THE AUTOMATIC PROCEDURE FOR THE UNAMBIGUOUS CHOICE OF LATTICE PARAMETERS AND THE BRAVAIS TRANSLATION LATTICE

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A complex method for the determination of: a) the orientation matrix between the crystallographic axes and the coordination system of the four-circle diffractometer; b) the smallest primitive cell; c) the Buerger and Niggli reduced cell; d) lattice parameters of the unit cell and the Bravais translation lattice (P, C, I, F, R); is described.

I. INTRODUCTION

The X-ray structure analysis of single crystals nowadays is highly automatized. Despite this fact it is possible to encounter in the current practice three main problems upon which the successful solution of the crystal structure depends.

The first problem is to find the lattice parameters (a, b, c, α, β, γ) and to choose the crystallographic system and the space group, respectively. This is the basic assumption of further procedure.

The second problem is to find the first atom(s). This procedure is today on a very good level which as regards the methodical and the software side (the heavy atom method, direct methods, programs SHELX76, SHELXS86, XTAL, MULTAN, DIRDIF).

The third problem is (considering the used X-rays and the therewith connected diffraction on electrons) the location of hydrogen atoms. Here the suitably chosen weight schemes, the calculating methods for their analysis, resp. (e. g. the SHELX76 program), should be taken into account, various limitations and corrections regarding the observed structural factors or programs of calculation for generating the hydrogen atoms.

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The authors of this article deal with the analysing and the solving of the first outlined problem of the structural analysis of single crystals by the four-circle diffractometer.

II. DETERMINATION OF THE CRTYSTAL ORIENTATION AND THE ORIENTATION MATRIX

To be able to adjust any plane (hkl) to the diffraction position it is neccessary to know the crystal orientation regarding the x, y, z axes of the diffractometer (Fig. 1). This condition should be fulfilled by 10—25 diffractions registered by chance.

From the Fig. 1 it follows that the x, y, z coordinates of the reciprocal vector $\bar{d}^*$ can be expressed by the relations

$$\begin{aligned} x &= a_x^* h + b_x^* k + c_x^* l \\ y &= a_y^* h + b_y^* k + c_y^* l \\ z &= a_z^* h + b_z^* k + c_z^* l, \end{aligned} \tag{1}$$

where $\bar{a}^* = (a_x^*, a_y^*, a_z^*)$, $\bar{b}^* = (b_x^*, b_y^*, b_z^*)$, $\bar{c}^* = (c_x^*, c_y^*, c_z^*)$ are reciprocal lattice vectors.

In the matrix notation

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} a_x^* b_x^* c_x^* \\ a_y^* b_y^* c_y^* \\ a_z^* b_z^* c_z^* \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix} \quad \text{or} \quad \mathscr{X} = \mathscr{A}\mathscr{H} \tag{2}$$

$\mathscr{X}$ is the column vector representing in the instrumental orthogonal coordination system of the diffractometer the reciprocal vector which fulfils the Bragg condition $2d\sin\Theta = n\lambda$, $\mathscr{A}$ is the orientation matrix and $\mathscr{H}$ is the column vector of integers which correspond to indices of the diffraction in question.

Busing and Levy [1] showed that

$$\mathscr{A} = \mathscr{U}\mathscr{B}, \tag{3}$$

where $\mathscr{U}$ is the orthogonal matrix of the 3×3 type which describes the orientation of the crystallographic axes and $\mathscr{B}$ is defined as

$$\mathscr{B} = \begin{pmatrix} a^* & b^* \cos\gamma^* & c^* \cos\beta^* \\ 0 & b^* \sin\gamma^* & -c^* \sin\beta^* \cos\alpha \\ 0 & 0 & 1/c \end{pmatrix}, \tag{4}$$

where a^*, b^*, c^*, β^*, γ^* are reciprocal lattice parameters and c, α are direct lattice parameters.

