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THE CRYSTAL LATTICE CONSTANTS REFINEMENT: A LEAST-SQUARES PROCEDURE FOR THE DIRECT OR THE RECIPROCAL CASE

ABSTRACT. — A Least-Squares procedure for the crystal lattice constants refinement is described. The crystal unit-cell is expressed in terms of direct or reciprocal lattice: accordingly the refinement is carried out with equations involving explicitly the direct or the reciprocal parameters. In this way lattice constants and their associated variances are estimated inside their proper (direct or reciprocal) case. Expressions accounting for systematic errors are considered; alternatively an internal standard correction procedure is provided. Using a trial approximatively known unit-cell the X-ray diffraction peaks may be tentatively indexed, according to a space group and a 2θ tolerance, and accepted or rejected in the successive refinement cycles.

An application of a computer program which has been written for the Olivetti P 652 is illustrated.

RIASSUNTO. — Viene presentato un metodo di affinamento delle costanti reticolari dei cristalli che procede su due linee separate: se si vogliono ottenere le costanti del reticolo diretto l'affinamento è condotto su formule che coinvolgono la cella unitaria diretta; se si ha interesse alle costanti reticolari del reticolo reciproco le formule usate sono fondate sulla cella unitaria reciproca. In tale modo costanti e loro varianze vengono stimate facendo uso delle espressioni più appropriate. Si tiene altresì conto della correzione degli errori sistematici sia tramite funzioni di correzione sia tramite l'uso della tecnica dello standard interno. Inoltre è previsto un procedimento di autoindicizzazione dei riflessi ai quali, nella fase iniziale, non è stato possibile assegnare un appropriato indice hkl.

Si illustra con un esempio, il programma di calcolo realizzato per la Olivetti P 652.

General considerations

As a rule the Least-Squares refinement of the direct unit-cell constants in crystals of low symmetry (triclinic or monoclinic) is carried out using the reciprocal lattice and often the quadratic form of the Bragg law.

Ideally the observation equation to be used for the Least-Squares minimization procedure of the random errors should contain the actual parameters to be estimated, the actual observation experimentally obtained and the appropriate observation weight. Any « manipulation » on the proper observation equation causes parameters and their variances that are not the best statistical estimates. If an X-ray diffracto-

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meter system is used the observation available from it is the Bragg's angle 2ϑ, and the correct form of sum of squares to be minimized is

$$\sum_{1}^{r} w_i \left(2\vartheta_{obs} - 2\vartheta_{calc}\right)_i^2 = \text{minimum} \tag{1}$$

where w_i is the weight of the i-th observation. With the Bragg's law eq. 1 becomes

$$\sum_{1}^{r} w_i \left(2\vartheta_{obs} - 2\arcsin\frac{\lambda}{2}\frac{1}{d}\right)_i^2 = \text{minimum} \tag{2}$$

Calling $F(a_o, b_o, c_o, \alpha_o, \beta_o, \gamma_o, h_i, k_i, l_i)$ and $F^*(a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*, h_i, k_i, l_i)$ the two functions relating $1/d_i$ to the direct or reciprocal triclinic unit-cell constants respectively, we can write eq. 2 as

$$\sum_{1}^{r} w_i \left(2\vartheta_{obs} - 2\arcsin\frac{\lambda}{2}F\right)_i^2 = \text{minimum} \tag{3}$$

in the direct space and

$$\sum_{1}^{r} w_i \left(2\vartheta_{obs} - 2\arcsin\frac{\lambda}{2}F^*\right)_i^2 = \text{minimum} \tag{4}$$

in the reciprocal space.

Both eqs. 3 and 4 are intrinsically non linear in the unit-cell parameters but Least-Squares normal equations linear-i.e. in the parameter corrections $\Delta a_o, \ldots, \Delta\gamma_o$ or $\Delta a^*, \ldots, \Delta\gamma^*$-can be respectively obtained with some linearization procedure. In such way however there is a difference between the true sum of squares in eq. 3 or eq. 4 (the appropriate non linear « Model ») and the sum of squares in the approximating linear expression of the « Model ». When the direct unit-cell constants are in evaluation, eq. 3 seems preferable as starting equation because the minimum reached handling eq. 3 may be — in principle — not strictly the same minimum obtained through eq. 4. On the other hand in a X-ray powder camera the observations are lenghts on film so that the correct form of sums of squares to be minimized is

