Diffractometry of Closely Superimposed Twins and Clusters: A Method and a Program for Establishing UB Matrices of Single-Crystal Individuals

By K. Tichý AND J. Beneš

Institut für Reaktortechnik ETHZ, EIR, CH-5303 Würenlingen, Switzerland

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Abstract

The diffractometer measurement of twinned and clustered crystals requires an accurate knowledge of $Q_i = U_iB_i$ matrices of single-crystal individuals contained in the sample. A determination of the $Q_i$ matrix is best done from several accurately centered orienting reflections diffracted by the $i$th single-crystal individual. The assignment of the orienting reflections to the individuals is easy for well-resolved reciprocal lattices; for closely superimposed ones a method is presented which facilitates this assignment.

Introduction

Three methods were published recently for diffractometer measurements of samples, where reflections are accompanied by one or several reflection satellites. We have published (Beneš & Tichý, 1975; Tichý & Beneš, 1977) a method for an optimum resolution of reflection satellites by bringing their reciprocal vectors into the equatorial plane of a four-circle diffractometer. A similar method was published by Rothbauer (1976), while the method of Denner, d'Amour, Schultz & Stoeger (1977) uses bisecting geometry and is confined to a check only, on whether a particular reflection is affected by an overlap from its satellites or not.

In all these papers, it is tacitly assumed that the unit cells and orientations, represented by $Q = UB$ matrices (Busing & Levy, 1967) are already known for all single-crystal individuals which are contained in the measured sample. This paper describes procedures leading to establishing of these $Q$ matrices, especially in a difficult case when reciprocal lattices of single-crystal individuals are closely superimposed.

Experimental

Let us assume that a sample we investigate is a cluster of single-crystal individuals ($i = 1, 2, ..., I$) and that we know, at least approximately, their unit cells, which are characterized by matrices $B_i$. Their orientations referred to a coordinate system rigidly attached to the $a$ axis of a diffractometer are described by orienting matrices $U_i$. We shall be interested in the product matrix $Q_i = U_iB_i$ only, as its knowledge is sufficient for computing the reciprocal vector components $u_{pi}$ from diffraction indices $h_i k_i l_i$ (components of column vector $h$):

$$u_{pi} = U_iB_ih_i = Q_ih_i.$$
Reflections determine the $Q_i$ matrix of the $i$th individual, the problem is essentially solved. We compute a preliminary $Q_i$ matrix (Busing & Levy, 1967) and from it we can compute indices $h_p$ of all orienting reflections, $r=1,2,...,R$ for the $i$th individual

$$h_p = Q_i^{-1} \Phi_i^{-1} X_i^{-1} \Omega_i^{-1} (2 \sin \theta_i/\lambda)(-\sin \theta_i \cos \theta_i, 0)^T.$$

(All matrices used in this paper, the coordinate system and diffractometer angles are defined in the paper of Hine, Richards & Tichý, 1975.)

There are significant differences in orienting reflections which belong to the $i$th individual and those which do not. According to our experience, if the diffraction indices $h_p$ differ by more than $\varepsilon_2 = 0.07$ from the integers, it may be safely assumed that the reflection does not belong to this individual, while if $h_p$ differ by less than $\varepsilon_1 = 0.03$ from the integers, then it very probably does belong to this individual (but it may belong to some other individual as well). The given values of $\varepsilon_1$ and $\varepsilon_2$ depend on the accuracy (our values are for reflection settings centered on a neutron diffractometer) and on the type of twinning, but we think that they can be used as starting values at the beginning of the procedure.

With a part of orienting reflections thus assigned we recompute the $Q_i$ matrices by a least-squares procedure (Busing & Levy, 1967; Shoemaker & Bassi, 1970; Tichý, 1970) and repeat several times the steps 2 and 3 with adjusted values of $\varepsilon_1$ and $\varepsilon_2$ if necessary.

**Intuitive assignment of establishing reflections to the individuals for distinctly separated reciprocal lattices**

How difficult this assignment will be depends very much on the type of twinning and how judiciously (or luckily) the clusters of orienting reflections were chosen.

(a) **Systematic coincidences of reflections for clusters in a plane of the reciprocal lattice**

If reflection satellites in one reciprocal plane coincide, the assignment is greatly facilitated. Orienting reflections of one cluster lying outside this plane are arbitrarily numbered and used (together with coinciding reflections of two ‘clusters’ in this plane) as establishing reflections for $Q_i$ matrices of all individuals.

