SHORT COMMUNICATIONS

The calculation of errors in a least squares estimate of unit-cell dimensions

A LEAST squares technique for evaluating unit-cell dimensions from measurements of the d-spacings of indexed powder lines has been described by Smith (1956). The relationship between d-spacing and indices is given in the general triclinic case by the equation

$$Q(hkl) = d_{hkl}^{-2} = h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+ \\ +2klb^*c^*\cos\alpha^*+2lhc^*a^*\cos\beta^*+2hka^*b^*\cos\gamma^*$$

which can be written in the form

$$Q(hkl) = h^2x_1+k^2x_2+l^2x_3+klx_4+lhx_5+hkx_6.$$

Smith derived least squares estimates of $x_1,..., x_6$, together with the estimated standard deviation $\hat{\sigma}$ of Q for the measured lines, from the expression: $\hat{\sigma}^2 = \sum(Q_{\text{obs}}-Q_{\text{calc}})^2/(M-N)$, where M is the number of lines measured and N is the number of variables to be estimated (6 for the triclinic). Smith then evaluates the standard deviation, σ_i, of the least squares estimates of each x_i from the relationship $\sigma_i = \hat{\sigma}\sqrt{c_{ii}}$, where c_{ii} is the appropriate element on the principal diagonal of the covariance matrix (Smith, 1956, p. 56). It would be more interesting to have estimates of the standard deviations of the calculated parameters of the direct lattice, a, b, c, α, β, and γ.

The errors in x_i are interdependent, the relationship between the standard deviations of a function F of the least square estimates of $x_1,..., x_6$ being given by $\sigma_F^2 = \hat{\sigma}^2 . \sum_{j=1}^{6}\sum_{k=1}^{6} c_{jk}.(\partial F/\partial x_j).(\partial F/\partial x_k)$ (Deming, 1938, p. 167), where c_{jk} is the element in the jth row of the kth column of the covariance matrix. If the function F is taken to be each of the direct lattice parameters in turn, the standard deviation of the calculated parameters a, b, c, α, β, and γ can be evaluated from this expression.

The partial derivatives of the direct lattice parameters with respect to the estimated variables are set down in table I. The calculation of each of the six σ_F's involves 36 triple products, which reduces to 21 since $c_{jk} = c_{kj}$. A programme for calculating least squares estimates of unit-cell dimensions and their estimated standard deviations was therefore written for the Cambridge University digital computer

TABLE I. Partial derivatives of direct lattice parameters in the triclinic system

F	$\partial F/\partial x_1$	$\partial F/\partial x_2$	$\partial F/\partial x_3$	$\partial F/\partial x_4$	$\partial F/\partial x_5$	$\partial F/\partial x_6$
a	$-\frac{1}{2}a^3$	$-\frac{1}{2}ab^2\cos^2\gamma$	$-\frac{1}{2}ac^2\cos^2\beta$	$-\frac{1}{2}abc\cos\beta\cos\gamma$	$-\frac{1}{2}a^2c\cos\beta$	$-\frac{1}{2}a^2b\cos\gamma$
b	$-\frac{1}{2}a^2b\cos^2\gamma$	$-\frac{1}{2}b^3$	$-\frac{1}{2}bc^2\cos^2\alpha$	$-\frac{1}{2}b^2c\cos\alpha$	$-\frac{1}{2}abc\cos\alpha\cos\gamma$	$-\frac{1}{2}ab^2\cos\gamma$
c	$-\frac{1}{2}a^2c\cos^2\beta$	$-\frac{1}{2}b^2c\cos^2\alpha$	$-\frac{1}{2}c^3$	$-\frac{1}{2}bc^2\cos\alpha$	$-\frac{1}{2}ac^2\cos\beta$	$-\frac{1}{2}abc\cos\alpha\cos\beta$
α	$a^2A/2\sin\alpha$	$\frac{1}{4}b^2\sin 2\alpha$	$\frac{1}{4}c^2\sin 2\alpha$	$\frac{1}{2}bc\sin\alpha$	$\frac{1}{2}ac\sin\alpha\cos\gamma$	$\frac{1}{2}ab\sin\alpha\cos\beta$
β	$\frac{1}{4}a^2\sin 2\beta$	$b^2B/2\sin\beta$	$\frac{1}{4}c^2\sin 2\beta$	$\frac{1}{2}bc\sin\beta\cos\gamma$	$\frac{1}{2}ac\sin\beta$	$\frac{1}{2}ab\sin\beta\cos\alpha$
γ	$\frac{1}{4}a^2\sin 2\gamma$	$\frac{1}{4}b^2\sin 2\beta$	$c^2C/2\sin\gamma$	$\frac{1}{2}bc\sin\gamma\cos\beta$	$\frac{1}{2}ac\sin\gamma\cos\alpha$	$\frac{1}{2}ab\sin\gamma$

$$A = 2\cos\beta\cos\gamma - \cos\alpha(\cos^2\beta + \cos^2\gamma)$$
$$B = 2\cos\alpha\cos\gamma - \cos\beta(\cos^2\alpha + \cos^2\gamma)$$
$$C = 2\cos\alpha\cos\beta - \cos\gamma(\cos^2\alpha + \cos^2\beta)$$

