

Zeitschrift: Helvetica Physica Acta
Band: 50 (1977)
Heft: 4

Artikel: A method and a computer program for measurement of intensities from twinned and clustered crystals on a 4-circle diffractometer
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DOI: <https://doi.org/10.5169/seals-114874>

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A method and a computer program for measurement of intensities from twinned and clustered crystals on a 4-circle diffractometer¹⁾

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(5. V. 1977)

Abstract. For measurements of twinned crystal samples on a 4-circle diffractometer the best experimental resolution is achieved when a reciprocal vector to be measured and its satellite reciprocal vector are brought into equatorial plane of the diffractometer and thus intersect the Ewald's reflection sphere with greatest possible lag in rotation of ω -axis of the diffractometer. When the measured sample contains more than two individuals (clustered crystal), each reciprocal vector is accompanied by several satellites and an optimum resolution is achieved when the vector to be measured and its nearest satellite lie in equatorial plane. A computer program for these calculations can avoid reflection settings in which primary or diffracted beams are obstructed by mechanical parts of the diffractometer.

1. Introduction

For diffractometry purposes twinned samples can be divided into two main categories:

- (a) twins in which reciprocal lattices of both single-crystal individuals do not coincide for all reciprocal lattice vectors,
- (b) twins which have reciprocal lattices exactly superimposed.

Samples in the second category have a diffraction pattern like a real single crystal and information about structure factors of individuals cannot be obtained experimentally. The solution of the twinning has to be done by purely mathematical means (e.g. [1]).

A characteristic feature of twins in the first category (see Fig. 1) is that in a close vicinity of a reciprocal vector \mathbf{r} (1), which belongs to the single-crystal individual (1), lies a vector \mathbf{r} (2) belonging to the individual (2). When the reciprocal vector \mathbf{r} (1) to be measured is swept through Ewald's reflection sphere, its satellite \mathbf{r} (2) will give rise to a satellite reflection which may interfere with the measurement of the vector \mathbf{r} (1). It is obviously desirable to minimize the effect of such an interference. Earlier we have pointed out [2] that the most effective way to do this is to bring both satellite vectors \mathbf{r} (1) and \mathbf{r} (2) into equatorial plane of a 4-circle diffractometer and

¹⁾ A short version of this paper (for twinned crystals only) was presented at the 10th International Congress of Crystallography, Amsterdam, 1975.

