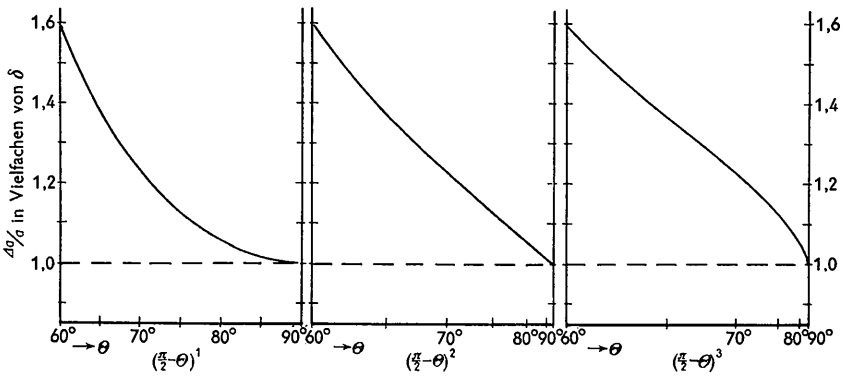

Fig. 3. Die Brechungskorrektur, ausgedrückt in $\Delta a/a$, aufgetragen über einigen hypothetischen Extrapolationsfunktionen, für sehr kleine Teilchen - - - - - - -, für sehr grosse Teilchen mit ebenen Oberflächen ————.

die Täler gerade das Umgekehrte gilt. Der Beitrag zur reflektierten Intensität ist aber für die Berge höher als für die Täler, da für eine gegebene Eindringtiefe der Strahlenweg innerhalb des Teilchens und damit die Absorption bei den Bergen kleiner ist als bei den Tälern. Im Mittel über die ganze, aufgerauhte Oberfläche erhält man also eine gegenüber Gl. (8) verringerte B.K. Mit ähnlichen Argumenten kann man für sehr kleine Teilchen zeigen, dass eine schwache, aber nicht zu vernachlässigende Absorption zu einer Erhöhung der B.K. gegenüber Gl. (9) führt. Solange über Gestalt und Grösse der Pulverteilchen nichts näheres bekannt ist, bleibt also die Differenz zwischen Gl. (8) und Gl. (9) als Unsicherheit der B.K.

Bei Anwendung einer Extrapolationsmethode liegen die Verhältnisse günstiger. In Fig. 3 sind die beiden Grenzen der B.K., ausgedrückt in $\Delta a/a$, über verschiedenen, hypothetischen Extrapolationsfunktionen aufgetragen. Bei der Funktion $(\frac{1}{2}\pi-\theta)^2$, die im Rückstrahlbereich etwa proportional $\cos^2\theta$ ist, extrapoliert sich $\Delta a/a$ mit $\theta \to 90°$ nahezu streng linear auf den richtigen Wert $\Delta a/a = \delta$ wie es bei dem Korrekturverfahren nach Wilson vorausgesetzt wird. Bei den beiden anderen Abszissenfunktionen kann bei ungünstiger Lage der letzten Interferenzen eventuell ein Fehler entstehen. Dieser ist aber wohl meist zu vernachlässigen, da die B.K., wie weiter vorne begründet, im allgemeinen zwischen den Extremen liegt.

Zusammenfassung

Es wird die Brechungskorrektur für Pulverpräparate untersucht. Die Korrektur liegt zwischen zwei Grenzwerten, deren Differenz bei hohen Winkeln Θ klein ist, mit fallendem Winkel Θ aber zunimmt. Die Korrektur der Gitterkonstanten nach der Extrapolation auf $\Theta = 90°$ ist jedenfalls dann unbedenklich, wenn die Extrapolationsfunktion etwa wie $(\frac{1}{2}\pi-\theta)^2$ gegen Null geht mit $\theta \to 90°$.

Literatur

Frohnmeyer, G. & Glocker, R. (1953). *Acta Cryst.* **6**, 19.

James, R. W. (1954). *The optical principles of the diffraction of X-rays*. London: Bell.

Straumanis, M. E. (1955). *Acta Cryst.* **8**, 654.

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

Acta Cryst. (1960). **13**, 828

Determination of lattice parameters with the aid of a computer.

By Melvin H. Mueller, LeRoy Heaton and K. T. Miller, *Argonne National Laboratory, Lemont, Illinois, U.S.A.*

(*Received* 12 *June* 1959)

The determination of precision lattice parameters was originally coded for the Argonne AVIDAC computer and has now been programmed for the Argonne GEORGE digital computer and for IBM-704. The present program permits the determination of lattice parameters and standard errors for the orthorhombic system and all other crystal systems of higher symmetry using a method of least squares. The angular measurements of lines or spots for several different wave lengths obtained from various types of cameras or a diffractometer may be used.

Provision has been made for using as many as three separate correction terms for eccentricity, absorption, divergence, etc.; however, one, two, three or none at all, may be used. The exact trigonometric function or functions used in these correction terms may be selected from a number of those previously suggested; for example,

$$\sin^2 2\theta,\ \varphi \sin 2\varphi,\ \cos^2\theta \sin 2\theta,\ \sin^2 2\theta(1/\sin\theta + 1/\theta),$$
$$\cos^2\theta \sin^2 2\theta \text{ or } \cos 2\theta .$$

If desired, a weighting factor (Hess, 1951) may also be used for each reflection, which may include an observation weight and/or a trigonometric function appropriate for the particular instrument, such as $1/\sin^2 2\theta$ for a Debye–Scherrer camera, and in addition a refraction correction may also be used.

