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Triclinic Cell Parameters from One Crystal Setting

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A general approach to determining triclinic cell parameters from one single-crystal setting is described, which has advantages over the method of angular lag. The procedure has been developed graphically, using a few chosen reflexions, but is also programmed for least-square computation, when a greater number of reflexions may be considered.

Introduction

In examining compounds of particular chemical interest one is frequently presented with ill-formed crystals of low stability. In consequence, there are no faces to aid orientation, while time permits only a limited number of photographs to be taken before decomposition occurs. Buerger (1942) prescribes an angular lag procedure, but his treatment suffers from the practical defect that it requires two superposed Weissenberg exposures (zero and first layer), as well as depending upon measurements involving low index reflexions of type $h00$, $h0l$ (if oscillating about the c axis, for example) which may very well be unobservedly weak. The present method involves measurements between general hkl reflexions and requires only that there be taken one oscillation photograph, one zero layer and one first layer equi-inclination Weissenberg photograph. The use of generalized Patterson and electron-density syntheses may then elucidate the essential features of the structure. Indeed, if the crystal is very unstable, an oscillation photograph plus a 100° first layer Weissenberg photographs is sufficient to define cell parameters. Another advantage of the present procedure is that it works equally well whether or not the film holder is split into halves, as is customary in some forms of low temperature integrating cameras (*e.g.* Wiebenga & Smits, 1950; Kreuger, 1955).

Geometrical procedure

Let a crystal oscillate about the c axis. ζ_c may be measured from an oscillation photograph, and ξ_a, ξ_b and γ^* are best measured from the zero layer Weissenberg photograph. Now consider the reciprocal lattice (Fig. 1) where O is the true origin and D the origin of the nth layer projected down to N.

ND is perpendicular to the a^*b^* plane, and so corresponds to the direction of the c axis.

DP is drawn perpendicular to Oa^* and QN perpendicular to DP. QN will be the direction of the b axis.

Thus $b\hat{N}c=\alpha$; therefore $Q\hat{P}N=Q\hat{N}D=180°-\alpha$ and $\tan\ Q\hat{P}N=\tan\ (180°-\alpha)=-\tan\ \alpha=DP/PN=n\zeta_c/\delta_b$ where δ_b is the shift of the nth layer origin perpendicular to Oa^*.

Now the angular distance, φ_1, between any two reflexions h_1k_1l and h_2k_2l passing through the sphere of reflexion is readily measured from an n-layer equi-inclination photograph, *e.g.* λ between $1\bar{1}1$ and $\bar{1}21$ in Fig. 2. It will, in general, differ from the angle between h_1k_10 and h_2k_20 because of the layer origin displacement.

We may thus construct on the nth layer of the reciprocal lattice the locus of points (a circle) at which the chord, P_1P_2 (Fig. 3), subtends the angle φ_1. When $\varphi_1 < 90°$ this is most accurately achieved by joining P_1P_2, making P_2X perpendicular to P_1P_2 and $X\hat{P}_1P_2$ equal to $90-\varphi_1$. The bisector, U, of P_1X is then the centre of the required circle. If $\varphi_2>90°$ (say) then the angle $\frac{1}{2}(180°-\varphi_2)$ is constructed at P_3 and P_4, and two sides of the resultant triangle are bisected to give the centre, V, of the circumscribing circle.

Repetition for another pair of reflexions, angle φ_2', results in intersecting circles, and discrimination between the two points of intersection may be made by reference to a third pair of reflexions, angle φ_3', to obtain the projection of the displaced origin, N'.

δ_b, perpendicular to Oa^*, may then be measured and the direct angle α calculated. The best accuracy is obtained when the circles intersect close to right angles.

Computational procedure

The solution of the precise analytical expression is difficult, and a quickly converging iterative method is used.

Let the nth layer origin shifts *parallel* to the a^* and b^* axes (Fig. 4) be nA and nB (δ_b then equals $nB \sin\gamma^*$, *etc.*).

We may compute $(P_1P_2)^2$ in two ways to equal

$$(h_2-h_1)^2a^2+(k_2-k_1)^2b^2+2(h_2-h_1)(k_2-k_1)ab\cos\gamma^* \quad (1)$$

or

$$\alpha_1^2+\alpha_2^2-2\sqrt{\alpha_1^2\alpha_2^2}\,.\,\cos\varphi_1 \quad (2)$$

where

$$\alpha_1^2=(h_1a+nA)^2+(k_1b+nB)^2+2(h_1a+nA)(k_1b+nB)\cos\gamma^*$$

and similarly for α_2.