EDSAC II. The results of the application of the programme to Smith's measurements on the Spanish Peak andesine are given in table II. The value of $\hat{\sigma}$ $6{\cdot}47\times10^{-5}$ calculated from $(\hat{\sigma})^2 = \sum (Q_{\text{obs}}-Q_{\text{calc}})^2/(M-6)$ differs from that obtained by Smith, $\hat{\sigma}$ $20{\cdot}66\times10^{-5}$, who used the expression:

$$(\hat{\sigma})^2 = (\sum Q^2_{\text{obs}}-nx_1-ox_2-px_3-qx_4-rx_5-sx_6)/(M-6),$$

where n, o,... are quantities used in forming the normal equations (Smith, 1956, p. 55). Recalculation of $\hat{\sigma}$ from data given by Smith on

TABLE II. Direct lattice parameters and their standard deviations for Spanish Peak andesine

	a (Å)	b (Å)	c (Å)	α	β	γ
Smith	8·160	12·848	7·121	93·72°	116·36°	89·52°
New values	8·1583	12·8471	7·1204	93·708	116·352	89·538
	σ_a	σ_b	σ_c	σ_α	σ_β	σ_γ
	0·0026	0·0017	0·0007	0·017	0·011	0·015

TABLE III. Partial derivatives of direct lattice parameters in the monoclinic system

F	$\partial F/\partial x_1$	$\partial F/\partial x_2$	$\partial F/\partial x_3$	$\partial F/\partial x_4$
a	$-\frac{1}{2}a^3$	0	$-\frac{1}{2}ac^2\cos^2\beta$	$-\frac{1}{2}a^2c\cos\beta$
b	0	$-\frac{1}{2}b^3$	0	0
c	$-\frac{1}{2}a^2c\cos^2\beta$	0	$-\frac{1}{2}c^3$	$-\frac{1}{2}ac^2\cos\beta$
β	$\frac{1}{4}a^2\sin 2\beta$	0	$\frac{1}{4}c^2\sin 2\beta$	$\frac{1}{2}ac\sin\beta$

a desk calculator using the former expression leads to the evaluation of $\hat{\sigma}$ as $6{\cdot}41\times10^{-5}$. The discrepancy of Smith's $\hat{\sigma}$ from these values is in large part due to his use of the alternative expression which introduces appreciable rounding-off errors in this case where the difference between $\sum Q^2_{\text{obs}}$ and $nx_1+ox_2+px_3+qx_4+rx_5+sx_6$ is of the order of 1 in 10^6; recalculation of $(\hat{\sigma})^2$ from this alternative equation on EDSAC II working to nine significant figures leads to a value of $\hat{\sigma}$ $6{\cdot}42\times10^{-5}$.

For data in systems of higher symmetry the computations become simpler. In the monoclinic system four variables are determined, a^{*2} b^{*2}, c^{*2}, and $2lhc^*a^*\cos\beta^*$. The expression for σ_F^2 is

$$\sigma_F^2 = \hat{\sigma}^2.\sum_{j=1}^{4}\sum_{k=1}^{4} c_{jk}.(\partial F/\partial x_j).(\partial F/\partial x_k).$$

The expressions for $\partial F/\partial x_j$ and $\partial F/\partial x_k$ are given in table III. In the orthorhombic system further simplification occurs since a, b, and c depend only on a^{*2}, b^{*2}, and c^{*2} respectively; the standard deviations there reduce to expressions of the form $\sigma_a = \frac{1}{2}\sqrt{c_{11}}\,\hat{\sigma}a^3$.

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Plagioclase reactions

During experiments with plagioclase feldspars, two unexpected effects were observed that do not appear to have been reported elsewhere. Sufficient work was carried out to ensure that the effects were real, but no further investigation is intended: the results are merely reported here as interesting phenomena.

Reactions with NaCl. Powders of crystalline plagioclase and rock-salt were mixed in equal proportions by weight and heated in a covered platinum crucible to 700° C for a day or so and then quenched in air. X-ray powder photographs showed the following crystalline components after the heat-treatment:

Albite (0·5 % An)+NaCl → sodalite
Oligoclase (22·1 % An)+NaCl → sodalite+nepheline
Bytownite (71·3 % An)+NaCl → nepheline,

while a subsidiary experiment showed that a naturally occurring nepheline heated with rock-salt under the same conditions gave:

Nepheline+NaCl → sodalite,

and so the primary product in the plagioclase reactions might always be nepheline. However, although albite was heated with very small proportions of rock-salt (about 10 % by weight) so that no excess NaCl would be left for further reaction if nepheline *were* formed first, only traces of the *sodalite* pattern were found: thus nepheline does not seem to be the primary product with albite.

The albite reaction was studied in slightly more detail. Powdered albite glass and rock-salt also produced sodalite at 700° C, but at temperatures of 650° C and below neither glassy nor crystalline albite showed any reaction after heating for 1 day. At 700° C all mixtures