Rosa Farinato *, Lucio Loreto*

## A LEAST-SQUARES REFINEMENT OF THE CRYSTAL LATTICE CONSTANTS AND EVALUATION OF THEIR ERRORS, USING THE DIRECT UNIT-CELL


#### Abstract

A Least-Square refinement procedure allowing a straightforward estimation of the crystal lattice constants and of their associated variances is described. The Least-Squares Principle has been used on a truncated Taylor's series expansions of the function which involves the $Q_{n \times 1}$ 's, the reflection indexes hkl and the constants $a_{0}, b_{0}, c_{0}, \alpha_{0}, \beta_{0}, \gamma_{0}$ in the triclinic direct unit-cell. This procedure simplifies the calculation of the direct unit-cell constants and saves most complications connected with an estimate of their joined variances.

Riassunto. - L'uso del metodo dei Minimi Quadrati applicato ad espressioni delle costanti reticolari espresse in termini di reticolo reciproco conducono a procedimenti di affinamento delle costanti stesse in modo abbastanza agevole. Tuttavia, qualora si vogliano valutare dalle varianze associate alle costanti reticolari reciproche le corrispondenti varianze nei parametri stimati della cella unitaria diretta, il procedimento di calcolo diventa molto laborioso. Nel presente lavoro viene discussa una utilizzazione del metodo dei Minimi Quadrati che, applicato a funzioni espresse unicamente in termini di reticolo diretto, richiede - in sostanza - soltanto la soluzione del sistema delle equazioni normali.


## Introduction

In the practice of crystal lattice constants refinement the Least-Square procedure is widely used, In most cases the expression to be minimized contains essentially two kinds of terms: i) the observations and the unit-cell constants; ii) other terms, which are up to the Researcher's option, relate to the geometrical and physical factors affecting the observations.

The present work deals with the i) subject only, neglecting the treatment of the systematic errors.

A standard statistical treatment, as suggested by Jetre and Foore (1935), can be applied estimating the errors in the unit-cell parameters and now this course has been adopted by many Authors.

For crystal symmetries lower than orthorombic the use of the reciprocal lattice yields an expression for the normal equations simple enough even in the triclinic

[^0]system. When the normal equations are solved by the inverse-matrix method, the reciprocal unit-cell parameters are calculated and their variances estimated from the variance-covariance matrix ( ${ }^{( }$). Classic formulas (Buerger, 1962) are used to obtain the direct unit-cell constants from the reciprocal ones. At the same time, if the variances in the refined reciprocal parameters are to be transformed into corresponding direct unit-cell constants variances, complications arise (Burnham, 1962; Kelsey, 1963; Langford, 1973).

The present paper describes a Least-Square treatment based on direct unit-cell constants, which allows a more immediate estimation of the parameters and their associated-variances.

## 1. Theoretical Approach

From X-ray diffraction experiments concerning the Bragg's law the quantities «actually measured» are lenghts on films or on paper of chart-recorders or angles on wheels, according to X-ray apparatus. These quantities are the «observations» which, strictly speaking, should be used in the minimization procedure of the Least-Squares Principle, as Hess (1951) has reminded in his discussion on the Cohen's (1935) method. The use of the $\mathrm{d}_{\mathrm{hk}}$ 's obtained from the quantities actually measured may result chiefly in an understimation of the precision in the estimated lattice constants, but not in all the cases as Langford (1973) has pointed out. However the $\mathrm{d}_{\mathrm{kk} 1}$ 's are retained here as «observations» owing to the following discussion is greatly simplified and because the precision may be improved by appropriate weighting functions. Thus we write the «observation equations» in the form:

$$
\begin{align*}
& Q_{\text {rob. }} \text { : f }\left(h_{r}, k_{r}, l_{r} ; a_{0}, b_{0}, c_{0}, a_{0}, B_{0}, y_{0}\right) \tag{1}
\end{align*}
$$

where the symbol $\xlongequal{\circ}$ means «observed equal to...» and $Q_{\text {lob. }}=1 / \mathrm{d}^{2}{ }_{h_{1} k_{1} 1_{1} \ldots} \ldots$, $Q_{\text {rob. }}=1 / d^{2}{ }_{h_{r} k_{r} l_{r}}$. In eqs. (1) the $a_{0}, \ldots . ., \gamma_{0}$ are the unknown direct unit-cell constants and $h_{i}, k_{i}, l_{i}(i=1, \ldots, r)$ are the exactly known reflection indexes.

The function f in eqs. (1) for the i-th observation may be expressed in the triclinic system (Warren, 1969) as
where
$R=\left(1-\cos ^{2} a_{\theta}-\cos ^{2} \beta_{\theta}-\cos ^{2} \gamma_{0}+2 \cos \alpha_{0} \cos \beta_{0} \cos \gamma_{0}\right)$
$m=\left(\cos B_{0} \cos \gamma_{0}-\cos a_{0}\right)$
$n=\left(\cos \gamma_{0} \cos a_{0}-\cos \beta_{0}\right)$
$p=\left(\cos a_{0} \cos B_{0}-\cos \gamma_{0}\right)$