For convenience in defining the problem, the difference, v, between the computed $\sin^2\theta$ and the observed $\sin^2\theta$ for each reflection, i, may be defined as:

$$v_i = \sin^2\theta_i(\text{computed}) - \sin^2\theta_i(\text{observed}) .$$

This may also be written:

$$v_i = [(A_0 + \Delta A)g\alpha_i + (B_0 + \Delta B)\beta_i + (C_0 + \Delta C)\gamma_i]L_i - (\sin^2\theta_i + \Delta\theta_i \sin 2\theta_i) ,$$

where

A_0, B_0 and C_0 are adopted values for $\lambda^2/(4a_0^2)$, $\lambda^2/(4b_0^2)$ and $\lambda^2/(4c_0^2)$, respectively,
$g = 4/3$ for hex. and 1 for all other systems,
α_i, β_i and γ_i have the usual meaning related to Miller indices,
$L_i = \lambda^2(\text{read})/\lambda^2(\text{used in computing parameters})$ and
$\Delta\theta_i \sin 2\theta_i = \Delta D\delta_j(\theta_i) + \Delta E\varepsilon_k(\theta_i) + \Delta F\zeta_l(\theta_i)$.

The problem is then to minimize the following:

$$\sum_n W_i v_i^2(\Delta A, \Delta B, \Delta C, \Delta D, \Delta E, \Delta F) ,$$

where

W_i = the weighting factor.

The best values for the particular delta terms used are determined by matrix methods using the computers.

The lattice parameters and their standard errors are then calculated according to the following:

$$a_0 = \left[\frac{\lambda^2}{4(A_0 + \Delta A)} g\right]^{\frac{1}{2}} \qquad S_{a_0} = \frac{0{\cdot}6745 a_0 g}{2A} \sigma_{\Delta A} .$$

The b_0, S_{b_0}, c_0 and S_{c_0} are calculated in the same way except that no g term is necessary.

The input data necessary therefore for a solution of a lattice parameter problem are: (1) number of lattice parameters to be determined, one, two or three; (2) number of drift constants, ΔD, ΔE, ΔF, ranging from zero to three; (3) type of trigonometric function,

$$\delta_j(\theta_i),\ \varepsilon_k(\theta_i),\ \zeta_l(\theta_i) ,$$

to be used with each drift constant; (4) type of weighting factor, W_i, if used; (5) value of g; (6) value of L_i; (7) wave length to be used in calculation; (8) α_i, β_i, γ_i which are related to the Miller indices in the usual manner; (9) θ_i in degrees or radians; (10) starting values for A_0, B_0 and C_0 as appropriate and (11) number of observations, n.

The present program calls for a print out of the following: (1) the input data; (2) ΔA, ΔB, ΔC and drift constants together with their σ^2 values; (3) lattice parameters and standard errors; (4) the v for each i; (5) $\sum_n W_i v_i^2/(n-k-1)\sum_n W_i$ where n = number of observations and k = degrees of freedom. This last term, the σ^2 of the v_i, is useful in evaluating the fit.

For each set of data a solution is first carried out for the lattice parameters only without the use of systematic correction terms and with equal weight for each observation. A plot of v versus θ for each observation is then made which incorporates some of the advantages of the graphical extrapolation method. From this plot it is possible (1) to detect the degree of systematic errors and to aid in the selection of the most suitable type of systematic correction, (2) to indicate the degree of randomness, (3) to pick out large deviations in individual observations which indicate errors in θ or incorrect indexing or (4) to determine indeed if any systematic correction is necessary.

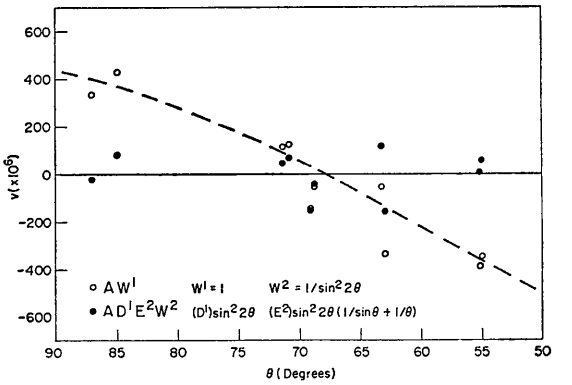

Fig. 1. Plot of v against θ for cubic UN pattern.

Fig. 1 is a plot of v versus θ obtained from a UN pattern, using Cu $K\alpha$ filtered radiation ($\lambda_{K\alpha 1} = 1{\cdot}54051$ Å), 114·59 mm. diameter camera, using asymmetric loading. The open circles indicate the results obtained without the use of a systematic correction term using unit weights, W^1, whereas the closed circles were obtained using two separate correction terms, D^1E^2, and a trigonometric weighting, W^2. Although this is not high precision data it illustrates many of the features of the plotting indicated above.

Since the calculation time for a single solution of a problem is a matter of a few sec., in practice it is usually advantageous to obtain several solutions to the problem at the same time using different combinations of correction terms and weighting factors in order to pass judgment on the fitting process and the accuracy of the lattice parameters. It is not surprising that in many cases the same or very nearly the same precise lattice parameters are obtained using different correction terms or combinations of terms.

Experience thus far indicates a weighting factor usually gives a better fit with a smaller standard error; however, exceptions have been observed. It has not been found necessary to use an iterative method with the program thus far, since the convergence is very rapid even though the starting values, A_0, B_0 and C_0, were in error by a factor of ten.

The authors are indebted to W. Greenhow for programming and to H. W. Knott for assistance in film measurement and tabulation. This work was performed under the auspices of the United States Atomic Energy Commission.

Reference

HESS, J. B. (1951). *Acta Cryst.* **4**, 209.