Table 7. *Environments of* H_2O *and* NH_4: *distances from neighboring oxygen atoms, with angles of interest*

H_2O–O(1)	3·170 Å
H_2O–O(2)	2·783
H_2O–O(3)	2·827
H_2O–O(4)	2·758
NH_4–O(1)	3·140
NH_4–O(2)	3·095
NH_4–O(3)	3·677
NH_4–O(4)	2·962
O(2)–H_2O–O(2′)	110·3°
O(4)–H_2O–O(4′)	109·7
O(3)–H_2O–O(3′)	80·0
O(2)–NH_4–O(2′)	119·2
O(4)–NH_4–O(4′)	107·9

together too small. The angles O(2)–H_2O–O(2′) and O(4)–H_2O–O(4′) are close to the tetrahedral value, but bonding to either O(2) or O(4) would bring the hydrogen atoms in towards the yttrium. The question of the bonding of the water molecule must therefore remain open.

We wish to acknowledge the valuable help and advice given to us by Dr. P. Clarke during the refinement stages of this work.

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An Accurate Correction Procedure for Equi-inclination Weissenberg Diagrams

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A method is presented by which the inclination error and the goniometer setting error can be derived from the deviations from linearity of lines of reciprocal-lattice points in upper-layer equi-inclination Weissenberg patterns. The method is most suitable for crystals having large unit cells and for rotation axes close to reciprocal-lattice directions.

Introduction

For crystals having large unit cells, the low-order reflexions in upper-layer equi-inclination Weissenberg patterns are quite close to the trace of the undeviated beam, or central axis. Even though the crystal alignment and inclination angle seem to be correct, these reflexions are often displaced from their proper positions. These displacements may serve as particularly sensitive diagnostic tools for improving these adjustments.

We shall here treat only the situation when the rotation axis is intended to coincide with a reciprocal-lattice axis. If this is not the case, the lack of coincidence could be treated as a known error, and we would be only interested in deviations from this. If this lack of coincidence were large, the reflexions involved would not be near the central axis of the Weissenberg diagram where all the sensitivity of this technique resides, so this method would not be recommended.

In the case treated here, the upper-layer zone is intended to rotate about a central reciprocal-lattice point which should remain stationary on the Ewald sphere. If all adjustments are correct, all straight lines of reciprocal-lattice points in the upper-layer zone that pass through the central stationary point become parallel straight lines on the Weissenberg pattern. If there is only an inclination error, the upper-layer zone rotates about the central stationary reciprocal-lattice point which is displaced from the surface of the Ewald sphere. If there is only a goniometer-setting error, the central reciprocal-lattice point rotates about the point on the Ewald sphere where it would be had there been no error. When each type of error occurs, the straight lines of reciprocal-lattice points that pass through the central point are no longer straight lines on the Weissenberg pattern. The resultant curves approach the undeviated straight lines far from the central axis of the pattern. The more closely the points on each curve approach the central axis, the more they deviate from

the line, this deviation being on opposite sides of the line above and below the central axis. We shall here derive these curves and relate them to the errors causing them.

This problem has been treated by Sayre (1954) for inclination angle errors only. His relation is considerably simpler than those presented here, but it involves more drastic small-angle approximations in its derivation. His method has not gone into general use, probably because, as has been our experience, goniometer setting errors are usually also involved, and different corrections would be implied by different reciprocal lattice lines on the same patterns, none of them being necessarily correct. The part of the method presented here that involves finding the inclination-angle error when the goniometer is perfectly aligned requires fewer measurements and provides greater accuracy than the Sayre technique, so it can be considered as a refined version of the latter.

Inclination-angle error

Let us first consider that the only error is that of the inclination angle.