[^1]Also note that
where V is the unit-cell volume.
A suitable linear form for eq. (2) can be achieved if appropriate approximations a,..., $\boldsymbol{\gamma}$ are available for the $a_{0}, \ldots ., \gamma_{o}$, so that the differences

| $\Delta a_{*}=a_{*}-a$ |  |
| :--- | :--- |
| $\Delta b_{*}=b_{*}-b$ | $(5 a)$ |
| $\Delta c_{*}=c_{*}=c$ | $(5 b)$ |
| $\Delta a_{*}=a_{*}-a$ | $(5 c)$ |
| $\Delta B_{*}=b_{*}-s$ | $(5 d)$ |
| $\Delta Y_{*}=r_{*}-r$ | $(5 e)$ |
|  |  |

become small numbers. Then, by Taylor's theorem, it is possible to approximate the right hand member in eq. (2) expanding it in a truncated power series. Calling $Q_{1}$ the right hand member in eq. (2), we have thus
where the terms with powers higher than 1 are neglected. In the expression (6) vertical lines emphasize that the function $\mathrm{Q}_{\mathrm{i}}$ and its partial derivatives must be numerically evaluated in the points $a_{0}=a, \ldots, \gamma_{0}=\gamma$. The quantity $\mathrm{Q}_{\mathrm{i} \mid} \mid, \ldots, \gamma$, $\boldsymbol{i}^{2}$ a numerical value matching the corresponding observation $\mathrm{Q}_{\mathrm{iab}}$, if $a, \ldots, \gamma$ have been intelligently chosen and if the observations are consistent (Pugh and Winslow, 1966). Thus the differences

$$
\begin{align*}
& Q_{\text {lob }}-\left.Q_{1}\right|_{a, \ldots, r}=\Delta o_{1}  \tag{7}\\
& \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \\
& a_{\text {rob }}-\left.o_{r}\right|_{a, \ldots, r}=\Delta o_{r}
\end{align*}
$$

are small numerical quantities with the same $\mathrm{Q}_{\mathrm{iob}}$ 's residuals, $(\mathrm{i}=1, \ldots, \mathrm{r})$.
Considering the $\Delta \mathrm{Q}$ 's as new observations, the observation equations are now:

$$
\begin{equation*}
\Delta Q_{1}=\left.\frac{\partial Q_{1}}{\partial a_{0}}\right|_{a_{,}, \ldots, r} \Delta a_{*}+\left.\frac{\partial Q_{1}}{\partial b_{*}}\right|_{a_{1}, \ldots, r} \Delta b_{*}+\left.\frac{\partial Q_{1}}{\partial c_{*}}\right|_{a_{1}, \ldots, r} \Delta c_{*}+\left.\frac{\partial Q_{1}}{\partial a_{*}}\right|_{a, \ldots, r} \Delta a_{0}+\left.\frac{\partial Q_{1}}{\partial B_{*}}\right|_{a, \ldots, r} \Delta B_{*}+\left.\frac{\partial Q_{1}}{\partial r_{*}}\right|_{a, \ldots, \gamma} \Delta r_{*} \tag{8}
\end{equation*}
$$

and they are all linear in the unknowns $\Delta \mathrm{a}_{\mathrm{o}}, \ldots, \Delta \gamma_{\mathrm{o}}$. If there are more observation equations than unknowns and if the reflection indexes set is appropriate, a LeastSquares solution can be applied,

In order to achieve such solution on statistical grounds, the «Model» underlying the observation equations (8) must be specified.

Using matrix algebra notation, we can write:

$$
\begin{align*}
& \mathbf{Y}=\left[\begin{array}{c}
\Delta 0_{1} \\
\vdots \\
\\
\vdots \\
\Delta Q_{r}
\end{array}\right] \tag{x}
\end{align*}
$$

$$
\begin{aligned}
& \text { (9b) } \beta=\left[\begin{array}{l}
\mathrm{soc} \\
\Delta \mathrm{bc} \\
\Delta c \cdot \\
\mathrm{sec} \\
\Delta s_{0} \\
\Delta r e c
\end{array}\right]
\end{aligned}
$$

where $\mathbf{Y}$ is a $(r \times 1)$ vector of random observable variables, $\mathbf{X}$ is a $(r \times 6)$ matrix of variables without errors $(r>6)$, and $\boldsymbol{\beta}$ is a $(6 \times 1)$ vector of unknown parameters.

The variance of $\mathbf{Y}$ is $\sigma^{2}$, where $\sigma^{2}$ does not depend on the elements of $\mathbf{X}$ and $\boldsymbol{\beta}$.
Thus the «Model» for eqs. (8) is assumed to be

$$
\begin{equation*}
\mathbf{Y}=\mathbf{X} \boldsymbol{\beta} \cdot \boldsymbol{\varepsilon} \tag{10}
\end{equation*}
$$

where

$$
\varepsilon \cdot\left[\begin{array}{c}
c_{1}  \tag{11}\\
\vdots \\
\vdots \\
c_{r}
\end{array}\right]
$$

is an $(r \times 1)$ vector of unobservable random perturbations for which we assume:

| $E(\varepsilon)=0$ | (12a) |
| :--- | :--- |
| $E\left(\varepsilon \varepsilon^{\prime}\right)=\sigma^{2} I_{r}$ | (12b) |

where E is the expectation operator and r the order of the unit-matrix $\mathbf{I}$, while the apex means the matrix transposition operation. The quantity $\sigma^{2}$ is the unkonwn variance of the perturbations $\varepsilon_{1}(i=1, \ldots, r)$.

