support for TNB was provided by the Daresbury Laboratory of the Science and Engineering Research Council.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1983). A**39**, 170–171

Refinement of cell and orientation parameters in four-circle diffractometry: the selection of orientation parameters.

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(*Received* 11 *May* 1982; *accepted* 26 *August* 1982)

Abstract

A reliable and automatic method of selecting three orientation parameters is presented. The refinement of these and of the symmetry-constrained unit-cell parameters from four-circle diffractometer data is described.

Two basic methods are generally used for the refinement of cell and orientation parameters in four-circle diffractometry. The method of Tichý (1970) is a linear least-squares refinement of the nine independent elements of the orientation matrix **UB**. Busing & Levy (1967*a*) (hereafter BL) refine instead the six unit-cell parameters (a, b, c α, β, γ) and three orientation parameters; the refinement is non-linear, and normally requires two–three cycles. Both methods use as observations the optimum setting angles measured for a selection of reflections. The first method has the advantages of speed and simplicity; the BL method, although slower, allows for the application of symmetry constraints on the cell parameters, permits a simple and sensible empirical weighting scheme (*e.g.* χ values are inherently less precise than ω values, and can be assigned a lower weight), and can be used with partial information (*e.g.* 2θ values only, if orientation is not refined). It is generally accepted that the Tichý method, or an equivalent procedure, gives the 'best' orientation matrix for intensity data collection (allowing for some alignment errors), but the BL method provides more reliable cell parameters (Sparks, 1976). An alternative method described by Shoemaker & Bassi (1970) is similar to the Tichý method, but also allows for symmetry constraints: these, however, are much less simple than in the BL method and considerably complicate the otherwise linear refinement.

The orientation parameters for BL are three of the angles ω_1, χ_1, φ_1, ω_2, χ_2, φ_2 for two specific reflections (Busing, 1970). The choice of these reflections, and of the three parameters from among the possible six, is discussed by Busing & Levy (1967*b*), and summarized by them in a table. An automatic selection of these parameters by the refinement program would be much more convenient. In the BL method, the orientation matrix **UB** is made up of two components: **B** is an orthogonalization matrix, which relates the reciprocal-cell axes to an arbitrary orthogonal Cartesian axis set, and depends only on the cell parameters; **U** is an orthogonal rotation matrix, which relates this crystal Cartesian axis set to an axis set fixed to the diffractometer φ axis, and which can be calculated from the unit-cell parameters, together with the indices and setting angles for the two orienting reflections (for the basic definitions and equations, see BL; we use the same convention here, by which $\omega = 0$ for a reflection in bisecting geometry).

Hamilton (1974) has suggested an alternative method of selecting three orientation parameters: they are the ω_s, χ_s, and φ_s angles through which the crystal must be rotated from the setting with $\omega = \chi = \varphi = 0$ to an orientation in which the crystal Cartesian-axis set and the φ-axis set are coincident. Hamilton demonstrates how initial values for these three parameters are extracted from the known (preliminary) **UB** matrix, so that the procedure can be automated. [The preliminary **UB** matrix can itself be set up from known approximate cell parameters and the indices and setting angles of any two non-colinear reflections, from the angles of three indexed reflections (BL), or by various more automatic procedures, as summarized, for example, by Gabe (1980).] The drawback of Hamilton's procedure is the high correla-

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tion which can exist among these parameters for certain values of them; if $\chi_s = 0$, ω_s and φ_s rotations are equivalent, and a matrix singularity results. For small values of χ_s, the high correlation hampers the refinement. The same problem occurs if three other rotations (*e.g.* about mutually orthogonal axes) are chosen as parameters instead of ω_s, χ_s and φ_s.

A clue to a reliable automation of the procedure is given in Busing's (1970) remark that the orientation parameters of the BL method 'simply define the orthogonal matrix **U** and need not correspond to any reflections actually observed'. Indeed, we can take this further: they need not correspond even to points of the reciprocal lattice, *i.e.* to reflections with integral indices.

