Table 1. *Data for copper*(II) *sulphate pentahydrate*

Cell parameters determined by Brooker & Nuffield (1966)

$$a = 6{\cdot}122,\ b = 10{\cdot}695,\ c = 5{\cdot}962\ \text{Å},\quad \alpha = 97{\cdot}58,\ \beta = 107{\cdot}17,\ \gamma = 77{\cdot}55°$$
$$a^* = 0{\cdot}1740,\ b^* = 0{\cdot}0960,\ c^* = 0{\cdot}1760\ \text{Å}^{-1},\ \alpha^* = 85{\cdot}80,\ \beta^* = 74{\cdot}00,\ \gamma^* = 100{\cdot}75°$$

(*a*) Cell parameters obtained from φ measurements using three reflections

Data from Hulme's (1966) Table 2					Results		
hkl	φ_m	hkl	φ_m	hkl	c^*	α^*	β^*
1 0 1	81·0	0 2 1	83·8	$\bar{1}$ 0 1	0·1760	86·1	73·9
1 0 1	85·5	0 3 1	79·5	$\bar{1}$ 0 1	0·1760	86·2	73·9
$\bar{2}$ $\bar{1}$ 1	103·0	0 3 1	108·0	1 $\bar{1}$ 1	0·1756	85·7	74·5
$\bar{1}$ 1 1	71·0	$\bar{2}$ $\bar{2}$ 1	84·2	$\bar{1}$ 2 1	0·1758	84·7	74·7
1 $\bar{1}$ 1	103·0	0 2 1	83·8	$\bar{1}$ 0 1	0·1762	86·0	73·7
0 3 1	79·5	$\bar{1}$ 0 1	85·0	$\bar{1}$ $\bar{3}$ 1	0·1765	86·2	73·3

(*b*) Cell parameters calculated from ξ derived from Brooker & Nuffield's data

hkl	ξ^2	$\xi^2_{hkl} - \xi^2_{hk0}$	c^*	α^*	β^*
3 8 0	0·7128	0·0732			
3 8 1	0·7860	(0·073)	0·1759	85·81	73·99
2 $\bar{7}$ 0	0·6599	0·0193	(0·1758)	(85·79)	(74·06)
2 $\bar{7}$ 1	0·6792	(0·019)			
$\bar{6}$ $\bar{2}$ 0	1·0520	−0·1034			
$\bar{6}$ $\bar{2}$ 1	0·9486	(−0·103)			

Let

$$\tan\rho = \frac{d^*_{12}\sin\varphi_{23}}{d^*_{23}\sin\varphi_{12}},$$

then,

$$\tan\frac{\sigma-\tau}{2} = \tan(45-\rho)\tan\frac{\sigma+\tau}{2}. \qquad (9)$$

The angles σ and τ can be calculated from their sum (8) and difference (9). Now, with three elements known in both triangles P_2P_1O and P_2P_3O, the ξ's can be calculated and c^*, β^* and α^* derived from (7).

Examples

The parameters c^*, α^* and β^* of copper(II) sulphate pentahydrate have been calculated for both methods described above. The data for this compound given by Brooker & Nuffield (1966) are quoted below. In Table 1(*a*), the values of φ_m have been taken from Hulme's (1966) Table 2 and these lead to estimates that are generally within ±0·3% for c^* and ±0·5° for α^* and β^*. In Table 1(*b*), the values of ξ have been calculated from Brooker & Nuffield data. The values of $(\xi^2_{hkl} - \xi^2_{hk0})$ in parentheses have been rounded and give the parameters in parentheses: evidently, this method of estimation is not unduly sensitive to experimental errors.

I am grateful to Professor D. Rogers for discussions.

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Diffractometric angles for rotation around the diffraction vector.

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Abstract

It is shown that the azimuthal angle ψ of rotation around the diffraction vector and the four angles χ_0, χ, φ' and $90-\omega$, all belong to one right spherical triangle from which the new relations $\sin\psi = \sin\chi\sin\varphi'$ and $\cos\varphi' = \cos\omega\cos\psi$ are derived. These angles are in fact related by ten trigonometric equations which can also be derived by matrix methods. The setting angles for a full ψ rotation of 360° are easily determined when results of both methods are used together.