Beside the eqs. (12a) and (12b) we also assume $\left(^{2}\right)$ that:
the rank of $\mathbf{X}$ is 6 .
(12c)
The elements of $\boldsymbol{\beta}$ have to be first estimated.
Calling

(13)
the $(6 \times 1)$ vector of estimate for $\boldsymbol{\beta}$ we can write:

$$
\mathbf{Y}=\mathbf{X} \hat{\beta}+\mathbf{e}
$$

${ }^{(2)}$ cf. Noble (1969).
where $\mathbf{e}$ is the $(\mathrm{r} \times 1)$ vector of the r residuals $(\mathbf{Y}-\mathbf{X} \hat{\boldsymbol{\beta}})$. The Least-Squares estimate of $\boldsymbol{\beta}$ is then the value of $\widehat{\boldsymbol{\beta}}$ which minimizes the following sum of square of the residuals SS:

The minimum for eq. (15) is reached setting to zero the partial derivatives $\partial\left(\mathbf{e}^{\prime} \mathbf{e}\right) / \partial \widehat{\boldsymbol{\beta}}$. This, Draper and Smith (1966), yields the normal equations

$$
\begin{equation*}
X^{\prime} X \hat{\beta}=X^{\prime} Y \tag{116}
\end{equation*}
$$

If the normal equations system (16) is solved by the inverse-matrix method, the vector $\widehat{\boldsymbol{\beta}}$ estimating $\boldsymbol{\beta}$ in eq. (10) is given by

$$
\hat{\beta}=\left(\mathbf{x}^{\prime} \mathbf{x}\right)^{-1} \mathbf{X}^{\prime} \mathbf{Y}
$$

(17)

In order to obtain an estimate of the variances in the elements of $\widehat{\boldsymbol{\beta}}$, further developments are needed, Johnston (1963). From eqs. (10) and (17) we have

$$
\hat{\beta}=\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1} \mathbf{X}^{\prime}(\mathbf{X} \beta+\boldsymbol{\varepsilon})
$$

110
from which ( ${ }^{3}$ )

$$
\begin{equation*}
(\hat{\beta}-\beta)=\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1} \mathbf{X}^{\prime} \boldsymbol{\varepsilon} \tag{19}
\end{equation*}
$$

${ }^{(3)}$ Proof: from eq. (18) we have

$$
\begin{aligned}
\hat{\beta} & -\left(\mathbf{X}^{\prime} \mathbf{x}\right)^{-1} \mathbf{X}^{\prime} \mathbf{X} \beta+\left(\mathbf{X}^{\prime} \mathbf{x}\right)^{-1} \mathbf{x}^{\prime} \varepsilon \\
& -\left(\mathbf{x}^{\prime} \mathbf{x}\right)^{-1}\left(\mathbf{X}^{\prime} \mathbf{X}\right) \beta+\left(\mathbf{X}^{\prime} \mathbf{x}\right)^{-1} \mathbf{X}^{\prime} \varepsilon \\
& -\mathbf{I}_{r} \beta+\left(\mathbf{x}^{\prime} \mathbf{x}\right)^{-1} \mathbf{x}^{\prime} \varepsilon
\end{aligned}
$$

namely

$$
\hat{\beta}-\beta+\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1} \mathbf{X}^{\prime} \boldsymbol{\varepsilon}
$$

We have also, taking the expectations in eq. (1s',

$$
\begin{gathered}
E(\hat{\beta})-E(\beta)+E\left[\left(\mathbf{X}^{\prime} \mathbf{X}\right)\right. \\
-\beta+\left(\boldsymbol{X}^{\prime} \mathbf{X}\right)^{-1} \mathbf{X}^{\prime} \mathrm{E}(\boldsymbol{\varepsilon})
\end{gathered}
$$

$$
18 \mathrm{c}
$$

and with eq. (12a)

$$
E(\hat{\beta})=\beta
$$

i.e. $\widehat{\boldsymbol{\beta}}$ is, as it's well known, an unbiased estimate of $\boldsymbol{\beta}$. By «Gauss Theorem » the Least-Squares linear estimators are also the minimum variance estimators (JOhnston, 1966).
then the variance of $\widehat{\boldsymbol{\beta}}$, called var $(\widehat{\boldsymbol{\beta}})$, is

$$
\begin{align*}
\operatorname{var}(\hat{\beta}) & =E\left[(\hat{\beta}-\beta)(\hat{\beta}-\beta)^{\prime}\right] \\
& =E\left[\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1} \mathbf{X} \boldsymbol{\varepsilon} \varepsilon^{\prime} \mathbf{X}\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1}\right] \\
& =\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1} \mathbf{X}^{\prime} E\left(\mathbf{E} \varepsilon^{\prime}\right) \mathbf{X}\left(\mathbf{x}^{\prime} \mathbf{X}\right)^{-1} \tag{20}
\end{align*}
$$

Using now eq. (12b), eq. (20) becomes

$$
\begin{equation*}
\operatorname{var}(\hat{\bar{\beta}})=\left(\mathbf{x}^{\prime} \mathbf{x}\right)^{-1} \mathbf{x}^{\prime} \sigma^{2} \mathbf{I}_{r} \mathbf{X}\left(\mathbf{x}^{\prime} \mathbf{x}\right)^{-1} \tag{21}
\end{equation*}
$$