$$\sum_{1}^{r} w_i \left(L_{obs} - L_{calc}\right)_i^2 = \text{minimum} \tag{5}$$

where the calculated lenghts (L_{calc}) can be expressed in terms of camera radius, wave-lenght, reflection indices and direct (or reciprocal) unit-cell constants. Again, to overcome mathematical difficulties, approximated expressions are obtained to build normal equations linear in the parameter corrections. However from the measured lenghts on film the Bragg's angles are usually obtained and eq. 5 is not used. The departure from an ideal Least-Square situation is now more pronounced

than in the above mentioned case. The use of the $Q = 1/d^2$ as « observation » is, of course, a worst choice.

The problem has been often debated: HESS (1951) has pointed out with some examples that an unappropriate observation equation can alter the precision of the estimated parameters up to weigh on statistical tests; LANGFORD (1973) remarks that the use of $sen^2\theta$ in the error equation is unfavorable only « ... if the cell is small or the system has high symmetry ». A systematic survey of the entire subject is still lacking.

The above outlined state of affairs however, is disquieting only when very high precision determinations are necessary. In the mineralogical and petrological routine works a compromise is the most reliable choice, so that $Q = 1/d^2$ is widely used as « observation » indipendently of how the lattice interplanar spacings are obtained. The quantity Q is retained as « observation » also in the present work but here a two-ways procedure has been adopted. Thus the lattice constants refinement is performed in terms of direct unit-cell if the direct parameters are required, or in terms of reciprocal unit-cell when the reciprocal constants are of interest. This strategy simplifies all the calculations smoothing also some mathematical and statistical complications.

Outline of the procedure

The Least-Squares unit-cell constants determination involving the reciprocal lattice is well known. Among the various papers on the subject those of SMITH (1956), BURNHAM (1962), KELSEY (1963), APPLEMAN et Al. (1973), LANGFORD (1973) are of relevant interest. The use of the direct unit-cell is described in FARINATO and LORETO (1975).

Using the subscript « c » for a calculated quantity and the subscript « ex » for a quantity obtained from an experiment we can write for the i-th X-ray diffraction peak $h_ik_il_i$

$$\left(\sin^2\vartheta_i\right)_c \triangleq \left(\sin^2\vartheta_i\right)_{ex} - \Delta\left(\sin^2\vartheta_i\right)_{ex} \qquad (6)$$

where the symbol $\triangleq$ means « is observed to be equal to » and $\Delta(\sin^2\theta_i)_{ex}$ is a correction term accounting for systematic errors. Multiplying each term of eq. 6 for the factor $4/\lambda_i^2$ and rearranging, we can write our « i-th observation equation of unit weight » as

$$\left(\frac{1}{d_i^2}\right)_c + \frac{4}{\lambda_i^2}\Delta\left(\sin^2\vartheta_i\right)_{ex} \triangleq \left(\frac{1}{d_i^2}\right)_{ex} \qquad (7)$$

or, with an obvious simplified notation

$$Q_c + D_{ex} \triangleq Q_{ex} \qquad (8)$$

In the triclinic system the expression of Q_c in terms of direct unit-cell constants and reflection indices is

$$Q_c = \frac{1}{R}\left(\frac{\sin^2\alpha_o}{a_o^2} h_i^2 + \frac{\sin^2\beta_o}{b_o^2} k_i^2 + \frac{\sin^2\gamma_o}{c_o^2} l_i^2 + \frac{2m}{b_o c_o} k_i l_i + \frac{2n}{a_o c_o} h_i l_i + \frac{2p}{a_o b_o} h_i k_i\right) \tag{9}$$

where

$$R = \left(1 - \cos^2\alpha_o - \cos^2\beta_o - \cos^2\gamma_o + 2\cos\alpha_o \cos\beta_o \cos\gamma_o\right) \tag{9a}$$

$$m = \left(\cos\beta_o \cos\gamma_o - \cos\alpha_o\right) \tag{9b}$$

$$n = \left(\cos\gamma_o \cos\alpha_o - \cos\beta_o\right) \tag{9c}$$

$$p = \left(\cos\alpha_o \cos\beta_o - \cos\gamma_o\right) \tag{9d}$$

Alternatively in terms of reciprocal lattice parameters the expression of Q_c is

$$Q_c = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2klb^* c^* \cos\alpha^* + 2hla^* c^* \cos\beta^* + 2hka^* b^* \cos\gamma^* \tag{10}$$