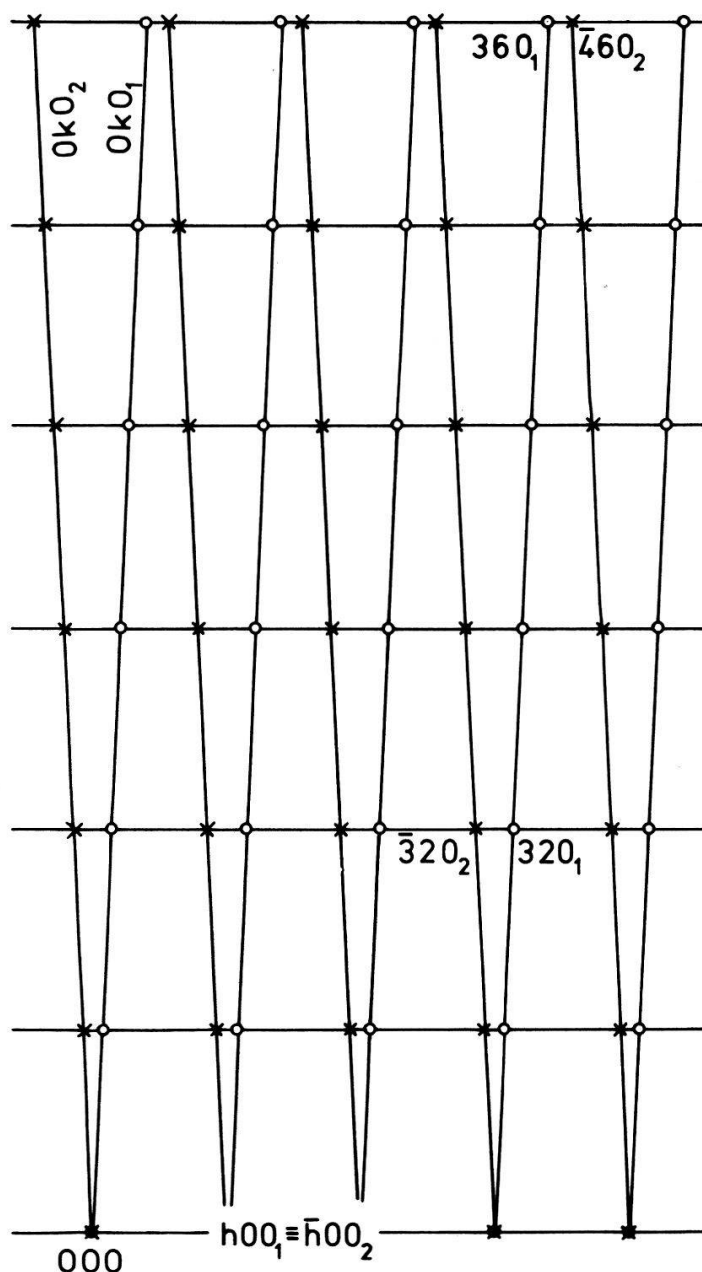


Figure 1

Reciprocal lattices of twinned crystal, $hk0$ plane. Nearest satellite reflections are $hk0_1$, $\bar{h}k0_2$ for $k < 3$ and $hk0_1$, $-(h+1), k, 0_2$ for $k \geq 4$.

to measure their intensities consecutively by rotating the sample around the ω -axis of the diffractometer. Similar conclusion, although not explicitly stated, was reached by [3].

This paper presents a method for data collection from twinned crystals and from samples containing more than two single crystal individuals (clustered crystals). A procedure of achieving a best possible resolution of satellite reflections while avoiding blind regions of the diffractometer is briefly described.

2. Determination of diffraction indices of satellite reflections

We assume that at this stage of crystal structure analysis not only the twinning has been recognized but that unit cells and orientations of all individuals have been

determined (as for necessary accuracy of determination see Remark I). Using matrix notation of Busing and Levy [4] we can describe each single-crystal individual by a metric matrix \mathbf{B}_i ²⁾ – and its orientation by a unit matrix \mathbf{U}_i . These two matrices transform diffraction indices $\mathbf{h}_i = hkl_i$ into components $\mathbf{u}_{\phi i}$ of reciprocal vector of i -th individual in ϕ -system of coordinates

$$\mathbf{u}_{\phi i} = \mathbf{U}_i \mathbf{B}_i \mathbf{h}_i \quad (1)$$

Without a loss of generality we shall derive the formulae for twinned crystal and point out differences for clustered crystals in a separate paragraph.

In order to determine from equation (1) the components of satellite reciprocal vector $\mathbf{u}_{\phi 2}$, we have to know its diffraction indices. It is not advisable to rely on simple rule of 'twinning law' as this may lead to errors as can be seen from Figure 1. A satellite nearest to 320_1 is $\bar{3}20_2$, i.e. 'twinning law' is that hkl_1 has a nearest satellite $\bar{h}kl_2$. This rule, however, is invalid for $k \geq 4$, as, e.g. 360_1 has a satellite $\bar{4}60_2$, i.e. hkl_1 and $-(h+1), k, l_2$. To avoid pitfalls of this sort, we recommend the following indexing procedure:

The vector $\mathbf{u}_{\phi 1} = \mathbf{U}_1 \mathbf{B}_1 \mathbf{h}_1$ (where \mathbf{h}_1 are integers) is expressed in terms of second individual

$$\mathbf{u}_{\phi 1} = \mathbf{U}_2 \mathbf{B}_2 \mathbf{h}'_2 \quad (2)$$

where \mathbf{h}'_2 are unknown non-integer indices. We obtain them by multiplying the equation (2) by $(\mathbf{U}_2 \mathbf{B}_2)^{-1}$

$$\mathbf{h}'_2 = (\mathbf{U}_2 \mathbf{B}_2)^{-1} \mathbf{u}_{\phi 1} = (\mathbf{U}_2 \mathbf{B}_2)^{-1} \mathbf{U}_1 \mathbf{B}_1 \mathbf{h}_1 \quad (3)$$

The diffraction indices \mathbf{h}_2 of nearest reciprocal vector of second individual are then obtained by rounding-off \mathbf{h}'_2 to their nearest integers.

3. Calculation of a reflection position with both satellite reciprocal vectors in equatorial plane

The method is analogous to that of Busing and Levy [4] to determine reflection settings for zero azimuth. By their definition the azimuthal angle is zero when the measured reciprocal vector is in the reflection position and both this vector and a reference vector, which is chosen arbitrarily, lie in the equatorial plane of the diffractometer. Using the satellite reciprocal vector $\mathbf{u}_{\phi 2}$ in place of a reference vector, the method can be adopted without any modification. The reciprocal vectors $\mathbf{u}_{\phi 1}$ and $\mathbf{u}_{\phi 2}$ are used for construction of a right-handed orthogonal unit vector triple, inverse matrix of which is the instrument-angle matrix

$$\mathbf{R} = \mathbf{\Omega X \Phi} \quad (4)$$

and setting angles ϕ , χ and ω are derived from its matrix elements R_{ij} (see also [4]). In order to bring the satellite vector $\mathbf{u}_{\phi 2}$ into reflection position as well, it is just necessary to continue the ω -rotation until this vector intersects the reflection sphere.

²⁾ When keeping individual \mathbf{B}_i matrices, the formulae derived here will also be valid for clustered crystals containing individuals of different phases or of different chemical composition. In majority of cases, however, all individuals will have the same unit cell and therefore all matrices \mathbf{B}_i will be identical.

It should be noted here that the resolution of reflection settings with azimuthal angles 0° and 180° is not the same when the vectors \mathbf{u}_{ϕ_1} and \mathbf{u}_{ϕ_2} have different lengths. As can be seen from Figure 2, both vectors \mathbf{u}_{ϕ_1} and \mathbf{u}_{ϕ_2} diffract almost simultaneously in case (b) and the intensity measurements of both vectors will be affected more by the other satellite than in case (a), where the resolution is more satisfactory.