If μ is the inclination angle and Δ is the angular error, then the radius of the circle of intersection between the upper-layer plane and the Ewald sphere (the radius of which is taken as 1) is

$$\varrho=\sqrt{1-[2\sin\mu-\sin(\mu+\Delta)]^2} \qquad (1)$$

and the radial distance in that plane between the circle circumference and the intersection (with the plane) of the axis of rotation of the reciprocal lattice is

$$\delta=\varrho-\cos(\mu+\Delta)\,. \qquad (2)$$

We consider Δ as positive if the inclination angle is too big, in which case δ is also positive, and the axis of rotation intersects the upper-layer plane inside the circle. If we assume that $|\Delta|$ is small (and is expressed in radians) then equations (1) and (2) reduce to

$$\varrho\simeq\cos\mu+\Delta\sin\mu \qquad (3)$$

and

$$\delta\simeq 2\Delta\sin\mu\,. \qquad (4)$$

The quantity δ/ϱ, which we shall refer to as the *error factor*, is plotted against the inclination angle μ for various angles of $|\Delta|$ in Fig. 2. The curves correspond to $0\leq|\Delta|\leq 1\frac{1}{2}°$ in increments of 5 minutes. Although δ/ϱ $(+\Delta)$ is not precisely equal to $-\delta/\varrho$ $(-\Delta)$, the difference is small enough to be neglected. This approximation is valid since in this range $(0\leq|\Delta|\leq 1\frac{1}{2}°$ and $|\delta/\varrho|<0{\cdot}018)$ $\cos\mu\gg\Delta\sin\mu$, so that equation (4) divided by equation (3) reduces to

$$\delta/\varrho\simeq 2\Delta\tan\mu\,. \qquad (5)$$

The sign of δ/ϱ is the same as that of Δ.

If γ is the angle between the projections down the axis of rotation (onto the upper-layer plane) of the incident and diffracted beams, and φ is the angle (as measured around the spindle shaft which holds the goniometer) between a given line of upper-layer reciprocal-lattice points that intersects the axis of rotation and the projection on the plane of the incident beam (*International Tables for X-ray Crystallography*, 1959), then for that line

$$\operatorname{cotan}\varphi=\tan\frac{\gamma}{2}-\frac{\delta}{\varrho\sin\gamma} \qquad (6a)$$

$$\text{or}\quad\operatorname{cotan}\omega=\left(\frac{2\varrho}{\delta}-1\right)\tan\frac{\gamma}{2} \qquad (6b)$$

where $\omega=\varphi+\gamma/2-\pi/2$, or the displacement in the φ direction from the line of perfect alignment at a particular γ on the Weissenberg film. These relations are readily derived by considering Fig. 1.

The upper-layer Weissenberg diagram can be considered as an orthogonal representation of γ *versus* φ (or a non-orthogonal representation of γ *versus* ω) for the various radial lines of reciprocal-lattice points. Such a plot of equation (6*a*) is shown in Fig. 3 for various values of the error factor δ/ϱ. For $2°\leq|\gamma|\leq 10°$, curves are plotted from $\delta/\varrho=+0{\cdot}016$ to $\delta/\varrho=-0{\cdot}016$ in increments of 0·002. For $10°\leq|\gamma|\leq 30°$, curves are plotted in increments of 0·005. For $30°\leq|\gamma|\leq 80°$, $\delta/\varrho=+0{\cdot}015$, 0 and $-0{\cdot}015$ are plotted.

The correction procedure to use is to find the appropriate error factor δ/ϱ by matching the Weissenberg film to Fig. 3, and then to find Δ from Fig. 2. The correction is the negative of the error Δ.

This matching procedure does not require complete lines of reciprocal-lattice points. All that is necessary

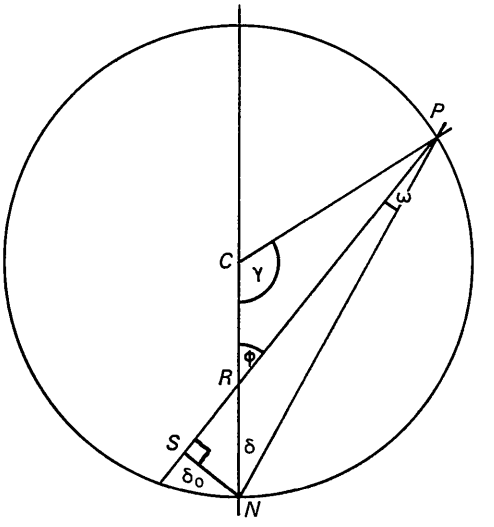

Fig. 1. Geometry in the upper-layer plane. *N* and *P* are on the circle of intersection between the upper-layer plane and the Ewald sphere; *CRN* is the projection of the undeviated beam; *CP* is the projection of the diffracted beam; *PRS* is the reciprocal-lattice line; *R* is the rotation axis if there were an inclination error only; *N* is the rotation axis if either there were no errors or if there were a goniometer error only; $CP=CN$ is the radius of the intersection circle$=\varrho$; $NR=\delta$; $NS=\delta'$.

is one reflexion on each side of the central axis of the film. While this central axis and that of Fig. 3 are kept superimposed, they are shifted relative to one another in the axis direction until the same error is indicated for each of these points.