From eq. (21) we obtain the important result:

$$
\operatorname{var}(\hat{\beta}) \cdot \sigma^{2}(\mathbf{X} \cdot \mathbf{X})^{-1}
$$

The var $(\widehat{\boldsymbol{\beta}})$ is called «variance-covariance» matrix.
The variance of the perturbations, $\sigma^{2}$, in eq. (21), can be estimated with the expression

$$
\hat{\sigma}^{2} \cdot \frac{e^{\prime} e}{r-6} \quad \text { (23) }
$$

Consequently the variance of each element $\Delta \hat{\mathrm{a}}_{\mathrm{o}}, \ldots . ., \Delta \hat{\boldsymbol{\gamma}}_{0}$ of $\widehat{\boldsymbol{\beta}}$ is obtained from the diagonal terms of $\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1}$, multiplied by $\hat{\sigma}^{2}$. If the model is correct the variances in $\Delta \hat{\mathrm{a}}_{o}, \ldots ., \Delta \hat{\gamma}_{0}$ are the same as the variances in the corresponding $\hat{\mathrm{a}}_{0}, \ldots ., \hat{\gamma}_{o}$, since a, ..., $\gamma$ are constants (Sićiliano, 1969).

When the initial parameters a,..., $\gamma$ are not appropriate, then from eqs. ( $5 a$ ), $\ldots .$. , ( $5 f$ ) the revised estimates of $a_{0}, \ldots . . . \gamma_{0}$ are obtained. A better approximation set is gained if these revised estimates are now applied to play the same role as the previous set a,..., $\gamma$ in the procedure just described. The whole process should be repeated until convergence is reached, i.e. when the differences between two succeeding «correction» cycles are lower than a fixed value.

If the observations are of unequal precision $\left({ }^{4}\right)$, we cannot consider them as coming from the same infinite parent distribution of perturbations. In this case to improve the «Model», instead of ( $12 b$ ) we use the statement $\mathrm{E}\left(\boldsymbol{\varepsilon} \varepsilon^{\prime}\right)=\sigma^{2} \mathbf{V}$, where

$$
\sigma^{2} \mathbf{V} \cdot\left[\begin{array}{lll}
\sigma_{1}^{2} & &  \tag{24}\\
& \ddots & \\
& & \ddots \\
& & \sigma_{r}^{2}
\end{array}\right]
$$

the off-diagonal terms all being zero.

[^2]With appropriate weights ${ }^{5}$ ) for each observation equation, the same foregoing «Model » can then be recovered (Draper and Smith, 1966).

Interval estimation for each refined parameter can be attained, for instance, on the basis of an error's Normal distribution law for the $\varepsilon_{1}(i=1, \ldots, r)$, namely changing the statement $(12 a)$ into $\mathrm{E}(\boldsymbol{\varepsilon})=(\mathrm{N}, \mathrm{O})$.

## 2-Some practical considerations

For the normal equations (16) it is necessary to build an expression for the partial derivatives appearing as elements in the matrix $\mathbf{X}$. For this purpose, according to the crystal system, expressions as those listed in Table 1 may be used.

In each refinement cycle the numerical value of all derivatives involved in the Jacobian (9b) are computed putting in the proper expression of Table 1, the set $\mathrm{a}, \ldots, \gamma$ available at the present refinement stage. The same set, of course, must be used evaluating the elements of $\mathbf{Y}$, by eqs. (7).

Provided a careful choice of the reflection indexes has been made to warrant a solution, the normal equations system is solved by the inverse-matrix method. Thus the quantities $\Delta \hat{\mathrm{a}}_{\mathrm{o}}, \ldots . ., \Delta \hat{\gamma}_{o}$ are the solution for that refinement stage and the relative estimated parameters $\hat{\mathrm{a}}_{\mathrm{o}}, \ldots, \hat{\gamma}_{o}$ are obtained from eqs. ( $5 a$ ), ,..., ( $5 f$ ). At the end of this iterative procedure the final refined parameters come out. The sum of the residuals is given by eq. (15) putting into them the final refined solutions $\Delta \hat{a}_{o}, \ldots ., \Delta \hat{\gamma}_{o}$.

The unknown variance $\sigma^{2}$ is estimated from eq. (23) and the variances $\sigma^{2} a_{0}$, $\ldots ., \sigma^{2} y_{0}$ in the refined unit-cell constants $a_{0}, \ldots ., \gamma_{0}$ are estimated from

$$
\begin{equation*}
\dot{\sigma}_{k}^{2}=\dot{\sigma}^{2} c_{k k} \quad(k=1, \ldots, 6) \tag{25}
\end{equation*}
$$

where $\hat{\sigma}_{1}{ }^{2}=\hat{\sigma}^{2} a_{0}, \ldots . ., ., \hat{\sigma}_{6}{ }^{2}=\hat{\sigma}^{2} \gamma_{0}$ and the $c_{k k}$ are the corresponding diagonal elements of $\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1}$.

If an estimate $\hat{\sigma}^{2}{ }_{\mathrm{v}}$ of the variance $\sigma^{2}{ }_{\mathrm{v}}$ in the unit-cell volume V is required, then the problem of interdipendence of the errors in the unit-cell constants arises. Apart from other considerations ( ${ }^{6}$ ), these errors cannot be considered independent because general hkl reflection indexes are employed throughout the method. Thus, disregarding special cases, the general expression for the error's propagation law accounting the covariances between the parameters must be used (Eadie et Al.,
(5) Whittaker and Robinson (1946); Hald (1952), Hamilton (1964).
(6) See Hey (1954).

