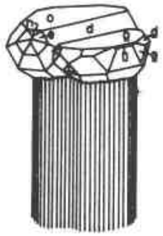

FIG. 2 (left). Group of three twinned colusite crystals oriented on an enargite prism. Leonard mine, Butte, Montana. Photograph by John W. Anthony.

FIG. 3 (center). Colusite twin oriented on enargite. Forms on the colusite twin are $o\{111\}$, $e\{012\}$, $n\{112\}$ and $d\{011\}$.

FIG. 4 (right). Colusite crystal oriented on enargite. This crystal lacks $o\{111\}$; other forms as in Fig. 3.

Thanks are due to Professor John W. Anthony, Department of Geology, University of Arizona, and Professor A. Pabst, Department of Geology, University of California, Berkeley, who read the manuscript and made a number of helpful suggestions.

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THE AMERICAN MINERALOGIST, VOL. 45, NOVEMBER-DECEMBER, 1960

A METHOD FOR THE DIRECT DETERMINATION OF LATTICE PARAMETERS

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Although the calculation of lattice parameters by Cohen's method of least squares (1) has proved a highly successful means of attaining accuracy and precision from *x*-ray powder data, it incorporates an analytical extrapolation of $\cos^2\theta$ to $\theta=90°$, as suggested by Bradley and Jay (2) to eliminate errors inherent in Debye-Scherrer type cameras. This dependence upon the error characteristics of a specific recording geometry may limit the universal applicability of the method to data obtained from other types of recording devices in which the systematic errors are either negligibly small (3), (4) or at any rate are not proportional to $\cos^2\theta$.

In the absence of systematic errors, it is still advantageous to minimize residual random errors, and this may be done conveniently and directly by finding values of Q_{hkl} (where $Q=1/d^2$) for each of the reflections concerned, and combining these by the method of least squares to yield the lattice parameters of the crystal in question.

The derivations of the method for the cubic, tetragonal and orthorhombic systems are as follows:

1. Cubic system (where $\alpha=h^2+k^2+l^2$, $A=1/a_0^2$, and Δ is the error) $Q=\alpha A+\Delta$, Rearranging and squaring, $\Delta^2=Q^2+\alpha^2A^2-2\alpha AQ$. Differentiating with respect to A, $2\alpha^2A=2\alpha Q$. Hence, for a series of observations,

$$A=\frac{\Sigma\alpha Q}{\Sigma\alpha^2} \tag{1}$$

2. Tetragonal system (where $\alpha=h^2+k^2$, $\gamma=l^2$, $C=1/c_0^2$ and the other terms have the same meanings as in the cubic case). $Q=\alpha A+\gamma C+\Delta$, Rearranging and squaring,

$$\Delta^2=Q^2+\gamma^2C^2+\alpha^2A^2-2\alpha AQ-2\gamma CQ+2\alpha A\gamma C$$

Differentiating with respect to A and C, respectively,

$$\begin{cases}2\alpha^2A-2\alpha Q+2\alpha\gamma C=0\\2\gamma^2C-2\gamma Q+2\alpha\gamma A=0\end{cases}$$

Hence, for a series of observations,

$$\begin{cases}A\Sigma\alpha^2+C\Sigma\alpha\gamma=\Sigma\alpha Q\\C\Sigma\gamma^2+A\Sigma\alpha\gamma=\Sigma\gamma Q\end{cases}$$

Solving by determinants,

$$A=\frac{\Sigma\gamma Q\cdot\Sigma\alpha\gamma-\Sigma\alpha Q\cdot\Sigma\gamma^2}{D^*} \tag{2}$$

and

$$C=\frac{\Sigma\alpha Q\cdot\Sigma\alpha\gamma-\Sigma\gamma Q\cdot\Sigma\alpha^2}{D^*} \tag{3}$$

where D* is the determinant of the system, *i.e.* $(\Sigma\alpha\gamma)^2-\Sigma\alpha^2\,\Sigma\gamma^2$

3. Orthorhombic system (where $\alpha=h^2$, $\beta=k^2$, $B=1/b_0^2$ and the other terms are as previously defined)

$$Q = \alpha A + \beta B + \gamma C + \Delta$$

Rearranging and squaring,

$$\Delta^2 = Q^2 + \alpha^2 A^2 + \beta^2 B^2 + \gamma^2 C^2 - 2Q\alpha A - 2Q\beta B - 2Q\gamma C$$
$$+ 2\alpha A\beta B + 2\alpha A\gamma C + 2\beta B\gamma C$$

Differentiating with respect to A,B, and C, respectively,

$$\begin{cases} 2\alpha^2 A - 2\alpha Q + 2\alpha\gamma C + 2\alpha\beta B = 0 \\ 2\beta^2 B - 2\beta Q + 2\alpha\beta A + 2\beta\gamma C = 0 \\ 2\gamma^2 C - 2\gamma Q + 2\alpha\gamma A + 2\beta\gamma B = 0 \end{cases}$$