**Example I: A twinned NH$_3$(CH$_2$)$_2$NH$_3$MnCl$_4$**

The crystals are monoclinic with $a = 8.609$, $b = 7.130$, and $c = 7.192$ Å, $\gamma = 92.69^\circ$. Reflections $h0l$ have no satellites. Two satellites 040 were denoted 0401 and 0402. The reflections 040, $h00_1$, and $00l_1$ established the $Q_1$ matrix of the first individual and the reflections 040 and $h00_2$ (identical with $h00_1$) and $00l_2$ (identical with $00l_1$) established the matrix $Q_2$.

(b) **No systematic coincidences of satellite reflections for individuals with identical unit cells**

We choose a reflection cluster which contains $I$ satellites and number them arbitrarily from 1 to $I$ thus assigning them to the individuals $i=1,2,...,I$. Reflections from a second, non-collinear cluster cannot be numbered arbitrarily but in accordance with assignment of reflections from the first cluster. We number them therefore symbolically, $j = j_1, j_2,..., j_I$ (a permutation of $1,2,...,I$). The angles $\alpha_{ij}$ subtended by reciprocal vectors in the first cluster $i = 1,2,...,I$ and in the second cluster $j = j_1, j_2,..., j_I$ are computed for all possible permutations of $j_1, j_2,..., j_I$, and for a particular permutation all angles $\alpha_{ij}$ are equal within an experimental error $\Delta \alpha$. As the unit cells of all individuals are identical, then just this particular permutation assigns correctly the reflections from the second cluster to the reflections of the first cluster (and to the individuals). The procedure is repeated for a third cluster (non-coplanar with either the first or the second) and thus we obtain for each individual three establishing reflections.

If clusters contain reflections with reciprocal vectors of unequal lengths, not all permutations have to be investigated, as the lengths of the reciprocal vectors eliminate some possibilities.

The angles $\alpha_{ij}$ are computed from the equation

$$\cos \alpha_{ij} = \frac{\mathbf{u}_{ij}^T \mathbf{u}_{ij}}{|\mathbf{u}_{ij}|^2},$$

where

$$\mathbf{u}_{ij} = \Phi_i^{-1} X_i^{-1} \Omega_i^{-1} (2 \sin \theta_i/\lambda)(-\sin \theta_i \cos \theta_i, 0)^T.$$

**Example II: A twinned NH$_3$(CH$_2$)$_2$NH$_3$CuCl$_4$**

The monoclinic unit cell has $a = 8.109$, $b = 7.158$, $c = 7.363$ Å, $\gamma = 92.37^\circ$. Reflections 004, and 040$_2$ were in the first selected cluster (their indices were derived from the lengths of their reciprocal vectors). Another pair of reflection satellites at an angle approximately $90^\circ$ to the first cluster contains two reflections which could also be 004 and 040. For one permutation the two angles $\alpha_{ij}$ were nearly equal and very close to $90^\circ$; for the second possible permutation the two angles $\alpha_{ij}$ differed significantly. The first permutation gave the indices and assignments of the reflections in the second cluster as 040$_1$ and 004$_2$. The indices of reflections thus assigned agreed with their $2\theta$ values. With reflections 040$_1$, 004$_1$, 004$_2$, and 040$_2$ assigned we turned to the reflections $h00$. These are in one cluster containing two reflection satellites as well and by the same procedure we have found for one permutation the angles to the assigned reflections were 90, 92-4, and 90, 87-6$^\circ$. The reflections in the third cluster were therefore given indices 300$_1$ and 300$_2$, which yield the same unit cell with angles 90, 90, 92$4^\circ$ for both twin individuals.
Closely superimposed reciprocal lattices

A different approach has to be adopted if the orienting reflections in the reflection clusters are so close that the differences in \( \alpha_{ij} \) are of the same magnitude as the uncertainty \( \Delta \alpha \) which is caused by experimental errors in the determination of reciprocal vector components, but are too far from one another to be regarded as a single overlapped peak. The methods described in the previous paragraph cannot be used as their results are not conclusive.