When $\mathscr{U}\mathscr{B}^{-1}$ is the inversion matrix of $\mathscr{U}\mathscr{B}$ and $(\mathscr{U}\mathscr{B}^{-1})^T$ is the transponed matrix in relation to $\mathscr{U}\mathscr{B}^{-1}$, then

$$(\mathscr{U}\mathscr{B}^{-1}).(\mathscr{U}\mathscr{B}^{-1})^T = 1/\lambda^2 \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}. \tag{5}$$

If the provided elements of the matrix $\mathscr{U}\mathscr{B}^{-1}$ are known, it is possible to calculate the unit cell parameters a, b, c, α, β, γ.

III. METHODOLOGY OF THE UNAMBIGUOUS CHOICE

The knowledge of the lattice parameters and the crystallographic system (P, C, I, F, R) enables immediately to begin data collecting of the integral intensities, which is the main aim of diffractometric measurements.

The process of determination and verification of the right choice of lattice parameters can be divided into three parts [3]

A — The reciprocal space

1. Determination of the smallest primitive cell.
2. Indexing of diffractions and refinement of the orientation matrix.
3. Verification of the smallest primitive cell.

B — The direct space

4. Calculation of the reduced form (S_{11}, S_{22}, S_{33}, S_{23}, S_{13}, S_{12}).
5. Determination of the reduced cell type (1—44).
6. The Bravais translation lattice.

C — The diffractometric tests

7. Confirmation of the crystal symmetry.
8. Check with respect to the extinction conditions.
9. Space group(s).

The aim of part A — the reciprocal space-is the choice of the primitive cell with the shortest vectors $\bar{a}^*$, $\bar{b}^*$, $\bar{c}^*$, which is the neccessary condition when determining the reduced and conventional cell in part B — the direct space. Part

C — the diffractometric tests deals with the verification of the right procedure in parts A and B.

III. 1. Determination of the smallest primitive cell

The refined angular values 10—25 the chance registered diffractions 2Θ, ω, φ, χ and the wave length λ of the X-ray used constitute the basic input data set. The further procedure of the calculations is divided into steps according to the algorithm:

a) The evaluation of the coordinates of reciprocal vectors x_i, y_i, z_i; $i = 1, n$ for n diffractions [2].
b) A vector can be constructed (Fig. 2) between every two points found in this way. The coordinates of the vectors will be denoted by capital letters (X_k, Y_k, Z_k), where $k = 1, p$ and $p = n(n-1)/2$ is the total number of vectors.
c) The vectors are ordered according to their magnitudes.
d) Let us take the shortest vector as $\bar{a}^*$ and find all vectors collinear to it. The absolute values of the compared vectors being taken into consideration.
e) Lets label a non-collinear vector to the $\bar{a}^*$ vector as $\bar{b}^*$ and again to it lets find all collinear vectors.
f) The shortest vector non-lying in the plane formed by vectors $\bar{a}^*$, $\bar{b}^*$ lets take as $\bar{c}^*$.
g) From the relation (2) it follows that the orientation matrix is formed of column vectors $\bar{a}^* = (X_1, Y_1, Z_1)$, $\bar{b}^* = (X_2, Y_2, Z_2)$ and $\bar{c}^* = (X_3, Y_3, Z_3)$

$$\mathcal{UB} = \begin{pmatrix} X_1 & X_2 & X_3 \\ Y_1 & Y_2 & Y_3 \\ Z_1 & Z_2 & Z_3 \end{pmatrix}. \tag{6}$$

If it moreover applies that the determinant of $\mathcal{UB} > 0$, the crystallographic coordination system of the vectors $\bar{a}^*$, $\bar{b}^*$, $\bar{c}^*$ in this sense is a righthand one.

III. 2. Indexing of diffractions and refinement of the orientation matrix

To all so far used diffractions (10—25) indices (hkl) are assigned which are calculated by means of the inversion matrix $\mathcal{UB}^{-1}$. By means of those diffractions to which for all three indices integers are assigned, the $\mathcal{UB}$ matrix is refined [4, 5].