## Table 1

## The partial derivatives of the function $Q$ in the crystal systems

$$
\begin{align*}
& Q=\frac{1}{k}\left(\frac{s i n^{2} a}{a^{2}} n^{2}+\frac{s \sin ^{2} s}{b^{2}} k^{2}+\frac{\sin ^{2} \gamma}{c^{2}} 1^{2}+\frac{2 n}{b c} k 1+\frac{2 n}{a c} n 1+\frac{2 p}{a b} n k\right) \\
& \text { where } \\
& R=\left(1-\cos ^{2} a-\cos ^{2} s-\cos ^{2} \gamma+2 \cos a \cos s \cos \gamma\right) \\
& m=(\cos B \cos \gamma-\cos a) \\
& n=(\cos \gamma \cos a-\cos s) \\
& p=(\cos a \cos \beta-\cos \gamma)
\end{align*}
$$

TRICLINAC $\left\{\right.$ eq. (2') with $\mathrm{a} \neq \mathrm{b} \neq \mathrm{ci} \mathrm{a} \times \mathrm{B}+\mathrm{y}+90^{\circ}$ )
$\frac{20}{30} \cdot \frac{-2}{3^{2} b c R^{2}} \mathrm{~h}\left[\mathrm{~h}\left(\mathrm{bcsin} \mathrm{n}^{2} \mathrm{a}\right)+1(\mathrm{abn})+k(\mathrm{acp})\right]$
$\frac{20}{3 b}=\frac{-2}{a b^{3} c \mathbb{R}} k\left[k\left(a c \operatorname{cin} n^{2} s\right)+1(a b e)+h(b c p)\right]$
$\frac{30}{3 c}=\frac{-2}{a b c^{3} R} 1\left[1\left(a b s \operatorname{in}^{2} y\right)+k(a c m)+h(b c n)\right\}$
$\frac{20}{2 a}=\frac{2 s i n a}{(a b c k)^{2}}\left[h^{2}\left[b^{2} c^{2}\left(R \cos a+m s i n^{2} a\right)\right]+k^{2}\left[a^{2} c^{2}\left(m s i n^{2} a\right)\right]+1^{2}\left[a^{2} b^{2}\left(m s i n^{2} y\right)\right]+k 1\left[s^{2} b c\left(R+2 n^{2}\right)\right]+h 1\left[a b^{2} c(2 m n-R \cos y)\right]+h k\left[a b c^{2}(2 m p-R \cos s)\right]\right)$
$\frac{20}{2 a}=\frac{2 s i n s}{(a b c R)^{2}}\left[h^{2}\left[b^{2} c^{2}\left(n s i n^{2} a\right)\right]+k^{2}\left(s^{2} c^{2}\left(R \cos s+n \sin n^{2} s\right)\right]+1^{2}\left[a^{2} b^{2}\left(n s\left\{n^{2} r\right)\right]+k 1\left[a^{2} b c(2 m n-R \cos r)\right]+h 1\left[a b^{2} c\left(R+2 n^{2}\right)\right]+h k\left[a b c^{2}(2 n p-R \cos a)\right]\right)\right.$
$\frac{3 Q}{\partial \gamma}=\frac{2 s i n \gamma}{(a b c R)^{2}}\left(h^{2}\left[b^{2} c^{2}\left(p s i n^{2} a\right)\right]+k^{2}\left[a^{2} c^{2}\left(p s i n^{2} b\right)\right]+1^{2}\left[a^{2} b^{2}\left(R \cos y+p s i n^{2} \gamma\right)\right]+k 1\left[a^{2} b c(2 m p-R \cos s)\right]+h 1\left[a b^{2} c(2 n p-R \cos a)\right]+h k\left[a b c^{2}\left(R+2 p^{2}\right)\right]\right)$

MONOCLINIC (eq. (2') with a 1 b \& $\mathrm{ci} \mathrm{a}=\mathrm{T}=90^{\circ} \neq \mathrm{g}$ )
$\frac{2 Q}{3 a}=\frac{-2}{a^{3} \operatorname{csin} n^{2} s} h(h c-1(a \cos B))$
$\frac{a Q}{a b}=\frac{-2}{b^{3}} k^{2}$
$\frac{a Q}{a c}=\frac{-2}{a c^{3} s \ln ^{2} s}[1 a-h(\cos s)]$
$\frac{2 Q}{2 B}=\frac{2}{a^{2} c^{2} s^{2} n^{3} s}\left\{h 1\left[a c\left(1+\cos ^{2} s\right)\right]-\cos s\left(h^{2} c^{2}+1^{2} a^{2}\right)\right\}$

ORTHORHOMBIC ( eq. (2') with $\mathrm{a}+\mathrm{b}+\mathrm{c} ; \mathrm{a}=\mathrm{s}=\gamma=90^{\circ}$ )
$\frac{a Q}{3 a}=\frac{-2}{a^{3}} h^{2} ; \quad \frac{3 Q}{a b}=\frac{-2}{b^{3}} k^{2} ; \quad \frac{3 Q}{\partial c}=\frac{-2}{c^{3}} 1^{2}$