In previous methods the decision whether all angles \( \alpha_{ij} (i,j=1,2,\ldots,I) \) are of the same magnitude or not relies on a comparison of pairs of observations. To improve the resolution capability of the method it is opportune to compare characteristics of the \( i \)th individual \((i=1,2,\ldots,I)\) based on all available observations which are applicable to this individual (orienting

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**Fig. 1.** A simplified flowchart of the program `ASSING`. Glossary of symbols: \( I \) = number of single-crystal individuals contained in the sample; \( R \) = number of orienting reflections measured; \( \varphi, \lambda, \omega, 2\theta \) = their diffractometer settings; \( \epsilon_1, \epsilon_2 \) = accuracy limits; other symbols see text.
reflections assigned to this individual). Obviously, such characteristics are the unit-cell parameters \(a, b, c\), \(\alpha, \beta, \gamma\) and three Eulerian angles \(\phi_{oi}, \chi_{oi}, \omega_{oi}\) which describe the orientation of the unit cell of the \(n\)th individual in the \(\varphi\) system of coordinates \((\phi_{oi}, \chi_{oi}, \omega_{oi})\). These are the angles through which the crystal must be rotated from \(\varphi = \chi = \omega = 0^\circ\) to bring the crystal system of coordinates of the \(n\)th individual into coincidence with the laboratory one. As a quality of fit of the observations to the characteristics of all individuals we adopt the criterion – how close to integers are the diffraction indices of orienting reflections when computed with \(Q_i\) matrices of individuals to which they are assigned?

As there is no other possibility, all possible permutations of establishing reflections have to be investigated. We thus select three non-coplanar reflection clusters (each containing \(i\) reflection satellites) and we can number arbitrarily the orienting reflections in the first cluster, \(i=1,2,\ldots, I\). The reflections in the second and third clusters are numbered symbolically \(j=j_1,j_2,\ldots,j_I\) and \(k=k_1,k_2,\ldots,k_I\) and operations of permutations of integers \(1,2,\ldots, I\) are performed on those numbers: \(j_1,j_2,\ldots,j_I\) and \(k_1,k_2,\ldots,k_I\). These permutations then yield three establishing reflections for each individual and there are therefore \((I!)^3\) possibilities which have to be examined unless the lengths of reciprocal vectors in the cluster differ enough to allow elimination of some possibilities.

A great volume of computation involved can be carried out with a program \textsc{ASSING} written for this purpose. The program requires the knowledge of preliminary matrices \(Q_i\). These are computed from input data which contain one of (a) either unit-cell dimensions \(a, b, c, \alpha, \beta, \gamma\) and the Eulerian angles \(\phi_{oi}, \chi_{oi}, \omega_{oi}\); (b) unit-cell dimensions and two orienting reflections \(h, k, l, \varphi_r, \chi_r, \omega_r, 2\theta\), with diffraction indices assigned or, (c) three or more non-coplanar orienting reflections.

On the basis of these input preliminary matrices \(Q_i\), the program \textsc{ASSING} generates the orienting reflections to individuals and recomputes \(Q_i\) matrices in an iterative procedure until all orienting reflections are assigned. The correct combination of establishing reflections can then be found from goodness-of-fit of the orienting reflections to \(Q_i\) matrices. A simplified flowchart of the program \textsc{ASSING} is presented in Fig. 1. Optimum values of \(\epsilon_1\) and \(\epsilon_2\) can be found tentatively to achieve maximum selectivity and assignment of all orienting reflections to the individuals at the same time. According to our experience (limited unfortunately to one structure only, which is given in Example III) one permutation has a better fit of the orienting reflections assigned to the individuals and their \(Q_i\) matrices than all other permutations and this permutation was adopted as a solution of the problem.

### Example III: A triplicated sample of high-temperature phase (\(T=404\) K) of \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{MnCl}_4\)

The substance is orthorhombic with \(a = 10.690, b = 7.218,\) and \(c = 7.337\) Å. 41 middle and strong orienting reflections were grouped in not more than three reflection satellites per reflection cluster and thus we concluded that the sample was triplicated.

In three chosen clusters approximately 90° apart we could differentiate between reflections 004 and 040 on the basis of their 2θ values. We denoted the reflections by capital letters and the first cluster thus contained 004\(_a\), 040\(_b\), 004\(_c\), the second cluster the reflections 004\(_r\), 040\(_s\), 040\(_t\) and the third cluster only two reflections 900\(_a\), 900\(_b\). The differences in angles subtended by reciprocal vectors of these reflections (see Table 1) are not conclusive enough to assign these reflections to the individuals and therefore the method described in the previous paragraph was applied.