III. 3. Verification of the smallest primitive cell

The calculation of the reduced form according to procedure outlined in chapter III, point 4, requires the cell which will be reduced so as to be primitive, generated by the shortest vectors.

The exact procedure requires the systematic check of possible lattices to be carried out in the reciprocal space [6]. The less exact but frequently sufficient procedure includes:

— the choice of weak, medium and strong diffractions from the polaroid film,
— the choice of three shortest non-coplanar vectors from the set of all vectors (Fig. 2). The occurrence of only integer indices indicates the right procedure.

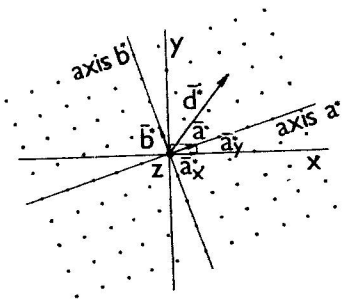

Fig. 1 An randomly oriented crystal on the goniometer.

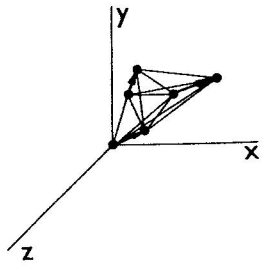

Fig. 2 Choice of the three shortest non-coplanar reciprocal vectors constructed from the set of given points including the origin.

If only too few diffractions are available, the fractional indices can occur when performing indexing. It means that between pairs of reciprocal points all the three shortest reciprocal vectors do not occur. In this case the indices h, k or l are to be integers or integers plus: 1/2, 1/3 or 2/3. The indices can be transformed into integers so that the corresponding axes are divided by 1/2 or 1/3, i.e. the column vector of the $\mathcal{UB}$ matrix in question is multiplied by 1/2 or 1/3.

If, at the same time more axes are to be changed, the reciprocal cell could diminish by more than the magnitude of the primitive cell. This fact could be hardly registered if the lattice parameters were not known before hand. It is most suitable to complete the input set of diffractions by further ones from the polaroid film.

III. 4. Determination of the reduced form

Three shortest non-coplanar vectors of the reciprocal spaces $\bar{a}^*$, $\bar{b}^*$, $\bar{c}^*$, which generate the orientation matrix $\mathcal{UB}$, are at the same time edges of the reciprocal cell. The direct lattice formed by these vectors is primitive again. According to relation (5) it is possible to determine the lattice parameters of this primitive cell in the direct space a_p, b_p, c_p, α_p, β_p, γ_p.

Under the Niggli cell [7, 8, 9] we understand such a cell of three dimensional Bravais translation lattices which is based on the reduction theory of positive definite ternary quadratic forms [10]. Niggli [11] showed that to every crystal lattice regardless of its symmetry it is possible to assign just one reduced cell defined by means of three shortest non-coplanar vectors $\bar{a}$, $\bar{b}$, $\bar{c}$, the scalar representation of which

$$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & S_{13} & S_{12} \end{pmatrix} = \begin{pmatrix} \bar{a}.\bar{a} & \bar{b}.\bar{b} & \bar{c}.\bar{c} \\ \bar{b}.\bar{c} & \bar{a}.\bar{c} & \bar{a}.\bar{b} \end{pmatrix} \tag{7}$$

fulfils the conditions derived from the reduction theory of the positive definite ternary quadratic forms [10].

A complete algorithm which is able to convert any primitive cell (in direct space) into the Niggli form was proposed by Křivý and Gruber [12].

III. 5. Determination of the reduced cell type

Mighell and Rodgers [3] classified reduced cells according to 44 forms, the corresponding Bravais cells being obtained on the basis of transformation matrices.

Remark. The theory of the reduced cell has been successfully used for the identification of crystallic powder materials from the Crystal Data file, a fast identification file ([8] with references).

III. 6 The Bravais translation lattice

The final phase is the determination of the Bravais (metric) lattice and the following comparison of the metric symmetry with that of the real symmetry of the crystal lattice. Transformation relations between the reduced cell and the Bravais lattice and conventions for a choice of the axes are given in [3] in table form. This table is very important for the next explanation.