TETRAGONL ( eq. (2') with $\Delta=b ; c ; a=8=r=90^{\circ}$ )
$\frac{20}{2 a}+\frac{-2}{a^{3}}\left(h^{2}+k^{2}\right) ; \quad \frac{3 Q}{2 c}=\frac{-2}{c^{3}} 1^{2}$
ISONETRIC ( eq. (2') with $a=b=c ; a=a=y=90^{\circ}$ )
$\frac{3 Q}{2 a}=\frac{-2}{a^{3}}\left(h^{2}+k^{2}+1^{2}\right)$
1971). In the triclinic system we have thus
where $q_{1}=a_{0}, \ldots, q_{6}=\gamma_{0}$. The covariances $\operatorname{cov}\left(q_{1}, q_{j}\right)$ are, of course, the elements of the variance-covariance matrix $\sigma^{2}\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1}\left({ }^{( }\right)$.

In the case of independent errors the expression (26) is simpler:

$$
\begin{equation*}
\left.\hat{\sigma}_{v}^{2} \cdot \sum_{1}^{6} \frac{x v}{x_{1}}\right|_{a_{1}, \ldots, i} ^{2} \cdot \dot{\sigma}_{1}^{2} \tag{27}
\end{equation*}
$$

The partial derivatives $\partial \mathrm{V} / \partial \mathrm{a}_{0}, \ldots, \partial \mathrm{~V} / \partial \gamma_{\circ}$ needed for each crystal system in eq. (26) and (27) are listed in Table 2.

Incidentally it is to be noted that uncorrelated variables are not necessarily independent (Cramer, 1974; Wonnacort and Wonnacott, 1970). The analysis of this problem is, however, beyond the scope of the present paper.

Concerning the use of a weighting scheme, the considerations of LangFord and Wilson (1973) are recommended.

## Table 2

The partial derivatives of the unit-cell volume $V$ required in estimating its variance

$$
V=a b c R^{\frac{1}{2}}
$$

where

$$
\begin{gathered}
R=1-\cos ^{2} a-\cos ^{2} \beta-\cos ^{2} \gamma+2 \cos a \cos \beta \cos \gamma \\
(m, n, p \text { as in Table 1) }
\end{gathered}
$$

|  | $\frac{2 V}{\text { ab }}$ | $\frac{\mathrm{aV}}{2 \mathrm{~b}}$ | $\frac{\partial V}{\text { ac }}$ | $\frac{\mathrm{aV}}{3 a}$ | $\frac{\mathrm{aV}}{} \mathrm{as}^{\text {S }}$ | $\frac{\mathrm{aV}}{} \mathrm{ar}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| TRICLINIC | $b c R^{\frac{1}{2}}$ | $a c R^{1}$ | $a b R^{\frac{1}{2}}$ | - $\mathrm{abcmR} \mathrm{R}^{-\frac{1}{2}}$ sina | -abcnR ${ }^{-\frac{1}{2}} \sin \beta$ | -abcpR ${ }^{-\frac{1}{2}} \sin$ y |
| MONOCLINIC | besing | acsing | absing |  | abecoss |  |
| ORTHORHOMBIC | bc | ${ }^{\text {ac }}$ | ab |  |  |  |
| TETRAGONAL | 2 ac |  | $\mathrm{a}^{2}$ |  |  |  |
| ISOMETRIC | $3 a^{3}$ |  |  |  |  |  |
| EXAGORAL | $6 \mathrm{cssin} 60^{\circ}$ |  | $3 \mathrm{a}^{2} \sin 60^{\circ}$ |  |  |  |
| RHOMBOHEDRAL | $3 a^{2} R^{\frac{1}{2}}$ |  | $-3 a^{3} \mathrm{~m}^{-\frac{1}{2}}$ sin $\alpha$ |  |  |  |

(7) In the calculation of $\hat{\sigma}^{2} \alpha_{0}$, $\hat{\sigma}^{2}{ }_{\beta o}$, $\hat{\sigma}^{2} \gamma_{\mathrm{o}}$, $\hat{\sigma}^{2}{ }_{v}$ it must be remembered that in the elements of $\left(\mathbf{X}^{\prime} \mathbf{X}\right)^{-1}$ radian measure are involved.

## Discussion

The method proposed in this paper will be now evaluated considering alternative procedures such as those developed, for instance, by Burnham (1962) and LangFord (1973). For simplicity, the three methods will be referred in this section as FL (Farinato-Loreto), B (Burnham), L (Langford). The original notations of the latter Authors have been slightly modified and their correction terms not considered.

The starting point of the B procedure is the same as in FL, but his curtailed expansion Taylor's series is applied in the reciprocal lattice expression for the Q's.