The correction term D_{ex} in eq. 8 may be made up of several functions according to the systematic errors to account for. Formally we will write

$$D_{ex} = \frac{4}{\lambda_i^2} \sum_1^k m \left[f_m(\vartheta_i)_{ex}\right] D_m \tag{11}$$

where $f_1(\theta_i)_{ex}, \ldots, f_k(\theta_i)_{ex}$ are the correction functions and the $D_1, \ldots, D_k$ are the « drift » constants. The equation 8 is intrinsically non linear in the lattice parameters (direct or reciprocal ones) but it is linear in the drift constants. An approximation of Q_c linear in terms of unit-cell parameter corrections can be obtained by a truncated Taylor's expansion, so that calling Q_i the i-th Q_c,

$$\sum_1^6 n \frac{\partial Q_i}{\partial x_n}\Bigg| \Delta x_n + \frac{4}{\lambda_i^2} \sum_1^k m \left[f_m(\vartheta_i)_{ex}\right] D_m \cong \Delta Q_i \tag{12}$$

is the new i-th observation equation for the triclinic case.

According to the case in eq. 12 Q_i comes out from eq. 9 or eq. 10, the x's are the direct or reciprocal unit-cell parameters and the Δx's are the corresponding parameter corrections. The vertical bar in eq. 12 points out that the partial derivatives must be numerically evaluated putting in their formulas the approximated unit-cell parameters. An expression of the partial derivatives of Q_c (eq. 9) in respect to $a_o, \ldots, \gamma_o$ is given in FARINATO and LORETO (1975), for all the crystal systems (1).

(1) See the Appendix for corrections of misprints in the FARINATO and LORETO (1975) paper.

In the reciprocal unit-cell case the partial derivatives of Q_c (eq. 10) in respect to $a^*, \ldots, \gamma^*$ are very simple for all the crystal systems and their expression will be not given here.

The meaning of ΔQ_i in eq. 12 is

$$\Delta Q_i = \left| \left(\frac{1}{d_i^2}\right)_{ex} - Q_i \right| \tag{13}$$

If there are more observation equations than unknown parameters, the Least-Squares method can be applied.
Let be

$$Y = \begin{bmatrix} \Delta Q_1 \\ \vdots \\ \Delta Q_i \\ \vdots \\ \Delta Q_r \end{bmatrix} \tag{14a}$$

$$X = \begin{bmatrix} \frac{\delta Q_1}{\delta x_1} \cdots \frac{\delta Q_1}{\delta x_6} & f_1(\vartheta_1)_{ex} \cdots f_k(\vartheta_1)_{ex} \\ \vdots \quad\quad \vdots & \vdots \quad\quad \vdots \\ \frac{\delta Q_i}{\delta x_1} \cdots \frac{\delta Q_i}{\delta x_6} & f_1(\vartheta_i)_{ex} \cdots f_k(\vartheta_i)_{ex} \\ \vdots \quad\quad \vdots & \vdots \quad\quad \vdots \\ \frac{\delta Q_r}{\delta x_1} \cdots \frac{\delta Q_r}{\delta x_6} & f_1(\vartheta_r)_{ex} \cdots f_k(\vartheta_r)_{ex} \end{bmatrix} \tag{14b}$$

$$\beta = \begin{bmatrix} \Delta x_1 \\ \vdots \\ \Delta x_6 \\ D_1 \\ \vdots \\ D_k \end{bmatrix} \tag{14c}$$

where $r > (6 + k)$, we can write the Least-Squares normal equation system as

$$X'X\hat{\beta} = X'Y \tag{15}$$

and if the matrix X'X is non singular the vector $\hat{\beta}$ estimating β of eq. 14*c* is given by

$$\hat{\beta} = (X'X)^{-1}X'Y \tag{16}$$

As it is well known, an iterative procedure is now applied until the Δx's of $\hat{\beta}$ are very close (if possible) to zero.