Goniometer-setting error

In the above discussion, the error was assumed to be completely in the inclination angle. With reference to Fig. 1, δ was kept constant and φ and ω were found as functions of γ. If this were true, all upper-layer straight lines of reciprocal-lattice points that go through the rotation axis would have the same functional shape (*i.e.* δ/ϱ=constant) in the Weissenberg diagram. If instead, all the error were in the alignment of the crystal axis with respect to the rotation axis, then δ/ϱ would be different for different lines of reciprocal-lattice points, being a maximum if the axis of the goniometer error happened to be parallel to the line of points. At this maximum, the values of δ and ϱ are related to the goniometer error by the same equations as for inclination-angle error [equation (1) and (2)], the goniometer error being about the same axis as that of the inclination angle. Let us call this value of δ at the maximum δ_0. For any particular line of reciprocal-lattice points, only the component δ' of the goniometer arc error that shifts the line normal to its length is effective in this context. In Fig. 1, δ' is kept constant when we are finding φ and ω.

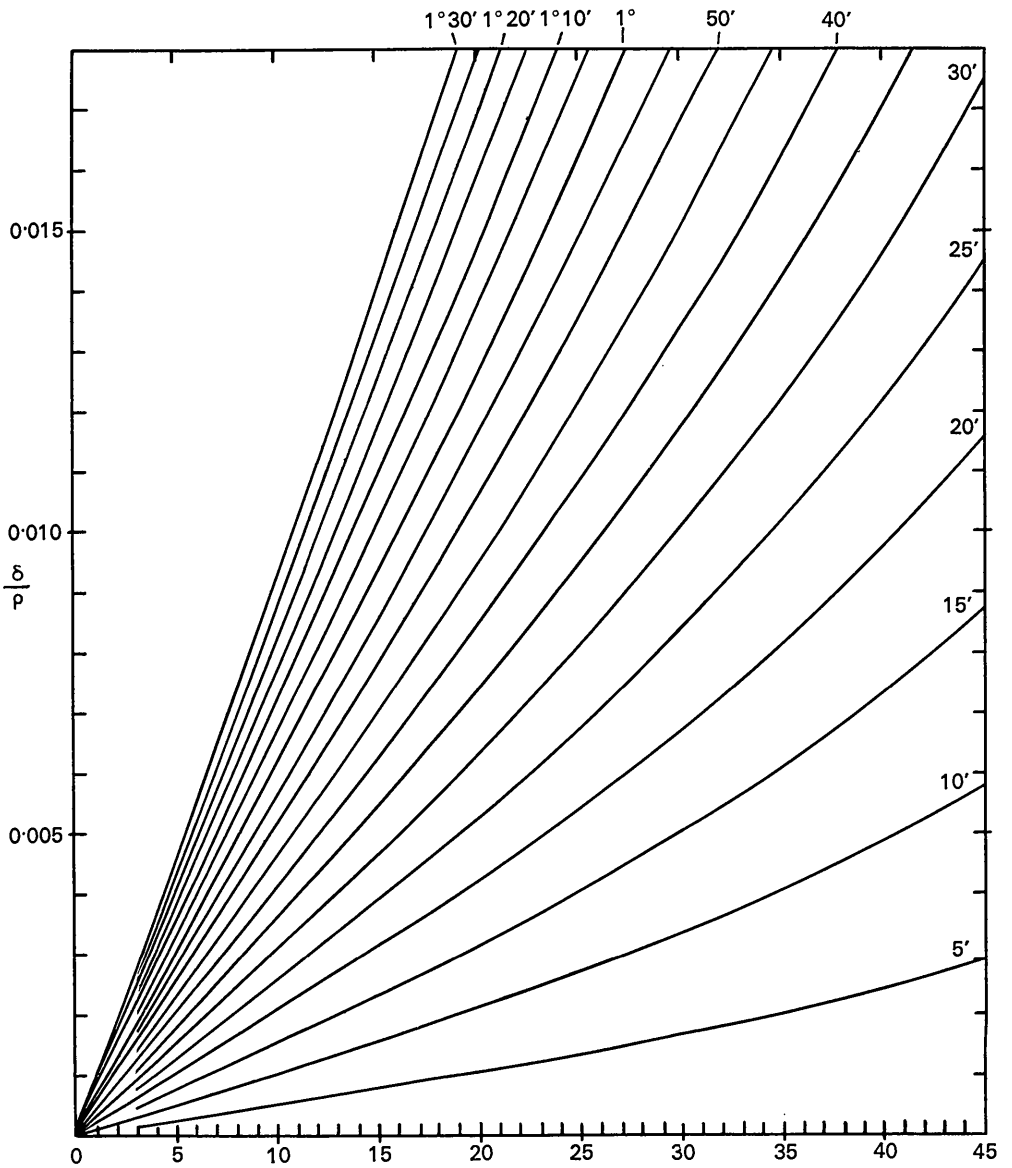

Fig. 2. Plot of the error factor δ/ϱ *versus* the inclination angle μ for various values of the error Δ. Curves of equal error Δ are shown for $0 \leq \Delta \leq 1\frac{1}{2}°$ at intervals of 5 minutes in Δ.

The relations between the variables that are analogous to equations (6) for this case are

$$\sin\varphi = \frac{\delta'}{2\varrho} + \operatorname{cotan}\frac{\gamma}{2}\sqrt{\sin^2\frac{\gamma}{2} - \left(\frac{\delta'}{2\varrho}\right)^2} \qquad (7a$$

$$\text{or } \sin\omega = \frac{\delta'}{2\varrho\sin\gamma/2} \,. \qquad (7b)$$