In B , for the i -th observation $\mathrm{Q}_{\text {iob }}$, the corresponding $\mathrm{Q}_{\text {leale. }}$. is
and the procedure minimizes the following sum of squares, called here BSS:
being $\mathrm{a}^{\prime *}, \ldots, \gamma^{\prime *}$ the trial parameters, and $\left(\Delta \mathrm{Q}_{\mathrm{i}}\right)_{\mathrm{B}}=\mathrm{Q}_{\text {iob, }}-\mathrm{Q}_{\text {icale. }}$. The B and FL methods differ in the type of function to be minimized though sharing the first step of the procedure which brings in the normal equations. The expressions of the derivatives are simpler in eq. (29) of B than in eq. (15) of FL, but once the normal equations system have been solved by the inverse-matrix method, in B only the estimated variances $\hat{\sigma}^{2}{ }_{\mathrm{a}}{ }^{*}, \ldots,, \hat{\sigma}^{2}{ }_{\gamma_{0}^{*}}$ are easily available whilst the corresponding estimates $\hat{\sigma}^{2}{ }_{a_{0}}, \ldots ., \hat{\sigma}^{2}{ }_{\gamma}$ o have to be reached by further elaborations.
In fact if

where the $\mathrm{f}_{\mathrm{k}}$ 's are the six functions each relating the direct to the reciprocal lattice constants, six expressions as

$$
\begin{equation*}
\left.\left.\dot{\sigma}_{k}^{2} \cdot \sum_{1}^{6} \sum_{1}^{6} \sum_{j}^{6} \frac{\partial f_{k}}{\partial p_{j}^{j}}\right|_{\dot{a}^{*}+\ldots, r^{*}} \frac{\partial f_{k}}{\partial p_{j}^{j}}\right|_{\dot{\sigma}^{*}, \ldots, r^{*}} ^{b_{i j}} \quad(k-1, \ldots, 6) \tag{31}
\end{equation*}
$$

must be still evaluated, where $\hat{\sigma}_{1}{ }^{2}=\hat{\sigma}^{2}{ }_{\mathrm{a}}^{0}$, ..., $\hat{\sigma}_{6}{ }^{2}=\hat{\sigma}^{2}{ }_{\gamma_{0}}, \mathrm{pl}_{1}{ }^{*}=\mathrm{a}^{*}, \ldots, \mathrm{pe}^{*}=\gamma^{*}$ and $b_{i j}$ 's are the elements of the variance-covariance matrix. Thus a new table of partial derivatives for the $f_{k}$ 's with respect to the variables $a^{*}, \ldots ., \gamma^{*}$, is needed now.

For the unit-cell volume variance estimation, the covariances among the direct unit-cell constants are required. Following Eadie et Al. (1971) and using a notation appropriate for case $B$, the covariance between two functions, say $f_{1}\left(a^{*}, \ldots, \gamma^{*}\right)$ and $\mathrm{f}_{2}\left(\mathrm{a}^{*}, \ldots, \gamma^{*}\right)$ is given by
and consequently the variance $\hat{\sigma}^{2}{ }_{v}$ of the unit-cell volume by
where the partial derivatives in eq. (33) are the same as in eq. (27).
The entire process is condensed by Burnham in an elegant compact matrix formulation.

The L method differs from B and FL, because no use is made of Taylor's approximate formulas, but the linearization is attained by another way. For the i-th observation $\mathrm{Q}_{\text {tob. }}$ the corresponding function is written as

$$
\begin{equation*}
a_{\text {tcalc. }}-m_{1}^{2} n+k_{1}^{2} 8+1_{1}^{2} c+k_{1}^{2} 1_{1}^{2} D+k_{1}^{1} 1_{1}^{1} k+k_{1} k_{1} F \tag{34}
\end{equation*}
$$

where


The following expression, called here LSS, is minimized:
where $\left(\Delta \mathrm{Q}_{\mathrm{i}}\right)_{\mathrm{L}}=\mathrm{Q}_{\text {iob. }}-\mathrm{Q}_{\text {icale. }}, \Delta \mathrm{A}=\mathrm{A}-\mathrm{A}^{\prime}, \ldots ., \Delta \mathrm{F}=\mathrm{F}-\mathrm{F}^{\prime}$ and $\mathrm{A}^{\prime}, \ldots ., \mathrm{F}^{\prime}\left(^{8}\right)$ are the trial parameters according to expressions (35). In the L mathematical development no explicit matrix-inversion appears and the following differences with the B and FL cases may be pointed out: i) only a simple summation over the appropriate product among the $\mathrm{h}, \mathrm{k}, \mathrm{l}$ and the $\mathrm{Q}_{\text {iob.' }}$ 's is required to perform the normal equations; the derivatives present at this stage in the B and FL procedures are lacking here; ii) once the normal equations system is solved, the variances and covariances concern quantities as $\mathrm{A}, \ldots ., \mathrm{F}$. The variances directly available in L are
${ }^{(8)}$ When $\mathrm{A}^{\prime}=\mathrm{O}, \ldots, \mathrm{F}^{\prime}=\mathrm{O}$ (but in this situation see Deming, 1938) the eq. (36) is the widely used one, cf. SMITH (1956), Lo GIudice (1971), and the «refinement» is attained changing only the hkl's set.
thus $\hat{\sigma}^{2}{ }_{\mathrm{A}}, \ldots, \ldots, \hat{\sigma}^{2}{ }_{\mathrm{F}}$. In order to calculate the variances $\hat{\sigma}_{\mathrm{a}_{0}}{ }^{2}, \ldots, \hat{\sigma}^{2}{ }_{\gamma_{0}}$, expressions similar to (30) are needed, namely

but, of course, the form of the functions $F_{k}$ is now different from the $f_{k}$ 's. Consequently the new relationship for the estimated variances $\hat{\sigma}^{2}{ }_{1}=\hat{\sigma}^{2}{ }_{a_{0}}, \ldots$, , $\hat{\sigma}^{2}{ }_{6}=\hat{\sigma}^{2}{ }_{\gamma_{0}}$ in the refined direct unit-cell parameters becomes
where $\mathrm{x}_{1}=\mathrm{A}, \ldots ., \mathrm{x}_{6}=\mathrm{F}$ and the $\mathrm{l}_{1 \mathrm{j}}$ 's are, after all, the elements of an actual variance-covariance matrix. As in B - but for the $\mathrm{F}_{\mathrm{k}}$ 's in respect the $\mathrm{A}, \ldots ., \mathrm{F}-\mathrm{a}$ table of partial derivatives is necessary at this calculation stage (Table 1 in Langrord, $1973\left(^{9}\right)$ ). Subsequently the procedure follows the same pattern as in B.