The variance σ^2 of the perturbations on the vector Y is estimated from the expression

$$\hat{\sigma}^2 = \frac{Y'Y - \hat{\beta}'X'Y}{r - (6 + k)} \tag{17}$$

and the variance σ_q^2 on each of the estimated parameters is estimated from

$$\hat{\sigma}_q^2 = \hat{\sigma}^2 c_{qq} \qquad (q = 1, 2, \ldots, 6, \ldots, 6+k) \tag{18}$$

where the c_{qq}'s are the diagonal elements in the matrix $(X'X)^{-1}$.
The variance σ_V^2 of the unit-cell volume V is estimated from

$$\hat{\sigma}_V^2 = \hat{\sigma}^2 \sum_1^6 \sum_1^6 \frac{\delta V}{\delta x_i} \frac{\delta V}{\delta x_j} c_{ij} \tag{19}$$

where the c_{ij}'s are the elements of the matrix $(X'X)^{-1}$.

If the r observation equations are of unequal weight, the same above outlined procedure can be followed multiplying each observation equation for the root square of its weight.

Because the variance σ^2 of Y does not depend on the X nor the β, its estimate $\hat{\sigma}^2$ has, of course, the same value in the direct or reciprocal refinement case. The value of $\hat{\sigma}^2$ is also independent from the refinement cycle. Starring to label the reciprocal unit-cell case, it may be useful to note that:

$$\hat{\sigma}_q^{*2} = \hat{\sigma}^2 c_{qq}^* \tag{20}$$

and that dividing eq. 18 by eq. 20:

$$\frac{\hat{\sigma}_q^2}{\hat{\sigma}_q^{*2}} = \frac{c_{qq}}{c_{qq}^*} \tag{21}$$

An example

A computer program has been prepared for the Olivetti P 652 Computer system. The program follows two ways separately i.e. the Least-Squares refinement is performed in the direct or in the reciprocal space.

c) the reflection indices $h_i k_i l_i$;

a) the crystal system code;

b) the approximations in the unit-cell parameters (direct or reciprocal ones);

c) the reflection indices $h_i k_i l_i$;

d) the angle $2\theta_i$ or the spacing d_i;

e) the wave-lenght λ_i;

f) the observation weight w_i;

g) the standard deviation $\sigma(\theta_i)$;

h) the code of the correction functions allowing for systematic errors (none or up to four functions simultaneously, if desidered. In tbale 1 are listed some common correction functions; other functions can be easily added).

If an internal standard whose unit-cell parameters are accurately known is used, the $2\theta_{ex}$'s are transformed in $2\theta_{obs}$ by a suitable subroutine. If not all the $2\theta_{obs}$ (or d_{obs}) are indexed, a preliminary unit-cell refinement is carried out with the $2\theta_{obs}$ already indexed and then a general indexing attempted within a specific space-group and a given tolerance. When no indices are found or the indexing is not unique, the corresponding 2θ (or d) is labelled « unknown ». The possibility of rejection of certain diffraction data from the calculation is also provided.

An example of listing of output data is displayed in the self-explanatory tables 2 and 3 concerning the Spanish Peak andesine quoted in SMITH (1956). Some useful « statistics » aid the criticism on the data used.

TABLE 1

Some systematic errors correction functions of common use:
see f.e. AZÀROFF and BUERGER (1958)

$$f_1(\vartheta) = \sin^2 2\vartheta \qquad f_5(\vartheta) = \frac{\sin^2 2\vartheta}{\vartheta}$$

$$f_2(\vartheta) = \vartheta_r \sin 2\vartheta$$

$$f_6(\vartheta) = \sin^2 2\vartheta \left(\frac{1}{\sin\vartheta} + \frac{1}{\vartheta}\right)$$

$$f_3(\vartheta) = \cos^2\vartheta \sin 2\vartheta$$

$$f_4(\vartheta) = \left(\frac{\pi}{2} - \vartheta_r\right) \sin 2\vartheta \qquad f_7(\vartheta) = \cos^2\vartheta \sin\vartheta$$

r = angle in radian measure

Appendix

« ERRATA CORRIGE » IN THE FARINATO AND LORETO (1975) PAPER

Page 494, Table 1:

— Under MONOCLINIC, the right hand member in the partial derivate $\partial Q/\partial c$ must be multiplied for the 1 index.

Page 495, Table 2:

— In the row « ISOMETRIC » read $3a^2$ instead of $3a^3$.

— In the row « HEXAGONAL » in the first column read $2a\sin\frac{\pi}{3}$ instead of $6a\sin 60°$, and in the third column read $a^2\sin\frac{\pi}{3}$ instead of $3a^2\sin 60°$.