Several methods have been proposed to calculate the setting angles ω, χ and φ for a given ψ rotation around the

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diffraction vector. Busing & Levy (1967) and Hamilton (1974) derived the setting angles from various elements of **R**, the matrix product of $\mathbf{\Omega X \Phi}$ which is equal to $\mathbf{\Psi X_0 \Phi_0}$ when the bisecting position is used to define $\psi = 0$. Santoro & Zocchi (1964), Arndt & Willis (1966) and Wang, Yoo, Pletcher & Sax (1976) deduced from Napierian triangles or tetrahedra a number of simple trigonometric equations relating five angles ω, χ, φ', χ_0 and ψ. It appears that both the matrix and the geometric methods can be simplified, leading to an easier determination of the setting angles for a full ψ rotation of 360°. Instead of two Napierian triangles (Arndt & Willis, 1966) or two tetrahedra (Wang, Yoo, Pletcher & Sax, 1976), it is shown that only one Napierian triangle needs to be considered. From it, one readily deduces the angles and their correct quadrants. Their signs, difficult to ascertain by the trigonometric method, are then obtained from two equations derived from the simpler matrix relation $\mathbf{\Omega X \Phi'} = \mathbf{\Psi X_0}$.

Let us consider (Fig. 1) a mobile orthogonal set of axes originating at the center of the crystal, with OY parallel to the diffraction vector and OZ parallel to the θ axis; OX is thus directed toward the detector when $2\theta = 0$. A r.l. point located at P when $\omega^* = \chi = 0$ and φ is at a certain angle depending on the crystal orientation (the origin of φ is arbitrary) must be brought on to the OY axis to be in the reflecting position. When ω is kept at 0, this is done through two successive rotations φ_0 and χ_0, corresponding to the path PGD, but, in doing so, the azimuth has not changed and ψ may be defined as 0 when $\omega = 0$. The azimuthal angle changes, however, when the path $PGAMD$ is followed (Santoro & Zocchi, 1964). This path corresponds to the successive rotations $\varphi = \varphi_0 + \varphi'$, then χ along a small circle of the sphere and, finally, ω in the direction opposite to that of φ'.

In practice, one wishes to determine the angles ω, χ and φ for a particular reflection from its known values of χ_0 and φ_0 and a chosen ψ. When φ_0, common to both routes, is not taken into consideration, only five angles are involved, and the problem reduces to the determination of ω, χ and φ' given χ_0 and ψ. It is now shown how these five angles are related in one Napierian triangle.

A trigonometric relation derived from matrices by Hamilton (1974),

$$\cos\chi = \cos\psi \cos\chi_0, \qquad (1)$$

indicates that a right spherical triangle may be constructed with sides χ_0 and ψ adjacent to the right angle C, and χ opposite to it. Since, in Fig. 1, the arc AC represents angle χ_0 and is perpendicular to the XY plane, ψ may be represented by an arc BC in this plane: here B has been arbitrarily taken between C and D. Then χ corresponds to the angle BOA in the great circle AB. Without resorting to spherical trigonometry, the location of B can be found at the intersection of the main circle in the XY plane with a line drawn tangent at E to a circle (not drawn in the figure), centered at F, of radius $EF = OA(\sin^2\chi - \sin^2\chi_0)^{1/2}$. Fig. 2 shows a classical construction allowing one to deduce the values of the spherical angles $A = \varphi'$ and $B = 90 - \omega$ from plane trigonometry. The triangle ABC, in which $a = \psi$, $b = \chi_0$, $c = \chi$, $A = \varphi'$ and $B = 90 - \omega$, gives immediately all the formulae* previously derived by various methods:

$$\sin\psi = \tan\omega \tan\chi_0 \qquad (2)$$

$$\sin\omega = \tan\psi \cot\chi \qquad (3)$$

$$\cos\chi = \tan\omega \cot\varphi' \qquad (4)$$

$$\cos\varphi' = \tan\chi_0 \cot\chi \qquad (5)$$

$$\sin\chi_0 = \tan\psi \cot\varphi' \qquad (6)$$

* ω is taken throughout this note to be zero when the bisecting mode is used, *i.e.* it follows Hamilton's (1974) first definition.

* The signs may differ owing to different conventions for positive rotations.