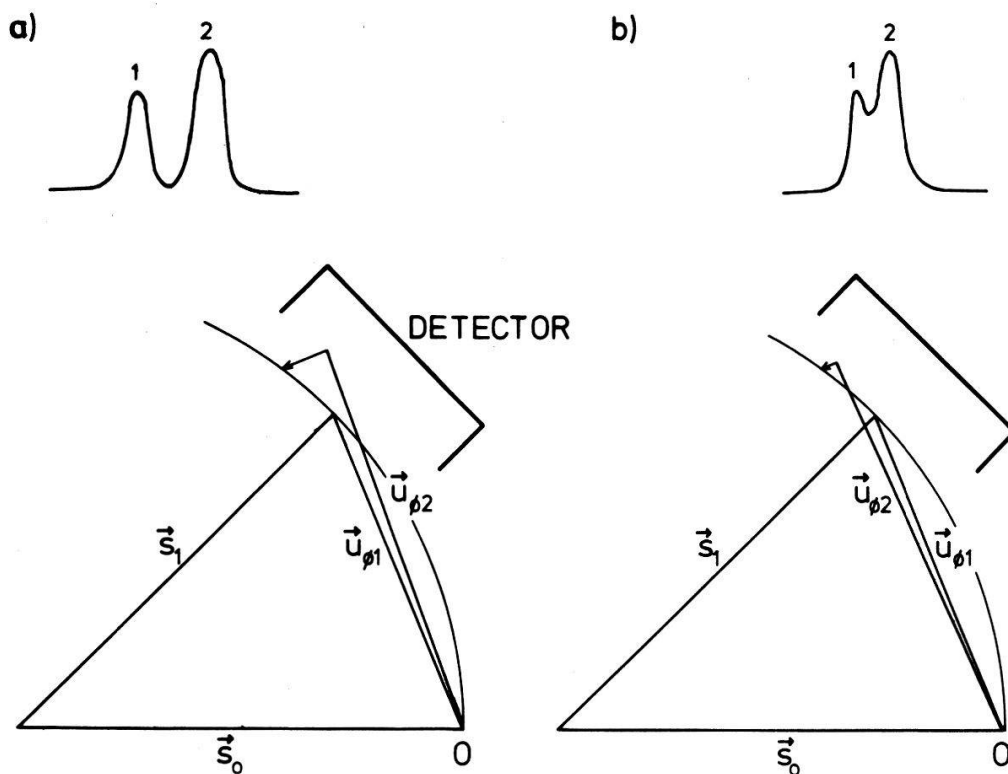


Figure 2

Different resolution in settings for azimuthal angles 0° and 180° for reciprocal vectors \mathbf{u}_{ϕ_1} and \mathbf{u}_{ϕ_2} of unequal lengths.

Reflection settings computed for two satellite vectors to be in the equatorial plane of the diffractometer bring more often than, e.g. bisecting geometry the diffractometer into positions where its mechanical parts obstruct the passage of primary or diffracted beams. To remedy this, either reflection settings of symmetry equivalent reflections are tried, and/or a tentative azimuthal scan $\pm 5^\circ$, $\pm 10^\circ$, ... is performed until a setting outside all of blind regions is found. The tentative azimuthal scan, of course, causes the satellite reciprocal vectors \mathbf{u}_{ϕ_1} and \mathbf{u}_{ϕ_2} to depart from the equatorial plane of the diffractometer, but as long as the offset angle of the tentative azimuthal scan is low, the resolution is not much worse than that of ideal case when both \mathbf{u}_{ϕ_1} and \mathbf{u}_{ϕ_2} are in the equatorial plane.

4. Problems arising when measuring clustered crystals

For twinned crystals a reflection setting with both measured satellite vectors \mathbf{u}_{ϕ_1} and \mathbf{u}_{ϕ_2} in equatorial plane can always be found (with exception of blind regions of diffractometer). For clustered crystals, however, this condition can be satisfied for reciprocal vectors of only two of N single crystal individuals and other $N-2$

vectors will necessarily lie outside the equatorial plane (unless several satellite vectors or all of them are coplanar).

The strategy for data collection from a clustered crystal depends on the purpose of the crystal analysis. If it is just to study the crystal structure of i -th individual, then always reciprocal vector $\mathbf{u}_{\phi i}$ and its nearest neighbour $\mathbf{u}_{\phi j}$ (see Fig. 3) will be brought into equatorial plane; other satellite reciprocal vectors will then interfere with measurement even less than the nearest vector $\mathbf{u}_{\phi j}$. In this case reflections from all other individuals are regarded as a ballast of no interest which only makes the measurement more difficult. If, however, individuals have the same structure, reflection peaks which are satellites to the reflection from i -th individual can supply equally valuable information about the structure. One can then perform the measurement with best possible resolution of two absolutely nearest reciprocal vectors ($\mathbf{u}_{\phi k}$ and $\mathbf{u}_{\phi l}$ in Fig. 3) or even better to find a setting for which the sum of squares of deviations of reciprocal vectors from equatorial plane is minimal and to measure intensities of all satellite reciprocal vectors during one scan. It should be perhaps noted here that diffraction indices of satellite reciprocal vectors associated in one vector cluster may be symmetry non-equivalent and that the measurement of all these reflections will yield several different structure factors F_{calc} . Therefore the data collection from a twinned or a clustered crystal need not necessarily mean doubled (or more than doubled) expense of the measuring time.