The curves for equations (7) differ from those of (6) primarily in their limits: the minimum $|\gamma|$ in (7) is 2 arcsin $(\delta'/2\varrho)$ while in (6) it is zero, and the minimum ω (at $\gamma=\pi$) in (7*b*) is arcsin $(\delta'/2\varrho)$ while in (6*b*) it is zero. Avoiding these limiting values, we find that, in the mid-region of primary concern (γ between 5 and 30°), the curves are remarkably close to being coincident, the difference between them being less than 3% of ω for $\delta/\varrho<0{\cdot}02$. Thus the curves of Fig. 3 can also be used to find the components of the goniometer arc error in the same way as the inclination error was found, and we will no longer distinguish between δ and δ'.

If we let φ_0 be the spindle angle of crystal rotation when the axis of the goniometer error is in the $\varphi=90°$ direction (when $\delta=\delta_0$), and φ_s be the general spindle angle, then

$$\frac{\delta}{\varrho} = 1 - \sqrt{\frac{\delta_0^2}{\varrho^2} - 2\frac{\delta_0}{\varrho}\cos(\varphi_s-\varphi_0) + 1} \,. \qquad (8)$$

If we consider $\dfrac{\delta_0^2}{\varrho^2} \ll 2\dfrac{\delta_0}{\varrho}\cos(\varphi_s-\varphi_0) \ll 1$, then

$$\frac{\delta}{\varrho} \simeq \frac{\delta_0}{\varrho}\cos(\varphi_s-\varphi_0) \,. \qquad (9)$$

Since the matching of Fig. 3 to the Weissenberg diagram is over a small range of φ, we can consider the resulting value of δ/ϱ to apply to the φ_s corresponding to $\varphi=90°$ for the particular line of reciprocal-lattice points. To solve equation (8) or (9) for the magnitude (Δ, which is obtained from δ_0/ϱ by Fig. 2) and the direction (φ_s) of the goniometer arc error, we need to measure δ/ϱ for two lines of reciprocal-lattice points: at $\varphi_s(1)$ and $\varphi_s(2)$. Equation (9) is accurate enough and particularly easy to apply. Analytically,

$$\varphi_0 = \arctan\left(\frac{\frac{\delta}{\varrho}(2)\cos\varphi_s(1) - \frac{\delta}{\varrho}(1)\cos\varphi_s(2)}{\frac{\delta}{\varrho}(1)\sin\varphi_s(2) - \frac{\delta}{\varrho}(2)\sin\varphi_s(1)}\right) , \qquad (10)$$

and then δ_0/ϱ comes out of equation (9) by substitution of the values for either of the lines.