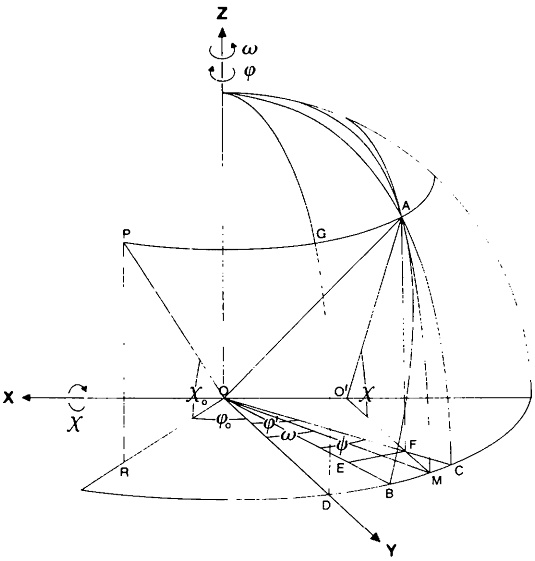

Fig. 1. Representation of the angles, all shown in the range 0 to 90° except φ_0 (0 to −90°). Arrows indicate positive angles. ψ is positive for a clockwise rotation looking toward O along the diffraction vector. The axis of the χ circle is shown coincident with the axis OX. This is true when the bisecting (symmetric) mode is used ($\omega = 0$). It is also true for the asymmetric mode during the φ and χ rotations but the final ω rotation moves the χ axis away from OX.

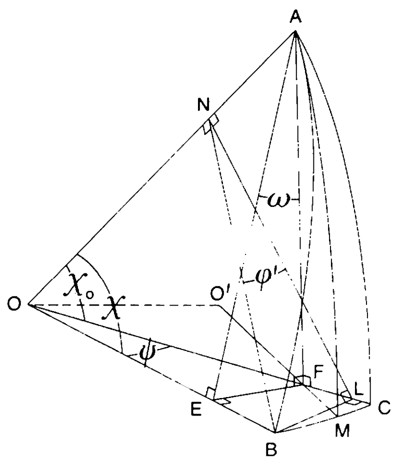

Fig. 2. Right spherical triangle with $a = \psi$, $b = \chi_0$, $c = \chi$; construction showing that $A = \varphi'$ and $B = 90 - \omega$.

$$\sin \omega = \sin \varphi' \cos \chi_0 \qquad (7)$$

$$\sin \chi_0 = \cos \omega \sin \chi; \qquad (8)$$

as well as two new relations:

$$\sin \psi = \sin \chi \sin \varphi' \qquad (9)$$

$$\cos \varphi' = \cos \omega \cos \psi. \qquad (10)$$

The similarity between (1) and (10) may be noted. It indicates that the triangle ABC implies the existence of another triangle $A'B'C'$ with $a' = \omega$, $b' = \psi$, $c' = \varphi'$, $A' = 90 - \chi_0$ and $B' = \chi$ (Arndt & Willis, 1966, Fig. 17, where three of the five elements were found).

It is now shown that these ten relations can all be derived by matrix methods. Two routes, *PGAMD* and *PGD*, were described above to bring the point P on to the Y axis. A certain ψ rotation was associated with the first of these. Thus, the successive rotations of the appropriate angles φ, χ and ω have an identical effect on the crystal orientation to that produced by the three successive rotations φ_0, χ_0 and ψ. If matrices are used to represent these rotations, one can write

$$\mathbf{\Omega X \Phi} = \mathbf{\Psi X}_0 \mathbf{\Phi}_0, \qquad (11)$$

where

$$\mathbf{\Phi} = (\cos \varphi \quad \sin \varphi \quad 0/-\sin \varphi \quad \cos \varphi \quad 0/0 \quad 0 \quad 1)$$

$$\mathbf{X} = (1 \quad 0 \quad 0/0 \quad \cos \chi \quad \sin \chi/0 \quad -\sin \chi \quad \cos \chi)$$

$$\mathbf{\Psi} = (\cos \psi \quad 0 \quad -\sin \psi/0 \quad 1 \quad 0/\sin \psi \quad 0 \quad \cos \psi).$$

$\mathbf{\Phi}_0$, $\mathbf{\Phi}'$ (see below) and $\mathbf{\Omega}$ are obtained by replacing φ in $\mathbf{\Phi}$ by φ_0, φ' and $-\omega$, respectively. $\mathbf{X}$ and $\mathbf{X}_0$ have the same form because at this stage OX still coincides with the χ axis. Relation (11), which is identical to the relation obtained by Busing & Levy (1967) in the particular case where ψ is defined to be 0 when $\omega = 0$, also allows one to deduce all Hamilton's (1974) equations involving the azimuthal angle.*