Equating and gathering terms leads to equations of the form

$$Ax + By = C_0\,,$$

where

$$C_0 = (-h_1h_2a^2 - k_1k_2b^2 - h_1k_2ab\cos\gamma^*$$
$$-\,h_2k_1ab\cos\gamma^*) + \cos\varphi_1\,.\,\sqrt{\alpha_1^2\alpha_2^2 - 2n^2AB\cos\gamma^*}$$
$$x = n\{(h_1a + h_2a + k_1b\cos\gamma^* + k_2b\cos\gamma^*) + nA\}$$
$$y = n\{(h_1a\cos\gamma^* + h_2a\cos\gamma^* + k_1b + k_2b) + nB\}.$$

There will be several such equations, depending on how many angular distances are measured. Commencing with rough values, A_0, B_0, for A and B, we may calculate $C_c = A_0x + B_0y$ so that

$$\Delta C = C_0 - C_c = \left(\frac{\partial C}{\partial A}\right)\Delta A + \left(\frac{\partial C}{\partial B}\right)\Delta B$$

whence

$$\Delta A = \frac{\Sigma\,\Delta C\,.\,x}{\Sigma\,x^2}\,; \qquad etc.$$

The strategy is to choose solutions, A_0 and B_0, compute C_0, x and y, and to derive improved A and B values by three minor rounds of refinement, so that $A_1 = A_0 + A_1$, *etc.* At this point C_0, x and y are recalculated (as they depend upon the magnitude of A and B) and another three rounds of refinement are carried out. By such an iterative process A and B are improved until they are no longer subject to significant changes between major rounds. At this point the resultant A and B values are output, together with the angles α and β. In addition, the final calculated input angles, φ_c, are printed out for comparison with the measured φ values employed.

In the program, written in Extended Mercury Autocode for the University of London Atlas Computer, starting values for A and B have been written in as 0·001 and 0·001. Provided that at least eight values of φ are introduced, which have values in the range 70–110° (so that $\cos\varphi$ is not too large) only about five rounds of major refinement are needed. With φ values around 40° some twenty rounds of refinement may be needful.

Accuracy

The accuracy obtainable is exemplified by some data, summarized in Table 1, relating to copper(II) sulphate pentahydrate which was oscillated in turn about each

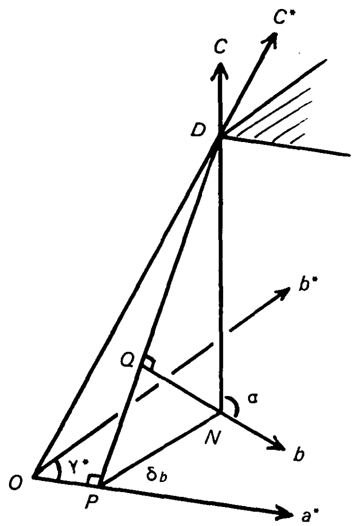

Fig. 1. General view of reciprocal lattice.

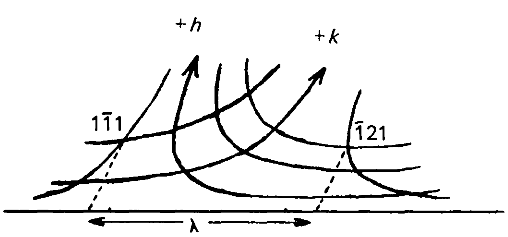

Fig. 2. Upper half of first layer equi-inclination Weissenberg photograph.

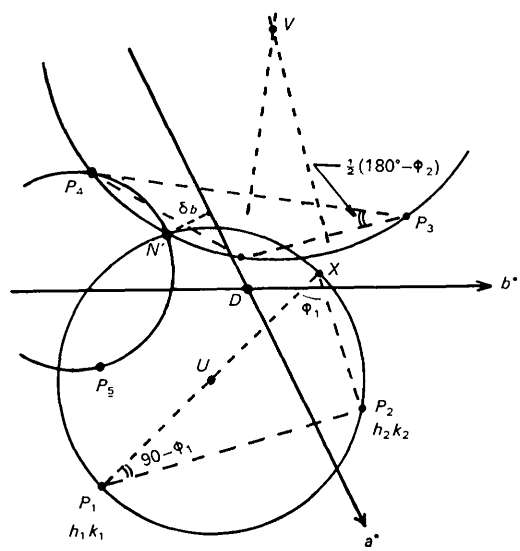

Fig. 3. *n*th layer of reciprocal lattice, showing constructions to obtain the projected origin, N'.