III. 7. Diffractometric tests

The crystal symmetry of a lattice can never exceed the metric symmetry determined from the reduced cell, it can be only lower [3]. If, for example, the reduced form corresponds to the triclinic system, the crystal lattice symmetry can be only triclinic. If the reduced form corresponds to the monoclinic lattice, the crystal system has to be either monoclinic or triclinic.

Mighell and Rodgers [3] showed that in 97% cases the reduced form leads direct to the right choice of the crystal lattice. In some exceptional cases in which the Bravais (metric) lattice symmetry exceeds the crystal symmetry it is neccessary to find structural reasons.

If the orientation matrix $\mathcal{UB}$, the lattice parameters and the Bravais lattice are known, it is possible to test the single crystal diffractometrically: a) the check of equivalent diffractions of suitable intensity is possible in each crystallographic system, e.g., the Friedel law always applies and therefore the intensity of each diffraction $I(hkl) = I(\bar{h}\bar{k}\bar{l})$ (pay attention to anomalous dispersion, b) the check regarding the conditions of the systematic absence diffractions concerns the centred Bravais lattices (C, F, I), i.e. general indices (hkl), c) if the checks are successful in points a) or b) resp., it is possible to search systematic absence diffractions on axes $(h00)$, $(0k0)$, $(00l)$, on planes $(hk0)$, $(h0l)$, $(0kl)$ and to find thus the space group(s) of symmetry.

IV. PRACTICAL PROCEDURE

IV. 1. Supplementary check by standard methods

Before placed on the goniometric head the crystal should be investigated by traditional optical methods (extinction in polarized light, a broken crystal, a twin crystal, etc.).

It is suitable to generalize the preliminary knowledge of the crystal by taking the oscillating photograph, a zero and a first layer one. From the oscillating photograph one direct lattice parameter is known (e.g. a) and from the Weissenberg photograph of the zero layer two reciprocal lattice parameters (e.g. b^*, c^*, interplanar distances d_{010}, d_{001}, resp.) and the angle between them α^* are known. From these data the volume of the unit cell can be calculated

$$V = a/(b^*c^* \sin \alpha^*) = (ad_{010}d_{001})/\sin \alpha^*, \tag{8}$$

which equals the volume calculated by means of the matrix $\mathcal{UB}$.

The Weissenberg photograph of the first layer shows a nonorthogonal lattice when the axes are bent:

a) triclinic, with the axis of rotation about the vector $\bar{a}$, $\bar{b}$, or $\bar{c}$;
b) monoclinic, with the axis of rotation about the vector $\bar{a}$ or $\bar{c}$;
c) rhombohedral, with the axis of rotation about the vector $\bar{a}$, $\bar{b}$ or $\bar{c}$;
d) hexagonal, with the axis of rotation about the vector $\bar{a}$ or $\bar{b}$.

The calculated value of volume (8) as well as the knowledge of the nonorthogonal or the orthogonal lattice, resp., helps to check the results.

IV. 2. Calculations

The program with the name UB was assorted for a Syntex $P2_1$ diffractometer. It is written in the FORTRAN IV, contains approximately 1800 statements, the neccessary memory is 140 kbytes and the computing time varies by about 5 s for one input set.

It is adjusted universally besides the subroutine COORD which precalculates the angular values 2Θ, ω, φ, χ to the vector coordinates x, y, z. Using the right relations for the given type of a diffractometer in the subroutine COORD it is possible to modify the program UB in this sense for any four-circle diffractometer.

The basic input data are always the wavelength of the X-rays used (LAMBDA), the refined angular values 2Θ, ω, φ, χ (TTHT, OME, PHI, CHI) for the maximal number of 30 diffractions and the parameter SIGMA, i.e. the absolute error for the individual members of the scalar representation of the primitive cell S_{ij} (chap. III.4).