Incidentally we can note that in FL the parameters to be refined play a separate role in each term of the observation equations.

## Conclusions

The minimization by the Least-Squares method, of an expression such as
in terms of direct unit-cell constants, instead of expressions like
or
(the latter two equations in terms of reciprocal lattice constants) makes it possible to perform a crystal lattice constants refinement and an estimate of the variance in these refined parameters in a more direct way.

[^3]The method explained in the present work, requires a shortened calculation procedure and therefore can be carried out by even a small computer. If such a computer system is able to automatically invert a matrix $\left({ }^{(10}\right)$, the procedure itself is very straightforward. Tha «convergence» is rapid, as proved by a computer program prepared by the Authors wich will be described in detail in a paper now under preparation.

Roma, may 1975, Istituto di Mineralogia e Petrografia dell'Università Centro Studio del C.N.R. per la Mineralogia e Petrologia delle Formazioni Ignee

## REFERENCES

Buerger M. J. (1962) - X-ray Crystallography. John Wiley \& Sons, New York.
Burnham C. W. (1962) - Lattice Constants Refinement. Carnegie Inst. Wash. Year book, 61, 132-135.
Chayes F. and Mackenzie W.S. (1957) - Experimental error in determining certain peack locations and distance between peacks in X-ray powder diffractometer patterns. Am. Min., 42, 534-547.
Cohen M. U. (1935) - Precision Lattice Constants from X-ray powder photograph. Rev. Sci. Instrum., 6, 68-74.
Cramér H. (1974) - Mathematical Methods of Statistics. Princenton University Press.
Deming W.E. (1938) - Statistical adjustment of data. Ist. edn., New York.
Draper N. R. and Smith H. (1966) - Applied Regression Analysis. John Wiley \& Sons Inc., New York.
Eadie W. T., Dryard D., James F.E., Roos M. and Sadoulet B. (1971) - Statistical Methods in Experimental Physics. North-Holland. Amsterdam.
Hald A. (1952) - Statistical Theory with Engineering Applications. John Wiley \& Sons. Inc., New York.
Hamilton W.C. (1964) - Statistics in Physical Science. Ronald Press, New York.
Hess J. B. (1951) - A modification of the Coben procedure for computing precision lattice constants from powder data. Acta Cryst., 4, 209-215.
Hey M.H. (1954) - A further note on the presentation of chemical analyses of minerals. Min. Mag., 30, 481-497.
Jette E. R. and Foote F. (1935) - Precision Determination of Lattice Constants. J. Chem. Phys., 3, 605-616.
Johnston J. (1963) - Econometric Methods. McGraw-Hill., New York.
Kelsey C. H. (1963) - The calculation of errors in a least squares estimate of unit-cell dimension. Min. Mag., 33, 809-812.

Langford J. I. (1973) - The Accuracy of Cell Dimension Determined by Cohen's Method of Least Squares and the Systematic Indexing of Powder Data. J. Appl. Cryst., 6, 190-196.
Langford J. I. and Wilson A. J. C. (1973) - Geometrical and Statistical Aspects of the Accuracy of Camera Powder Data. J. Appl. Cryst., 6, 197-202.
Lo Giudice A. (1971) - Un metodo di calcolo ed affinamento delle costanti reticolari dei cristalli monoclini. Rend. Soc. Ital. Mineral. Petrol., 27, 205-210.
Noble B. (1969) - Applied Linear Algebra. Prentice-Hall Inc.
Pugh E.M. and Winslow G.H. (1966) - The Analysis of Physical Measurements. AddisonWesley.
Siciliano A. (1969) - L'elaborazione dei dati sperimentali. Casa Editrice Ambrosiana, Milano.
Smith J. V. (1956) - The powder patterns and lattice parameters of plagioclase feldspars. I. The soda-rich plagioclases. Min. Mag., 31, 47-68.

Taupin D. (1973) - A powder-diagram automatic indexing routine. J. Appl. Cryst., 6, 380-385.
Visser J. W. (1969) - Some calculations for powder patterns. J. Appl. Cryst., 2, 142-143.
Warren B.E. (1969) - X-ray Diffraction. Addison-Wesley.
Whittaker E.T. and Robinson G. (1946) - Calculus of Observations. Blackie, London.
Wonnacott R. J. and Wonnacott Th. H. (1970) - Econometrics. John Wiley \& Sons, Inc. New York.


[^0]:    * Istituto di Mineralogia e Petrografia. Università degli Studi di Roma.

[^1]:    (1) For a different procedure see f.e. Taupin (1973).

[^2]:    (4) cf. Chayes and Mackenzie (1957).

[^3]:    (9) See also Kelsey (1963), Visser (1969).

