a 10 cm. back-reflection symmetrical focusing camera with unfiltered  $\text{Cu } K$  radiation. The resulting data from the ten lines having  $\phi < 60^\circ$  were calculated both by the Cohen procedure and by the modified procedure. The films were not exact duplicates even though the same specimen was used throughout. Owing to slight differences in intensities and spottiness, a particular line could not always be weighted the same in the duplicate determinations; and, of course, there were some differences in the ring-

diameter data themselves owing to different shrinkage of the successive films. Since all lines came from the range  $17^\circ < \phi < 54^\circ$ , where the difference between the

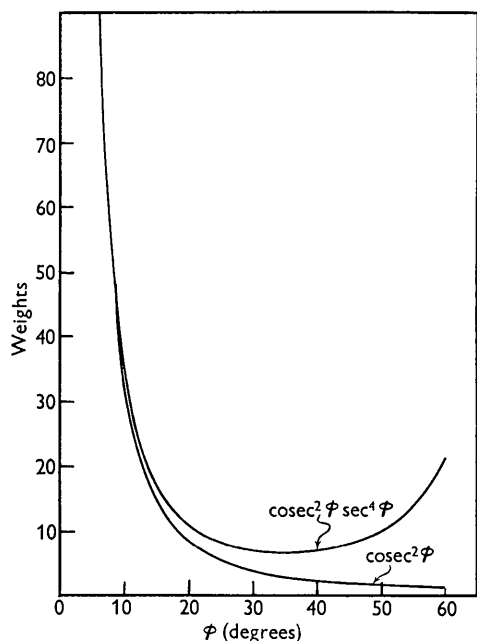


Fig. 1. Plot of the weighting functions assumed in the modified computation.

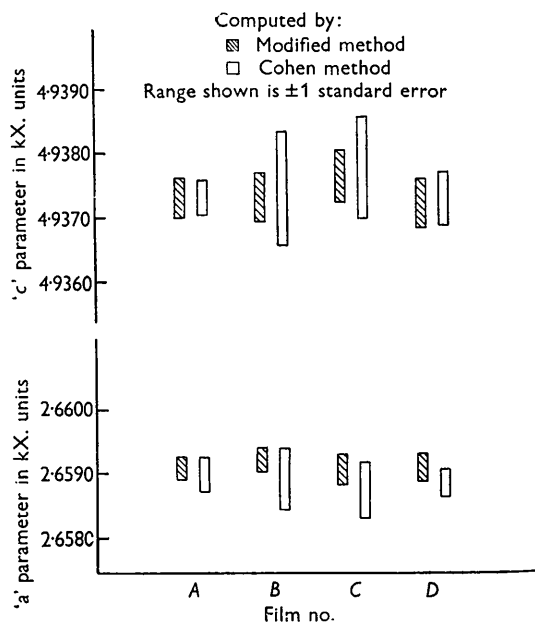


Fig. 2. A comparison of the Cohen and modified computations upon successive patterns of a single specimen of zinc.

weights  $w_\gamma$  and  $w_s \text{ cosec}^2 \phi$  is minor, the effect upon the calculated parameters is slight (see Fig. 2). However, it should be noted that the estimates of improved precision derived from the modified procedure are clearly substantiated by the consistency of the repeated determinations.

In cases where lines of smaller  $\phi$  are available in the patterns, then the effect of the difference in the inherent weights rapidly assumes importance. Fig. 3, for example, compares the two computation procedures on identical data from some typical patterns having lines in the region  $\phi = 6-10^\circ$ .

From these comparisons it is seen that the Cohen computation frequently yields parameters that differ from the most probable parameters calculated by the modified procedure, the difference being unpredictable both in magnitude and sign. An even more disquieting effect of the Cohen method is the frequent and unpredictable underestimation of the precision of the calculated parameters, as illustrated especially by the cases *B* and *C* of Fig. 2 and *D* of Fig. 3, where modified computation shows normal precision. The latter effect is

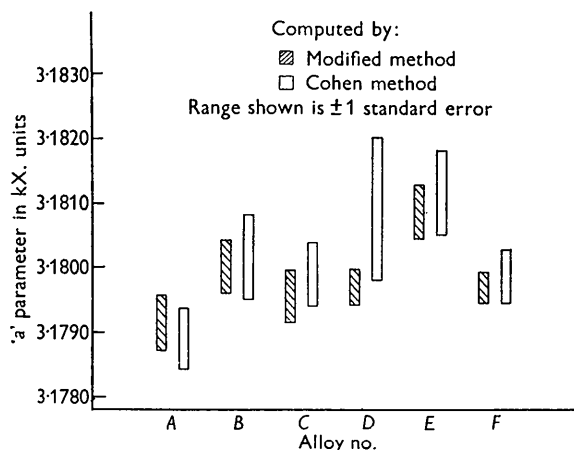


Fig. 3. Comparisons of the Cohen and modified computations for patterns of unrelated samples of magnesium-base solid solutions from a flat-film back-reflection camera. The comparison is shown only for the more precise 'a' parameter.