Taking into account that $\varphi = \varphi_0 + \varphi'$, *i.e.* $\mathbf{\Phi} = \mathbf{\Phi}' \mathbf{\Phi}_0$, (11) simplifies to

$$\mathbf{\Omega X \Phi}' = \mathbf{\Psi X}_0. \qquad (12)$$

Expansion of $\mathbf{M} = \mathbf{\Omega X \Phi}'$ and $\mathbf{N} = \mathbf{\Psi X}_0$ gives

$$\mathbf{M} = \begin{pmatrix} \cos \omega \cos \varphi' + \sin \omega \cos \chi \sin \varphi' & \cos \omega \sin \varphi' - \sin \omega \cos \chi \cos \varphi' & -\sin \omega \sin \chi \\ \sin \omega \cos \varphi' - \cos \omega \cos \chi \sin \varphi' & \sin \omega \sin \varphi' + \cos \omega \cos \chi \cos \varphi' & \cos \omega \sin \chi \\ \sin \chi \sin \varphi' & -\sin \chi \cos \varphi' & \cos \chi \end{pmatrix},$$

* The right-hand side of Hamilton's equation (2) in section 3.3.2 should read $\cos \chi_0 \cos \varphi_0$ instead of $\cos \chi_0 \sin \varphi_0$.

$$\mathbf{N} = \begin{pmatrix} \cos \psi & \sin \psi \sin \chi_0 & -\sin \psi \cos \chi_0 \\ 0 & \cos \chi_0 & \sin \chi_0 \\ \sin \psi & -\cos \psi \sin \chi_0 & \cos \psi \cos \chi_0 \end{pmatrix}.$$

Since $\mathbf{M} = \mathbf{N}$, $m_{ij} = n_{ij}$ and the ten Napierian equations are easily obtained in the same order as above: $m_{33} = n_{33}$; $m_{13} n_{23} = n_{13} m_{23}$; $m_{13} n_{33} = n_{13} m_{33}$; $m_{21} = n_{21}$; $m_{32} n_{33} = n_{32} m_{33}$; $m_{31} n_{32} = n_{31} m_{32}$; $m_{13} n_{31} = n_{13} m_{31}$; $m_{23} = n_{23}$; $m_{31} = n_{31}$; $m_{23} n_{32} = n_{23} m_{32}$.

The angles ω, χ and φ' may be calculated from (12) as follows: since ψ is chosen and χ_0 and φ_0 are known (*e.g.* by manually centering the reflection at $\omega = 0$), all n_{ij} are easily obtained and the angles ω, χ and φ' are those which satisfy $m_{ij} = n_{ij}$. An easier procedure would be to use the properties of Napierian triangles. The angles ω, χ and φ' may first be calculated, *e.g.* by successive use of (2), (3) and (4). If the angles χ_0 and ω are limited to their usual range, 0 to 90°, the laws of Napierian triangles indicate that χ, φ' and ψ are all either acute or obtuse, irrespective of their signs. The angles calculated from (2) – (4) are thus transformed if necessary to lie in their correct quadrant. Their signs are then checked through the two following equations taken from (12).

$$\cos \omega \cos \varphi' + \sin \omega \cos \chi \sin \varphi' = \cos \psi, \qquad (13)$$

$$\cos \omega \sin \varphi' - \sin \omega \cos \chi \cos \varphi' = \sin \psi \sin \chi. \qquad (14)$$

Only one set* of signs for ω, χ and φ' will satisfy their right-hand sides. For example, the following data, $\chi_0 = 39{\cdot}55$, $\varphi_0 = 151{\cdot}05$ and $\psi = 210°$, give for (2) – (4): $\omega = -31{\cdot}19$, $\chi = -48{\cdot}11$ and $\varphi' = -42{\cdot}20°$. With $\psi = 210°$, equivalent to $-150°$, χ and φ' must both be obtuse, *i.e.* 131·89 and 137·80°, respectively. Then (13) and (14) indicate that ω and φ' are both negative and χ positive. The angles sought are thus: $\omega = -31{\cdot}19$, $\chi = 131{\cdot}89$ and $\varphi' = -137{\cdot}80°$. Finally, $\varphi = 13{\cdot}25°$ is obtained from $\varphi = \varphi_0 + \varphi'$.

I thank Professor D. Rogers for discussions.

* Of the four, ω and φ' must always have the same sign if, as in Fig. 1, their sense of positive rotation is opposite.

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