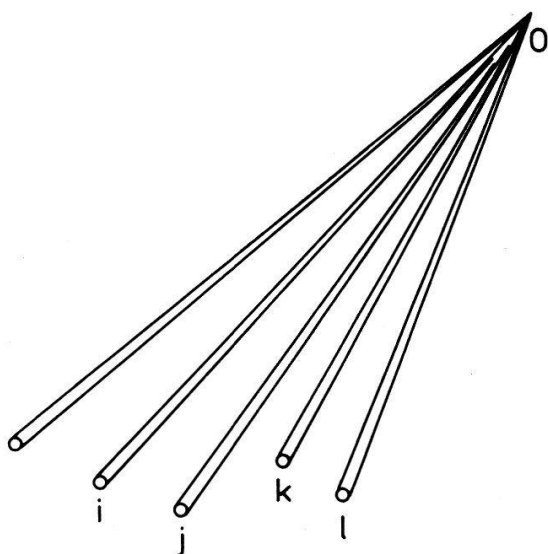


Figure 3
Spatial distribution of satellite reciprocal vectors in a vector cluster (O = origin of reciprocal lattice).

5. Reflection setting for reciprocal vectors outside the equatorial plane

For twinned crystals and reciprocal vectors in the equatorial plane (azimuths 0° and 180°) the reflection settings are given by the equation (4). For azimuthal angles other than 0° and 180° and for clustered crystals, some reciprocal vectors are outside the equatorial plane. Their reflection settings are those for 'normal-beam' method (see [5]). In order to be able to use them, it is necessary to compute first the components (ξ_i, η_i, ζ_i) of reciprocal vectors $\mathbf{u}_{\mathbf{L}i}$ in the laboratory system of coordinates

after the diffractometer circles were set to angles ϕ_0 , χ_0 , ω_0 derived from matrix **R**

$$\mathbf{u}_{Li} = (\xi_i, \eta_i, \zeta_i)^T = \mathbf{R}\mathbf{U}_i\mathbf{B}_i\mathbf{h}_i \quad (5)$$

To register the diffracted beam, the detector arm is then set to the angle Y_i in the equatorial plane and the detector is tilted in vertical plane to the angle v_i

$$v_i = \sin^{-1}(\lambda\xi_i) \quad (6)$$

$$Y_i = \cos^{-1}(1 + \cos^2 v_i - \lambda^2[\xi_i^2 + \eta_i^2])/(2 \cos v_i) \quad (7)$$

The ϕ - and χ -circles remain set to ϕ_0 and χ_0 respectively, ω -circle is set for each satellite peak to ω_i

$$\omega_i = 180^\circ - \rho_i - \Omega_i \quad (8)$$

where

$$\Omega_i = \cos^{-1}([\xi_i^2 + \eta_i^2]\lambda^2 + 1 - \cos^2 v_i)/(2\lambda\sqrt{\xi_i^2 + \eta_i^2}) \quad (9)$$

and

$$\rho_i = \tan^{-1}(\eta_i/\xi_i). \quad (10)$$

6. Application of the method and supplementary remarks

Neutron diffraction studies of following samples were done according to the procedure described:

- Twinned crystal of ethylenediammonium copper tetrachloride $\text{NH}_3(\text{CH}_2)_2\text{NH}_3\text{CuCl}_4$, monoclinic, $P2_1/b$, $a = 8.109$, $b = 7.158$, $c = 7.363$, $\gamma = 92.37^\circ$. Indices of reflection satellites: hkl_1 , $\bar{h}lk_2$. Systematic coincidences of reflections: $0kk$.
- Twinned crystal of ethylenediammonium manganese tetrachloride $\text{NH}_3(\text{CH}_2)_2\text{NH}_3\text{MnCl}_4$, monoclinic, $P2_1/b$, $a = 8.609$, $b = 7.130$, $c = 7.192$, $\gamma = 92.68^\circ$. Indices of reflection satellites: hkl_1 , $\bar{h}k\bar{l}_2$. Systematic coincidences of reflections: $h0l$.
- Quadruplicated sample of butylenediammonium manganese tetrachloride, $\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{MnCl}_4$, room temperature phase, monoclinic, $P2_1/b$, $a = 10.770$, $b = 7.177$, $c = 7.307$, $\gamma = 92.67^\circ$. Indices of reflection satellites: hkl_1 , $\bar{h}lk_2$, $\bar{h}k\bar{l}_3$, $\bar{h}\bar{l}k_4$.
- Triuplicated sample of butylenediammonium manganese tetrachloride, $\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{MnCl}_4$, high temperature phase $T = 404$ K, orthorhombic, $a = 10.631$, $b = 7.178$, $c = 7.297$. Indices of reflection satellites: hkl_1 , $\bar{h}\bar{l}k_2$, $\bar{h}\bar{l}k_3$.

Remark I: Accuracy of determination of orienting matrices and unit cells

The accuracy of these determinations should be at least three to five times better for twins than for single crystals and still higher for more complicated clusters, if one is to rely on pre-computed positions Y_i , v_i of diffracted beams and settings ω_i of individuals (for given values of ϕ and χ). According to our experience, computed reflection settings should not differ from those observed by more than $\frac{1}{3}$ of total

width of reflection profile measured in ω -scan, otherwise difficulties with assigning of reflection peaks to individuals will arise.

Remark II: Computer program CLUVER

The computer program written for this type of measurement has all the features described so far, some of its additional features are listed below:

- (a) The program checks whether satellite vectors do not coincide for practical purposes. As a measure of coincidence we adopt the accuracy with which one can determine the components of reciprocal vectors ($\Delta r^* \approx 0.0005 \text{ \AA}^{-1}$).
- (b) The program uses bisecting geometry if the angle subtended by two reciprocal vectors to be brought into equatorial plane is smaller than a certain limit below which it is regarded unsafe to construct right-handed orthogonal unit vector triple (we use 0.1 degree).
- (c) For practical purposes close reflections are measured as one overlapped peak if their $\Delta\omega$ separation is smaller than a certain fraction ($\sim \frac{1}{3}$) of total width of reflection profile.
- (d) For reflection settings lying in blind regions of the diffractometer, the search of other symmetry equivalent reflections and/or azimuthal scan is facultative. If, however, both are to be applied, the user can choose, whether he prefers the azimuthal scan to be done first and the test of symmetry equivalent reflections second or vice versa.
- (e) On the basis of supplied horizontal and vertical divergencies of the beam and widths of the detector window and computed inclination angles ν_i of diffracted beams, the program indicates whether a particular beam will be registered fully, partly or not at all by the detector. An optional scan over all satellite reflections, which will be registered at least partly, is possible.

Remark III: Overlapping of reflections

Depending on the character of twinning, there may be some systematic coincidences (e.g. lines or planes in reciprocal lattice) of reflections from both twin individuals and in spite of measures described above, reflections of some reciprocal vectors may remain unresolved. When these overlapping reflections have the same F_{calc} , they can be used in least-squares refinement (based on F or F^2) with separate scale factors which are not refined but constrained to the sum of scale factors of individuals contributing to the same reflection, provided that enough other resolved reflections are available. If overlapping reflections have different F_{calc} , they must be omitted from conventional least-squares refinement based on F or F^2 , or refinement based on intensities must be used.

Remark IV: Absorption and extinction

If these corrections are not negligible, an adequate treatment demands a knowledge of the spatial distribution of the volumes of single crystal individuals in the sample.

Data for two twinned structures mentioned above have been corrected on the assumption that both individuals were evenly distributed over the whole volume of the sample. Even with such a crude assumption and with absorption and extinction corrections 0.54 and 50% respectively the structures refined to 0.046 and 0.085 of weighted *R*-factor.

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