especially important in determining the effect upon the lattice constants of some experimental treatment of the specimen. An example is given in Table 1, where the 't-test' (Mills, 1938) has been applied to the results computed by both procedures from the measurements of two patterns secured, respectively, before and after a particular heat treatment of the specimen. On the basis of the parameters computed by the modified procedure, the lattice constants are shown to have been altered to a significant degree by the treatment (as was

Table 1. Comparison of the significance level of the difference between specimens when the parameters are computed by the Cohen procedure and by the modified method

	Before heat treatment	After heat treatment	Probability that the difference is not significant (%)
Modified method	$3.1792_1 \pm 0.0004_8$	$3.1807_0 \pm 0.0003_8$	$\leq 1$
Cohen method	$3.1795_4 \pm 0.0005_8$	$3.180_7 \pm 0.001_4$	$\sim 35$

also suggested by other physical tests). If, however, one were to rely upon the parameters computed by the Cohen procedure, it would be necessary to conclude that a difference as great as was measured must be expected experimentally about one-third of the time from chance alone, and, hence, that the measured change probably had no significance.

These examples of the effect of the Cohen computation method upon the lattice constants have been confirmed in many more specific cases where comparison computations have been carried out. In addition, some further practical confirmation has been indicated from many hundreds of lattice-constant determinations by the modified computation, which have been made in the last few years in the Magnesium Laboratories of The Dow Chemical Company. For example, it has been noted repeatedly in studies of the effect of various solute elements upon the lattice constants of magnesium-base solid solutions that the lattice constant  $v$ . composition data have exhibited less scatter than had been experienced previously in otherwise analogous studies when the Cohen computation was employed. In a few cases where earlier determinations were repeated, the error bands of the new curves were as much as 50% narrower. In still other studies, significant correlation was found between the X-ray parameters and the concurrent measurements of other properties, like electrical conductivity, where analogous earlier studies with the Cohen method had almost invariably proved insensitive. It seems fair to conclude that the slightly greater computational effort required for the modified procedure has been completely justified by detectible improvement in the precision of the computed lattice constants.

Much of the work reported here was carried out at The Dow Chemical Company. Helpful suggestions from Professor C. S. Barrett are gratefully acknowledged.

## APPENDIX I

### Modification for other cameras and other crystal systems

The treatment of the cubic system with back-reflection Debye camera has already been given. Extension of the method to the symmetrical focusing back-reflection camera is easily accomplished by modifying the substitutions of equation (6) to

$$\delta \equiv \frac{s}{2D} \sin \frac{s}{2D} \quad \text{and} \quad \gamma \equiv 1 + \cos \frac{s}{2D}.$$

The normal equations for this case then become identical with (13a).

For the flat-film symmetrical back-reflection camera, the specific observation equation for the cubic system can be written

$$\frac{1}{a_0^2} \frac{\lambda^2}{2} n^2 (h^2 + k^2 + l^2) + K_0 \frac{4ps^2}{(s^2 + 4p^2)^{\frac{3}{2}}} - \left\{ 1 + \frac{2p}{(s^2 + 4p^2)^{\frac{1}{2}}} \right\} = 0, \quad (15)$$

where  $p \equiv$  film-specimen distance. Hence the appropriate substitutions are

$$\delta \equiv \frac{4ps^2}{(s^2 + 4p^2)^{\frac{3}{2}}} \quad \text{and} \quad \gamma \equiv 1 + \frac{2p}{(s^2 + 4p^2)^{\frac{1}{2}}}.$$

The  $L$  coefficients can be approximated sufficiently well by

$$L \simeq \frac{1}{w_s} \operatorname{cosec}^2 \phi \sec^4 \phi = \frac{1}{w_s} \frac{(s^2 + 4p^2)^3}{s^2}, \quad (16)$$

by an argument analogous to the one used in developing equation (12a). The normal equations for this case thus become

$$\left. \begin{aligned} \Delta A \Sigma \alpha^2 \frac{w_s}{\sin^2 \phi \cos^4 \phi} + \Delta K \Sigma \alpha \delta \frac{w_s}{\sin^2 \phi \cos^4 \phi} \\ = \Sigma \alpha F_0 \frac{w_s}{\sin^2 \phi \cos^4 \phi}, \\ \Delta A \Sigma \alpha \delta \frac{w_s}{\sin^2 \phi \cos^4 \phi} + \Delta K \Sigma \delta^2 \frac{w_s}{\sin^2 \phi \cos^4 \phi} \\ = \Sigma \delta F_0 \frac{w_s}{\sin^2 \phi \cos^4 \phi}. \end{aligned} \right\} (17)$$