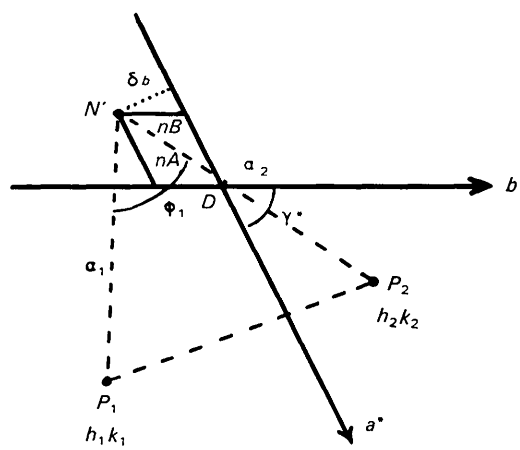

Fig. 4. *n*th layer of reciprocal lattice, showing a typical triangle used in computing the projected origin, N'.

Table 1. *Data for* $CuSO_4.5H_2O$

Experimental values obtained by angular lag about axis below	Graphical & programmed angles (°) α_g	α_p	β_g	β_p	γ_g	γ_p
a axis	—	—	107·4	108·1	76·8	77·9
b axis	97·1	97·7	—	—	77·1	76·8
c axis	97·4	97·5	107·3	107·2	—	—
Literature values	97·6		107·2		77·6	

principal axis after being set by the procedure of Brooker & Nuffield (1966). More detailed information is given for one axis in Table 2. In general the graphical method, provided some half-dozen values of φ are taken and the various close intersections are finally averaged, is accurate to about 1°. With the least-square computational procedure, a rather better accuracy is obtainable, particularly if φ angles are measured with a travelling microscope. The resultant cell angles are sensitive to errors in crystal setting.

Table 2. *Comparison of inter-reflexion angles, φ_m, measured with a ruler and those, φ_c, calculated from the final cell parameters deduced by programmed angular lag*

Values marked * were used for graphical evaluation

h	*k*	*l*	*h*	*k*	*l*	φ_m	φ_c
0	3	1	1	0	1	85·5°	85·4°
0	3	1	1	−1	1	108·0	107·7
0	3	1	0	0	1	67·0	66·7
0	2	1	1	0	1	81·0	81·0
0	2	1	1	−1	1	103·0	103·2
*0	1	1	1	0	1	69·6	69·6
*0	1	1	1	−1	1	92·0	91·9
1	2	1	0	−1	1	95·5	95·5
1	2	1	0	−2	1	111·0	111·2
*1	1	1	0	−1	1	76·6	76·7
1	1	1	0	−2	1	92·0	92·4
*0	0	1	0	−1	1	71·5	71·5
0	0	1	0	−2	1	87·5	87·3
−1	−3	1	−1	0	1	85·0	84·5
−1	−2	1	−1	0	1	72·0	71·5
−1	−2	1	−1	1	1	100·6	100·4
*−1	−1	1	−1	1	1	73·0	72·5
−1	−1	1	−1	2	1	86·1	86·0
−2	−2	1	−1	1	1	71·0	70·9
−2	−2	1	−1	2	1	84·2	84·4
−1	0	1	0	2	1	83·8	83·5
−1	0	1	0	3	1	79·5	79·0
−2	−1	1	0	3	1	103·0	103·2
−2	−1	1	0	2	1	107·2	107·6

The resulting α, β, γ^* values are used to calculate direct cell angles, and hence to obtain direct cell dimensions from ξ_a and ξ_b. At this stage a Delaunay reduction (Delaunay, 1933, Patterson & Love 1957,) may be applied to obtain the conventional triclinic cell, and to ensure that the crystal truly lacks elements of symmetry.

My thanks are due to various colleagues who have produced inconvenient unstable crystals, and to students who have used the graphical method during the last three years.

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