TABLE 2

Direct unit-cell parameters refinement. Listing of the output data.

University of Roma Institute of Mineralogy <> LEAST SQUARES CRYSTAL LATTICE CONSTANTS REFINEMENT <> by G. De Angelis - R. Farinato - L. Loreto (1976)

SAMPLE Andesine No 152 LOCALITY Spanish Peak, Calif. X RAY APP. NORELCO high-angle diff.meter INT. STD Quartz

NAME J. V. Smith OPERATOR G.D.A./R.F./L.L. REMARKS Min.Mag. 31 pg 52 (1956) DAY 14 sept 1976

REFINED PARAMETERS <> SYSTEM : TRICLINIC <> cicle No. 4 <> code 29

RECIPR CELL	a*	b*	c*	alpha*	beta*	gamma*	V*
ESTIMATE	0.13682555	0.07802211	0.15709378	86.09099606	63.62042855	88.67692807	0.00149887
STND DEV.	0.00003576	0.00000984	0.00001510	0.01728241	0.01107159	0.01442556	0.00000041
STND DEV.%	0.02613833	0.01260597	0.00961106	0.02007459	0.01740258	0.01626754	0.02741971
CORRECTION	0.00000000	0.00000000	0.00000000	0.00000000	-0.00000000	-0.00000000	
DIRECT CELL	8.15833952	12.84718370	7.12042200	93.70741725	116.35249997	89.53844077	667.17019882

No	h	k	l	dobs.	dcalc.	DIFF.	%	G	2THETAob	2THETAcd	DIFF.	%	G	lambda	weight	2THETAex	DIFF.	STND DEV.d
1	2	0	-1	4.03835	4.03692	0.001435	12.4	1.0	22.010	22.018	-0.0079	-8.2	-0.7	1.541800	1.00			
2	1	-1	1	3.87920	3.88006	-0.000862	-7.4	-1.5	22.925	22.920	0.0052	5.3	1.2	1.541800	1.00			
3	1	1	1	3.76111	3.75951	0.001607	13.9	1.2	23.655	23.665	-0.0103	-10.6	-1.0	1.541800	1.00			
4	1	-3	0	3.72618	3.72602	0.000162	1.4	-0.4	23.880	23.881	-0.0011	-1.1	0.3	1.541800	1.00			
5	1	3	0	3.65384	3.65179	0.002044	17.6	1.7	24.360	24.374	-0.0138	-14.3	-1.5	1.541800	1.00			
6	1	1	-2	3.48428	3.48215	0.002138	18.4	1.8	25.565	25.581	-0.0160	-16.4	-1.8	1.541800	1.00			
7	-1	1	2	3.36868	3.36774	0.000938	8.1	0.5	26.458	26.466	-0.0075	-7.7	-0.6	1.541800	1.00			
R	0	4	0	3.20451					27.840					1.541800	1.00			
R	0	0	2	3.18300					28.032					1.541800	1.00			
R	2	2	0	3.14639					28.365					1.541800	1.00			
8	1	-3	1	3.00496	3.00428	0.000684	5.9	0.2	29.730	29.737	-0.0069	-7.1	-0.5	1.541800	1.00			
9	1	3	1	2.84311	2.84233	0.000778	6.7	0.3	31.465	31.474	-0.0088	-9.1	-0.8	1.541800	1.00			
10	-1	3	2	2.64849	2.64843	0.000069	0.6	-0.5	33.815	33.816	-0.0009	-0.9	0.3	1.540510	1.00			
11	2	4	-1	2.53138	2.53168	-0.000299	-2.6	-0.9	35.430	35.426	0.0043	4.5	1.1	1.540510	1.00			
12	-2	4	1	2.48825	2.48835	-0.000094	-0.8	-0.7	36.065	36.064	0.0014	1.5	0.7	1.540510	1.00			
13	0	6	0	2.13599	2.13615	-0.000153	-1.3	-0.7	42.275	42.272	0.0032	3.3	0.9	1.540510	1.00			
14	2	2	2	1.87957	1.87975	-0.000183	-1.6	-0.8	48.385	48.380	0.0050	5.2	1.2	1.540510	1.00			
15	1	1	3	1.79689	1.79686	0.000038	0.3	-0.5	50.765	50.766	-0.0011	-1.2	0.3	1.540510	1.00			
16	2	0	-4	1.77618	1.77629	-0.000118	-1.0	-0.7	51.400	51.396	0.0037	3.8	1.0	1.540510	1.00			
						0.011602	100.0				0.0971	100.0						