The UB program enables:

1. The processing of the diffractometric measurements carried out in a nonsymmetrical setting ($\Theta \neq \omega$), i.e. obtaining the desired results for an unknown single crystal through diffractions from the polaroid film.
2. Working in a symmetrical setting ($\Theta = \omega$), i.e. testing the known single crystal monitored before on a diffractometer, applying the values 2Θ, ω, φ, χ. Point 1 is valid for an unknown single crystal, but now $\Theta = \omega$.
3. To remove fractional indices. If in the first run of the UB program diffractions are indexed by fractional indices (chap. III.2, III.3.), an individual input to the program is enabled with suitable modified vectors of the $\mathcal{UB}$ matrix (the application of the parameters LAMBDA, TTHT, OME, PHI, CHI and SIGMA is neccessary).
4. To test the input diffractions with regard to their preceding occurrence in the set. This possibility is suitable, since in the set if vectors a very short vector could occur that could be further considered as the shortest $\bar{a}^*$.

5. If the program UB does not choose three non-coplanar vectors, the (*hkl*) indices will be greater than 100. It is possible to change the COL and/or COP parameters (in default are 2.58). These are significant in a selection of the collinear and the coplanar vectors (e.g. COL and/or COP will be equal to 30) and the program can run again.
6. To change the error value SIGMA ($=0.12$ Å^2, default) for the scalar representation of the primitive cell S_{ij}.
7. To obtain the results in table form for the experiment (diffractometric measurements) and for publication by giving the summary formula and the density D_m.
8. In one run of the UB program it is possible to treat any number of structures with any combination of possibilities 1—7.

V. EXAMPLES

An example to illustrate calculations is NaCl. It crystallizes in the cubic system, space group Fm3m, $a = 5.6396$ Å, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, F(000) $=$ $= 112$, $V = 179.37$ Å^3, $M_r = 58.4428$ gmol^{-1}, $Z = 4$, $D_m = 2.16371$ Mgm^{-3}, $D_x = 2.16386$ Mgm^{-3}.

From the polaroid film 15 diffractions of weak, medium and strong intensities were chosen (Table 1). Point 16 is the origin. The example is described in detail and can serve as a test of the UB program. The UB program chose out of 120 vectors three shortest non-coplanar vectors between the points No. 16-4 ($\bar{a}^*$), 16-5 ($\bar{b}^*$), 4-2 ($\bar{c}^*$) and indexed the diffractions from Table 1. The indices in question are given in Table 2.

Applying the equation (5) to the refined orientation matrix the lattice parameters of the primitive cell in the direct space were calculated:

$$a_p = 3.988, \quad b_p = 3.990, \quad c_p = 3.989 \text{ Å}$$

$$\alpha_p = 119.92, \quad \beta_p = 60.06, \quad \gamma_p = 120.02°.$$

For the absolute error SIGMA $= 0.12$ Å^2 the transformations of the proposed primitive cell have run as follows- Table 3. From Table 3 it is evident that the Buerger and the Niggli cells are the same. The Niggli cell is positive (Typ I) with the parameters:

$$a_N = 3.988, \quad b_N = 3.988, \quad c_N = 3.988 \text{ Å}$$

$$\alpha_N = 60, \quad \beta_N = 60, \quad \gamma_N = 60°.$$

From the last line of Table 3 it follows that

a) $S_{11} = S_{22} = S_{33}$ (the reduced form No. 1—8)
b) $S_{23} = S_{11}/2$, $S_{13} = S_{11}/2$, $S_{12} = S_{11}/2$,
i.e. the reduced form has No. 1 and the lattice is cubic, F centered.

Table 1

Angles (o) and instrumental coordinates of diffractions from the polaroid film for the structure of NaCl.