Hence, for a series of observations,

$$\begin{cases} A\Sigma\alpha^2 + B\Sigma\alpha\beta + C\Sigma\alpha\gamma = \Sigma\alpha Q \\ B\Sigma\beta^2 + A\Sigma\alpha\beta + C\Sigma\beta\gamma = \Sigma\beta Q \\ C\Sigma\gamma^2 + A\Sigma\alpha\gamma + B\Sigma\beta\gamma = \Sigma\gamma Q \end{cases}$$

Solving by determinants,

$$AD^* = [\Sigma\gamma Q\ \Sigma\alpha\beta\ \Sigma\beta\gamma + \Sigma\beta Q\ \Sigma\beta\gamma\ \Sigma\alpha\gamma + \Sigma\alpha Q\ \Sigma\beta^2\ \Sigma\gamma^2]$$
$$- [\Sigma\alpha Q\ (\Sigma\beta\gamma)^2 + \Sigma\alpha\beta\ \Sigma\beta Q\ \Sigma\gamma^2 + \Sigma\alpha\gamma\ \Sigma\beta^2\ \Sigma\gamma Q] \qquad (4)$$
$$BD^* = [\Sigma\alpha\gamma\ \Sigma\beta\gamma\ \Sigma\alpha Q + \Sigma\alpha\beta\ \Sigma\gamma Q\ \Sigma\alpha\gamma + \Sigma\alpha^2\ \Sigma\beta Q\ \Sigma\gamma^2]$$
$$- [\Sigma\alpha^2\ \Sigma\gamma Q\ \Sigma\beta\gamma + \Sigma\alpha Q\ \Sigma\alpha\beta\ \Sigma\gamma^2 + \Sigma\beta Q\ (\Sigma\alpha\gamma^2] \qquad (5)$$
$$CD^* = [\Sigma\alpha\gamma\ \Sigma\alpha\beta\ \Sigma\beta Q + \Sigma\alpha\beta\ \Sigma\beta\gamma\ \Sigma\alpha Q + \Sigma\alpha^2\ \Sigma\beta^2\ \Sigma\gamma Q]$$
$$- [\Sigma\alpha^2\ \Sigma\beta\gamma\ \Sigma\beta Q + (\Sigma\alpha\beta)^2\ \Sigma\gamma Q + \Sigma\alpha\gamma\ \Sigma\beta^2\ \Sigma\alpha Q] \qquad (6)$$
$$D^* = [2(\Sigma\alpha\gamma\ \Sigma\alpha\beta\ \Sigma\beta\gamma) + \Sigma\alpha^2\ \Sigma\beta^2\ \Sigma\gamma^2]$$
$$- [\Sigma\alpha^2\ (\Sigma\beta\gamma) + \Sigma\beta^2\ (\Sigma\alpha\gamma)^2 + \Sigma\gamma^2\ (\Sigma\alpha\beta)^2]$$

In order to illustrate the ease and directness of application of this least squares treatment of the reciprocal lattice, equation (I) will be used to calculate the lattice parameter of sodium chloride. The data in this example were derived from a 2.4 cm. radius precision low angle device (4); the preliminary treatment of the data involved correction for film shrinkage, and the graphical conversion of *RZ* values (4) to *Q* values.

hkl	α	α^2	Q_{obs}	αQ_{obs}
111	3	9	.0936	.281
200	4	16	.1255	.502
220	8	64	.2510	2.008
311	11	121	.3475	3.823
222	12	144	.3765	4.518

$\sum\alpha Q = 11.132$, $\sum\alpha^2 = 354$, $A = 0.03145$, $a_0 = 5.639$ Å.

Acknowledgements

It is a pleasure to acknowledge the generous help provided by F. H. Kelly, M.O.B. in making available his computers. I also wish to thank Professor J. B. Polya and M. H. Ra-Stas for their valued discussions and advice.

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THE AMERICAN MINERALOGIST, VOL. 45, NOVEMBER–DECEMBER, 1960

THE DEVELOPMENT OF AN ACCURATE LOW ANGLE *X*-RAY POWDER DIFFRACTION CAMERA

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Introduction

Most attempts at increasing the degree of accuracy attainable from low powder angle powder diffraction data have hitherto been directed toward the recognition and mathematical correction of general systematic errors, toward the manual correction of collimation and recording geometry distortions and towards the construction of larger and more intricate cameras and diffractometers. There are limits to the practicability of attempting to eliminate errors entirely by these means; usually it is found that the random errors of observation become more serious at low angles than any or all of the systematic errors attributable to the nature of the recording instrument or to the specimen.

Random errors

Quantitative assessments of the effect of random errors may be obtained upon consideration of the instantaneous magnification, M_i, defined as the rate of change of measured film distance, S, with respect to the interplanar spacing, D, in the crystal. In the case of the familiar Debye-Scherrer type of camera, the measured film distance is proportional to θ, and, in the terms of Bragg's equation,

$$M_i = \frac{dS}{dD} = \frac{-4R}{n\lambda \cot\theta \csc\theta}$$

The magnitude of a random error of observation may be regarded as independent of ϕ, and its effect upon a derived lattice spacing is inversely proportional to M_i, that is,

$$\Delta \propto \frac{n\lambda \cot\theta \csc\theta}{4R}$$

Since $\cot\theta$ and $\csc\theta$ are functions which increase in value rapidly with