Crystal systems having more than one lattice parameter are more complicated in requiring additional normal equations. The treatment may be illustrated in terms of a tetragonal lattice and the back-reflection Debye camera. The specific observation equation for this case,

$$\frac{\lambda^2}{4} n^2 \left( \frac{h^2 + k^2}{a_0^2} + \frac{l^2}{c_0^2} \right) + K_0 \frac{s}{2D} \sin \frac{s}{D} = \cos^2 \frac{s}{2D}, \quad (18)$$

may be brought to the form

$$F = A_0 \alpha + B_0 \beta + K_0 \delta - \gamma, \quad (19)$$

by modifying certain substitutions of equation (6) to

$$\begin{aligned} A_0 &\equiv 1/a_0^2, \\ \alpha &\equiv \frac{1}{2} \lambda^2 n^2 (h^2 + k^2), \\ B_0 &\equiv 1/c_0^2, \\ \beta &\equiv \frac{1}{2} \lambda^2 n^2 l^2. \end{aligned}$$

The quantities  $\delta$  and  $\gamma$  remain identical with the earlier case. Then the normal equations analogous to (13a) become

$$\left. \begin{aligned} \Delta A \Sigma \alpha^2 \frac{w_s}{\sin^2 \phi} + \Delta B \Sigma \alpha \beta \frac{w_s}{\sin^2 \phi} + \Delta K \Sigma \alpha \delta \frac{w_s}{\sin^2 \phi} \\ = \Sigma \alpha F_0 \frac{w_s}{\sin^2 \phi}, \\ \Delta A \Sigma \alpha \beta \frac{w_s}{\sin^2 \phi} + \Delta B \Sigma \beta^2 \frac{w_s}{\sin^2 \phi} + \Delta K \Sigma \beta \delta \frac{w_s}{\sin^2 \phi} \\ = \Sigma \beta F_0 \frac{w_s}{\sin^2 \phi}, \\ \Delta A \Sigma \alpha \delta \frac{w_s}{\sin^2 \phi} + \Delta B \Sigma \beta \delta \frac{w_s}{\sin^2 \phi} + \Delta K \Sigma \delta^2 \frac{w_s}{\sin^2 \phi} \\ = \Sigma \delta F_0 \frac{w_s}{\sin^2 \phi}. \end{aligned} \right\} (20)$$

Here, too, exactly as was found for the cubic case, modification of the quantities  $\delta$  and  $\gamma$  permits extension to other cameras.

Buerger (1942) has adapted the Cohen extrapolation for single-crystal work to refine  $d$  spacings when  $\lambda$  and  $n$  are variable. In this case the generalized interplanar spacing  $d$  is retained in the observation equation. For example, for a back-reflection Debye camera the observation equation becomes

$$\frac{n^2\lambda^2}{4d^2} + K \frac{\phi}{2} \sin \phi = \cos^2 \frac{\phi}{2}. \quad (21)$$

This equation can, in turn, be recast into a form identical with (6) by modifying the  $A_0$  and  $\alpha$  substitutions to  $A_0 \equiv 1/d^2$  and  $\alpha \equiv \frac{1}{2}n^2\lambda^2$ . The normal equations of (13a) then become the appropriate solution.

## APPENDIX II

### Derivation of the systematic-errors function for the flat-film symmetrical back-reflection camera

A systematic error is introduced by any error in the measurement of the true film-specimen distance. Let  $p$  be the assumed film-specimen distance, and  $s$  be the diameter of a particular ( $hkl$ ) ring on the film. Then, the angle  $\phi$  for this particular ( $hkl$ ) plane is given by

$$\tan \phi = \frac{1}{2}s/p. \quad (22)$$

An error  $\Delta p$  in the distance  $p$  causes an error  $\Delta\phi_p$  in each of the calculated back-reflection angles  $\phi$ . This error is

$$\Delta\phi_p = -\frac{\Delta p}{p} \sin \phi \cos \phi. \quad (23)$$

Shrinkage of the film introduces an error  $\Delta s$  in the measurement of the line diameter  $s$ . Again employing equation (22), the error in each calculated angle  $\phi$  is given by

$$\Delta\phi_s = \frac{\Delta s}{s} \sin \phi \cos \phi. \quad (24)$$

There is line broadening, but no systematic error, due to the film being other than perpendicular to the incident X-ray beam if the film is rotated during exposure. Such rotation is normal practice, however, and the

abnormal case which introduces a systematic error can easily be avoided.

Cylindrical cameras are subject to a systematic error due to eccentric mounting of the specimen in the X-ray beam, but no such error can be incurred in the flat-film back-reflection method.

Systematic deviation of the intensity maximum of a diffracted line from the center of the 'geometric' diffracted beam, due to absorption in the specimen, is negligible unless the depth of penetration of the X-ray beam into the surface of the specimen is of the same order of magnitude as the diameter of the defining pinhole. This critical ratio is usually avoided with large margin of safety simply by employing normal pinholes of 0.020 in. or larger.

The total systematic error in  $\phi$  will be the sum of all the individual systematic errors. That is

$$\Delta\phi = \Delta\phi_p + \Delta\phi_s = (\Delta s/s - \Delta p/p) \sin \phi \cos \phi. \quad (25)$$

For uniform shrinkage,  $\Delta s/s$  is a constant for a given film. Similarly  $\Delta p/p$  is also a constant for a given film. The error function may consequently be reduced to the simple expression

$$\Delta\phi = K \sin \phi \cos \phi. \quad (26)$$

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