STATISTICS

Degrees of freedom (N-K)	=	10
Variance of the perturbations	=	0.0000000041
SQR of the variance	=	0.0000638746
Residual sum of squares	=	0.0000000408
Standard error of the fit on (1/d)**2	=	0.0000638746
Standard error of the fit on d	=	0.0012763209
Standard error of the fit on 2THETA	=	0.0094654840

DIFF.	E=MEAN	S=STND DEV.	E + S	E - S
2THETA	-0.0032272776	0.0069728457	0.0037455681	-0.0102001234
d	0.0005115893	0.0008982343	0.0014098236	-0.0003866451

NOTE :

% = contribution percent to the sum of the absolute DIFF.
G = "unit normal deviate form" = [DIFF.-MEAN(DIFF.)]/STND DEV.
R = rejected from the calculation

DET. = 3.47163919936000

RECIPROCAL VAR-COV MATRIX

0.00000000127906	-0.00000000015613	-0.00000000022889	0.00000000130887	0.00000000259333	0.00000000192200
-0.00000000015613	0.00000000009674	0.00000000002603	0.00000000025122	-0.00000000047015	-0.00000000011303
-0.00000000022889	0.00000000002603	0.00000000022796	0.00000000184601	-0.00000000159415	0.00000000079599
0.00000000130887	0.00000000025122	0.00000000184601	0.00000009098366	-0.00000001765407	0.00000003476682
0.00000000259333	-0.00000000047015	-0.00000000159415	-0.00000001765407	0.00000003734006	-0.00000001095751
0.00000000192200	-0.00000000011303	0.00000000079599	0.00000003476682	-0.00000001095751	0.00000006338986

Initial parameters: $a_o = 9$ Å, $b_o = 12$ Å, $c_o = 8$ Å, $\alpha_o = 93°$, $\beta_o = 117°$, $\gamma_o = 88°$

TABLE 3

Reciprocal unit-cell parameters refinement. Listing of the output data.

University of Roma Institute of Mineralogy ◇ LEAST SQUARES CRYSTAL LATTICE CONSTANTS REFINEMENT ◇ by G. De Angelis - R. Farinato - L. Loreto (1976)

SAMPLE Andesine No 152 LOCALITY Spanish Peak, Calif. X RAY APP. NORELCO high-angle diff.meter INT. STD Quartz

NAME J. V. Smith OPERATOR G.D.A./R.F./L.L. REMARKS Min.Mag. 31 pg 52 (1956) DAY 14 sept 1976

REFINED PARAMETERS ◇ SYSTEM : TRICLINIC ◇ cicle No. 4 ◇ code 29

DIRECT CELL	a	b	c	alpha	beta	gamma	V
ESTIMATE	8.15833952	12.84718370	7.12042200	93.70741724	116.35249997	89.53844078	667.17019882
STND DEV.	0.00253047	0.00166570	0.00068303	0.01720979	0.01129914	0.01447511	0.18622001
STND DEV.%	0.03101701	0.01296549	0.00959256	0.01836546	0.00971113	0.01616636	0.02791192
CORRECTION	-0.00000000	0.00000000	0.00000000	-0.00000000	-0.00000000	0.00000000	
RECIPR CELL	0.13682555	0.07802211	0.15709378	86.09099606	63.62042855	88.67692807	0.00149887