To take advantage of this, we can *define* the initial orienting reflection angles to be $\omega_1 = \chi_1 = \varphi_1 = \omega_2 = \chi_2 = 0$, $\varphi_2 = 90°$. The corresponding non-integral 'indices' are derived from the initial **UB** matrix: from BL equations (19) and (22), the desired indices are given by

$$\mathbf{UBh} = \begin{pmatrix}1\\0\\0\end{pmatrix} \quad \text{and} \quad \begin{pmatrix}0\\1\\0\end{pmatrix}$$

respectively, and are thus six of the elements of $\mathbf{V} = (\mathbf{UB})^{-1}$, *viz* v_{11}, v_{21}, v_{31} for the first, and v_{12}, v_{22}, v_{32} for the second dummy reflection (v_{13}, v_{23}, v_{33} represents a dummy reflection with $\omega = 0$, $\chi = 90°$ and arbitrary φ). The three parameters χ_1, φ_1 and χ_2 are refined, together with the cell parameters (1–6, depending on symmetry constraints) by the standard BL method. It should be noted (as is stated in BL) that, after the refinement, the two vectors corresponding to the orienting 'reflections' will no longer lie exactly in the equatorial plane. This is immaterial, as the purpose of refining the three orientation parameters is purely to obtain the best estimate for the matrix **U** subject to the unit-cell symmetry constraints, *i.e.* for the matrix which minimizes the least-squares function $\sum wA^2$, where $A = y_{obs} - y_{calc}$, and y is, in turn, 2θ, ω, and χ for each centred reflection (BL's type 1, 3 and 5 observations). We use a weighting scheme whereby $w = 1$ for χ, 2 for 2θ, and 4 for ω, which roughly reflects the relative precisions obtained for these measurements in our reflection centring method.

We have included this 'automated BL' method in the software for our four-circle diffractometer, written in Extended Basic for Data General Eclipse and Nova computers (Clegg, 1981). Reflection-angle data are obtained by an automatic centring routine and held on a computer disc file together with preliminary parameters. The only input required from the user is a command to perform refinement and a code number specifying the crystal symmetry. The method is indeed considerably slower (by a factor of about 5–15, depending on symmetry) than the Tichý method, which is also incorporated in the program, but it is just as simple to use. In any case, the slower refinement is no great drawback, as this refinement is performed normally only once for each crystal under investigation.

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Acta Cryst. (1983). A**39**, 171–173

Diffraction by a one-dimensionally disordered crystal. III. Relation between the matrix and the probability tree methods.*

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(*Received* 5 *January* 1982; *accepted* 16 *August* 1982)

Abstract

The calculation of the diffraction from a one-dimensionally disordered crystal is shown to be easier using the matrix (M) method than with the probability tree (PT) method. If the order of the difference equation is high, an analytical solution cannot be obtained by the PT method unless the model is highly simplified. There is no such limitation in the M method.

From the relations between mth and $(m+1)$th layers in the probability trees in Fig. 1 of Howard (1977), the **P** matrix (Kakinoki, 1967) is obtained as

$$\mathbf{P} = \begin{array}{c} \begin{matrix} A^+ & A^* & B^+ & B^* & C^+ & C^* \end{matrix} \\ \left(\begin{array}{cc:cc:cc} & & 1-p & 0 & 0 & p \\ \multicolumn{2}{c:}{0} & q & 0 & 1-q & 0 \\ \hdashline 0 & p & \multicolumn{2}{c:}{} & 1-p & 0 \\ \multicolumn{2}{c:}{1-q\quad 0} & \multicolumn{2}{c:}{0} & q & 0 \\ \hdashline 1-p & 0 & 0 & p & \multicolumn{2}{c}{} \\ q & 0 & 1-q & 0 & \multicolumn{2}{c}{0} \end{array}\right) \end{array} \begin{matrix} A^+ \\ A^* \\ B^+ \\ B^* \\ C^+ \\ C^* \end{matrix} \begin{matrix} w^+/3 \\ w^*/3 \\ w^+/3 \\ w^*/3 \\ w^+/3 \\ w^*/3 \end{matrix},$$

where Howard's second parameter q is used and where A^+, B^+ and C^+ denote the original or 2nd, 4th,... inserted layers and A^*, B^* and C^* denote the 1st, 3rd,... inserted layers.

* Part II: Kakinoki (1967).

0567-7394/83/010171-03$01.50