#### Table 1. Angle subtended by reciprocal vectors of reflections in three selected reflection clusters of the high-temperature phase of \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{MnCl}_4\)

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Angle 1</th>
<th>Angle 2</th>
<th>Angle 3</th>
<th>Angle 4</th>
<th>Angle 5</th>
<th>Angle 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>900(_a)</td>
<td>900(_b)</td>
<td>004(_c)</td>
<td>040(_b)</td>
<td>004(_r)</td>
<td>004(_t)</td>
<td>004(_s)</td>
</tr>
<tr>
<td>900(_a)</td>
<td>900(_b)</td>
<td>004(_c)</td>
<td>040(_b)</td>
<td>004(_r)</td>
<td>004(_t)</td>
<td>004(_s)</td>
</tr>
<tr>
<td>900(_a)</td>
<td>900(_b)</td>
<td>004(_c)</td>
<td>040(_b)</td>
<td>004(_r)</td>
<td>004(_t)</td>
<td>004(_s)</td>
</tr>
<tr>
<td>900(_a)</td>
<td>900(_b)</td>
<td>004(_c)</td>
<td>040(_b)</td>
<td>004(_r)</td>
<td>004(_t)</td>
<td>004(_s)</td>
</tr>
</tbody>
</table>

The reflections of the first cluster were numbered with \(C=2, D=1, \) and \(E=3\), so that the reflection 004\(_c\) = 004\(_2\) was assigned to the second individual, etc. Furthermore, in the first cluster there is only one reflection 040\(_i\) (i.e. 040\(_1\)) and in the second cluster there is only one reflection 004\(_r\). They must belong to the same individual and therefore \(F=1\). The remaining two reflections of the second cluster are numbered symbolically \(G=j_2, H=j_3\). In the third cluster there are two reflections only, 900\(_a\) and 900\(_b\); therefore one of them must be common to two individuals. There are therefore six possible different distributions of the reflections 900\(_a\) and 900\(_b\) among the individuals 1, 2, and 3 (see Table 2). We are left with only 12 permutations to examine instead of the \((3!)^3=36\) which would result from a blind application of the procedure, or if the clusters were chosen less judiciously.

From the comparison of the results of the method applied to the 12 permutations of establishing reflections and all remaining orienting reflections, the permutation with \(C=2, D=1, E=3, F=1, G=2, H=3, A=1+2, B=3\) emerged as that with the best fit and the individuals 1, 2, 3 were thus based on establishing reflections \{040\(_b\), 004\(_r\), 900\(_a\), 004\(_c\), 040\(_s\), 900\(_a\)\} and
Table 2. Possibilities of distributions of establishing reflections for the individuals in three selected clusters

<table>
<thead>
<tr>
<th>Reflection clusters</th>
<th>Possibilities of the distribution (in columns)</th>
<th>Number of possibilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>004c</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>0400</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>004e</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>004W</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>040e</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>040W</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>900e</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>900W</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

{004e, 0400, 900W} respectively. In the iterative procedure all orienting reflections were assigned to the individuals and their $Q_1$, $Q_2$, and $Q_3$ matrices were then based on 17, 13, and 14 orienting reflections respectively.

**Conclusion**

The method presented in the last paragraph is statistically more broadly based than direct methods of assignment of reflections to the single-crystal individuals, e.g. by comparing angles subtended by two reciprocal vectors computed from their diffractometer settings in reflection positions. As the information used by the two methods in different ways is essentially the same (the components of reciprocal vectors are in one method used to compute an angle, in the other they are used to build up the $Q_i$ matrices), it is evident that the statistical method is applicable to well-resolved twins and clusters as well.

A purely geometrical criterion was adopted here, namely that of goodness-of-fit of orienting reflections and $Q_i$ matrices ($i = 1, 2, ..., I$) of all single-crystal individuals, where the $Q_i$ matrix for the $i$th individual is based only on the orienting reflections assigned to it. Ultimate verification of the correctness of the assignment by comparison of intensities and especially space-group extinctions, if the structures of single-crystal individuals are identical, is beyond the slope of this paper.

**References**