No	h	k	l	dobs.	dcalc.	DIFF.	%	G	2THETAob	2THETAcd	DIFF.	%	G	lambda	weight	2THETAex	DIFF.	STND DEV.d
1	2	0	-1	4.03835	4.03692	0.001435	12.4	1.0	22.010	22.018	-0.0079	-8.2	-0.7	1.541800	1.00			
2	1	-1	1	3.87920	3.88006	-0.000862	-7.4	-1.5	22.925	22.920	0.0052	5.3	1.2	1.541800	1.00			
3	1	1	1	3.76111	3.75951	0.001607	13.9	1.2	23.655	23.665	-0.0103	-10.6	-1.0	1.541800	1.00			
4	1	-3	0	3.72618	3.72602	0.000162	1.4	-0.4	23.880	23.881	-0.0011	-1.1	0.3	1.541800	1.00			
5	1	3	0	3.65384	3.65179	0.002044	17.6	1.7	24.360	24.374	-0.0138	-14.3	-1.5	1.541800	1.00			
6	1	1	-2	3.48428	3.48215	0.002138	18.4	1.8	25.565	25.581	-0.0160	-16.4	-1.8	1.541800	1.00			
7	-1	1	2	3.36868	3.36774	0.000938	8.1	0.5	26.458	26.466	-0.0075	-7.7	-0.6	1.541800	1.00			
R	0	4	0	3.20451					27.840					1.541800	1.00			
R	0	0	2	3.18300					28.032					1.541800	1.00			
R	2	2	0	3.14639					28.365					1.541800	1.00			
8	1	-3	1	3.00496	3.00428	0.000684	5.9	0.2	29.730	29.737	-0.0069	-7.1	-0.5	1.541800	1.00			
9	1	3	1	2.84311	2.84233	0.000778	6.7	0.3	31.465	31.474	-0.0088	-9.1	-0.8	1.541800	1.00			
10	-1	3	2	2.64849	2.64843	0.000069	0.6	-0.5	33.815	33.816	-0.0009	-0.9	0.3	1.540510	1.00			
11	2	4	-1	2.53138	2.53168	-0.000299	-2.6	-0.9	35.430	35.426	0.0043	4.5	1.1	1.540510	1.00			
12	-2	4	1	2.48825	2.48835	-0.000094	-0.8	-0.7	36.065	36.064	0.0014	1.5	0.7	1.540510	1.00			
13	0	6	0	2.13599	2.13615	-0.000153	-1.3	-0.7	42.275	42.272	0.0032	3.3	0.9	1.540510	1.00			
14	2	2	2	1.87957	1.87975	-0.000183	-1.6	-0.8	48.385	48.380	0.0050	5.2	1.2	1.540510	1.00			
15	1	1	3	1.79689	1.79686	0.000038	0.3	-0.5	50.765	50.766	-0.0011	-1.2	0.3	1.540510	1.00			
16	2	0	-4	1.77618	1.77629	-0.000118	-1.0	-0.7	51.400	51.396	0.0037	3.8	1.0	1.540510	1.00			
						0.011602	100.0				0.0971	100.0						

STATISTICS

Degrees of freedom (N-K)	=	10
Variance of the perturbations	=	0.0000000041
SQR of the variance	=	0.0000638746
Residual sum of squares	=	0.0000000408
Standard error of the fit on (1/d)**2	=	0.0000638746
Standard error of the fit on d	=	0.0012763210
Standard error of the fit on 2THETA	=	0.0094654841

DIFF.	E=MEAN	S=STND DEV.	E + S	E - S
2THETA	-0.0032272776	0.0069728461	0.0037455684	-0.0102001237
d	0.0005115893	0.0008982344	0.0014098237	-0.0003866452

NOTE :

% = contribution percent to the sum of the absolute DIFF.
G = "unit normal deviate form" = [DIFF.-MEAN(DIFF.)]/STND DEV.
R = rejected from the calculation

DET. = 0.00000000001752

DIRECT VAR-COV MATRIX

0.00000640329273	-0.00000184274484	0.00000015941395	-0.00000002254410	0.00000030257965	0.00000004900699
-0.00000184274484	0.00000277455763	0.00000000232106	0.00000013197389	-0.00000009191479	-0.00000004676266
0.00000015941395	0.00000000232106	0.00000046653131	0.00000006726645	0.00000005373860	-0.00000003287912
-0.00000002254410	0.00000013197389	0.00000006726645	0.00000009022069	-0.00000001376789	-0.00000003262110
0.00000030257965	-0.00000009191479	0.00000005373860	-0.00000001376789	0.00000003889066	-0.00000000977517
0.00000004900699	-0.00000004676266	-0.00000003287912	-0.00000003262110	-0.00000000977517	0.00000006382613

Initial parameters: $a^* = 0.12$ Å^{-1}, $b^* = 0.08$ Å^{-1}, $c^* = 0.14$ Å^{-1}, $\alpha^* = 87°.65$, $\beta^* = 63°$, $\gamma^* = 91°$

— In the row «RHOMBOHEDRAL» the third space must be empty and the formula: $-3a^3mR^{-1/2}\sin\alpha$ shifted in the fourth column.

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— The last three terms of eq. 28 must be multiplied for the factor 2.

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