N°	2Θ	ω	φ	χ	x	y	z
1	14.47	359.06	230.46	9.40	0.2125	−0.1290	0.0407
2	14.47	359.11	136.54	20.65	−0.1347	−0.1939	0.0879
3	14.46	358.96	330.17	68.68	0.0136	0.0966	0.2320
4	12.51	359.81	190.39	56.43	0.0457	−0.1134	0.1804
5	12.51	359.82	76.24	40.04	−0.1668	0.0157	0.1393
6	20.52	359.28	89.53	7.68	−0.3471	−0.0650	0.0467
7	20.52	359.44	181.95	21.61	0.0779	−0.3228	0.1289
8	20.52	359.41	28.59	33.07	−0.1992	0.2253	0.1909
9	20.51	359.44	244.77	51.33	0.2262	−0.0327	0.2731
10	20.50	359.24	102.87	66.37	−0.1214	−0.0974	0.3200
11	25.19	359.56	178.20	58.23	0.0913	−0.2267	0.3612
12	29.17	359.72	310.39	72.56	0.0274	0.1929	0.4644
13	25.20	359.65	67.69	41.03	−0.3339	0.0313	0.2791
14	25.20	359.68	279.78	25.77	0.3608	0.1612	0.1849
15	12.52	359.92	2.23	13.66	−0.0323	0.2095	0.0512
16	origin				0.0	0.0	0.0

Table 2

Indices assigned to diffractions from the polaroid film for the structure of NaCl.

N°	h	k	l
1	0	1	−1
2	−1	0	−1
3	1	−1	0
4	0	0	−1
5	0	−1	0
6	−1	−1	0
7	−1	1	−2
8	1	−2	1
9	1	0	−1
10	0	−1	−1
11	0	0	−2
12	2	−2	0
13	0	−2	0
14	2	0	0
15	1	−1	1

The UB program uses Table 1 in [3]. For the wavelength λ used in the experiment, we get the basic lattice parameters of the Bravais (conventional) lattice (5):

$$a = b = c = 5.640 \text{ Å}$$

$$\alpha = \beta = \gamma = 90°.$$

Table 3

Transformations of the primitive cell for the structure of NaCl.

Cell	S_{11} (Å^2)	S_{22} (Å^2)	S_{33} (Å^2)	S_{23} (Å^2)	S_{13} (Å^2)	S_{12} (Å^2)	Type
proposed	15.906	15.906	15.906	−7.953	7.953	−7.953	
Buerger	15.906	15.906	15.906	7.953	7.953	7.953	
Niggli	15.906	15.906	15.906	7.953	7.953	7.953	+

Crystallographic lattice parameters agree with the calculated ones with a preciseness of 0.007%.

Knowing the lattice parameters and the Bravais lattice it is possible to begin immediately with the automatic measurement of integral intensities.

VI. CONCLUSION

The aim of the contribution was to describe in detail the procedure which enables from by change found diffractions of an arbitrary oriented single crystal with regard to the instrumental axes of a four-circle diffractometer to determine unambiguously the lattice parameters and the Bravais primitive or centered lattice. This knowledge permits immediately to begin measurements of integral intensities. The precision of the obtained results agrees very well with the experiment. On the basis of the above theory a program was written and tested on 15 structures. In 13 cases the calculated results agreed with experimental measurements carried out by other techniques (oscillating, the Weissenberg equiinclination, diffractometric). In two cases (monoclinic systems) the choice of an experimentally determined cell did not correspond with the cell found by the program UB by means of the theory of the reduced cell. Possibilities of the choice of another unit cell are described by Gruber [8].

The UB program can be obtained from the second author. If there are some problems in using this program, will you kindly send the output listing of the UB program to his address.

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ПРОЦЕДУРА АВТОМАТИЧЕСКОГО ОПРЕДЕЛЕНИЯ ОДНОЗНАЧНЫХ ПАРАМЕТРОВ РЕШЕТКИ И ТРАНСЛАЦИОННАЯ РЕШЕТКА БРЕВЕЙСА

В работе приведена полная методика определения: а) ориентационной матрицы между кристаллографическими осями и системой координат четырехосевого дифрактометра; б) наименшей примитивной клетки; в) клеток Биргера и Нигли; г) параметров решетки, показанных клеток и транслационной решетки (P, C, I, F, R) Бревейса.