Alternatively, equation (9) can be very easily solved graphically. We draw a radial line proportional in length to $\delta/\varrho(1)$ at angle $\varphi_s(1)$ on polar coordinate paper, do the same for $\delta/\varrho(2)$ at $\varphi_s(2)$, draw perpendiculars at the ends of these lines, and we find that δ_0/ϱ and φ_0 are the length and angle of the radial line to the intersection of the perpendiculars. The individual goniometer-arc error factors are, to a high enough degree of accuracy, equal to the vector projections of δ_0/ϱ at φ_0 onto the φ_s's at which the axis of each arc is parallel to $\varphi=90°$ (in each of these positions the relevant arc adjustment motion would be in the direction of the X-ray beam if $\mu=0$). The justification for this is that small angles are vectorially additive.

Inclination and goniometer-setting errors occurring simultaneously

If both a goniometer error and an inclination-angle error are simultaneously present, then a constant unknown term due to the latter (which we shall call δ_a/ϱ) must be added to equation (8) or (9). To solve this case, we need to measure δ/ϱ for three reciprocal-lattice lines at known φ_s's. Analytically, using equation (9),

$$\frac{\delta}{\varrho}(n) = \frac{\delta_0}{\varrho}\cos[\varphi_s(n)-\varphi_0] + \frac{\delta_a}{\varrho} \quad (n=1,\ 2 \text{ and } 3) \qquad (11)$$

we find that

$$\varphi_0 = \arctan \frac{\frac{\delta}{\varrho}(3)\cos\varphi_s(2) + \frac{\delta}{\varrho}(2)\cos\varphi_s(1) + \frac{\delta}{\varrho}(1)\cos\varphi_s(3) - \frac{\delta}{\varrho}(3)\sin\varphi_s(1) + \frac{\delta}{\varrho}(2)\sin\varphi_s(3) + \frac{\delta}{\varrho}(1)\sin\varphi_s(2) - \frac{\delta}{\varrho}(3)\cos\varphi_s(1) - \frac{\delta}{\varrho}(2)\cos\varphi_s(3) - \frac{\delta}{\varrho}(1)\cos\varphi_s(2)}{\frac{\delta}{\varrho}(3)\sin\varphi_s(2) - \frac{\delta}{\varrho}(2)\sin\varphi_s(1) - \frac{\delta}{\varrho}(1)\sin\varphi_s(3)} \qquad (12)$$

$$\frac{\delta_0}{\varrho} = \frac{\frac{\delta}{\varrho}(1) - \frac{\delta}{\varrho}(2)}{\cos[\varphi_s(1)-\varphi_0] - \cos[\varphi_s(2)-\varphi_0]} \qquad (13)$$

and then δ_a/ϱ can come directly from any one of equations (11).

For the geometrical solution, the three $\delta/\varrho(n)$'s are marked off at the $\varphi_s(n)$'s on polar coordinate paper as before. If $\delta_a/\varrho=0$, the three terminal perpendiculars would intersect at the one point corresponding to δ_0/ϱ at φ_0. In general, the three perpendiculars form a triangle, and the amount of equal expansion or contraction of the three $\delta/\varrho(n)$'s necessary to reduce the triangle to a point is the required δ_a/ϱ. The four intersections of the internal and external angle bisectors of the triangle are the possible solutions for this point. The correct choice amongst these four points involves finding the one that corresponds to expansion or contraction of all three $\delta/\varrho(n)$'s simultaneously.

When this is not intuitively obvious, rules for choosing the correct point can be formulated. These rules involve noticing that the three terminal perpendiculars

divide the plane into seven regions: the triangle interior, the three outside regions sharing edges with the triangle, and the three outside regions sharing only corners with the triangle.

Let us initially assume that all of the $\delta/\varrho(n)$'s are positive. Then, if the origin happens to be in one of the three outside regions sharing edges with the triangle, the desired point is the intersection of external angle bisectors in the same region. If the origin is in one of the three outside regions sharing only corners with the triangle, the desired point is the intersection of external angle bisectors in the outside region sharing

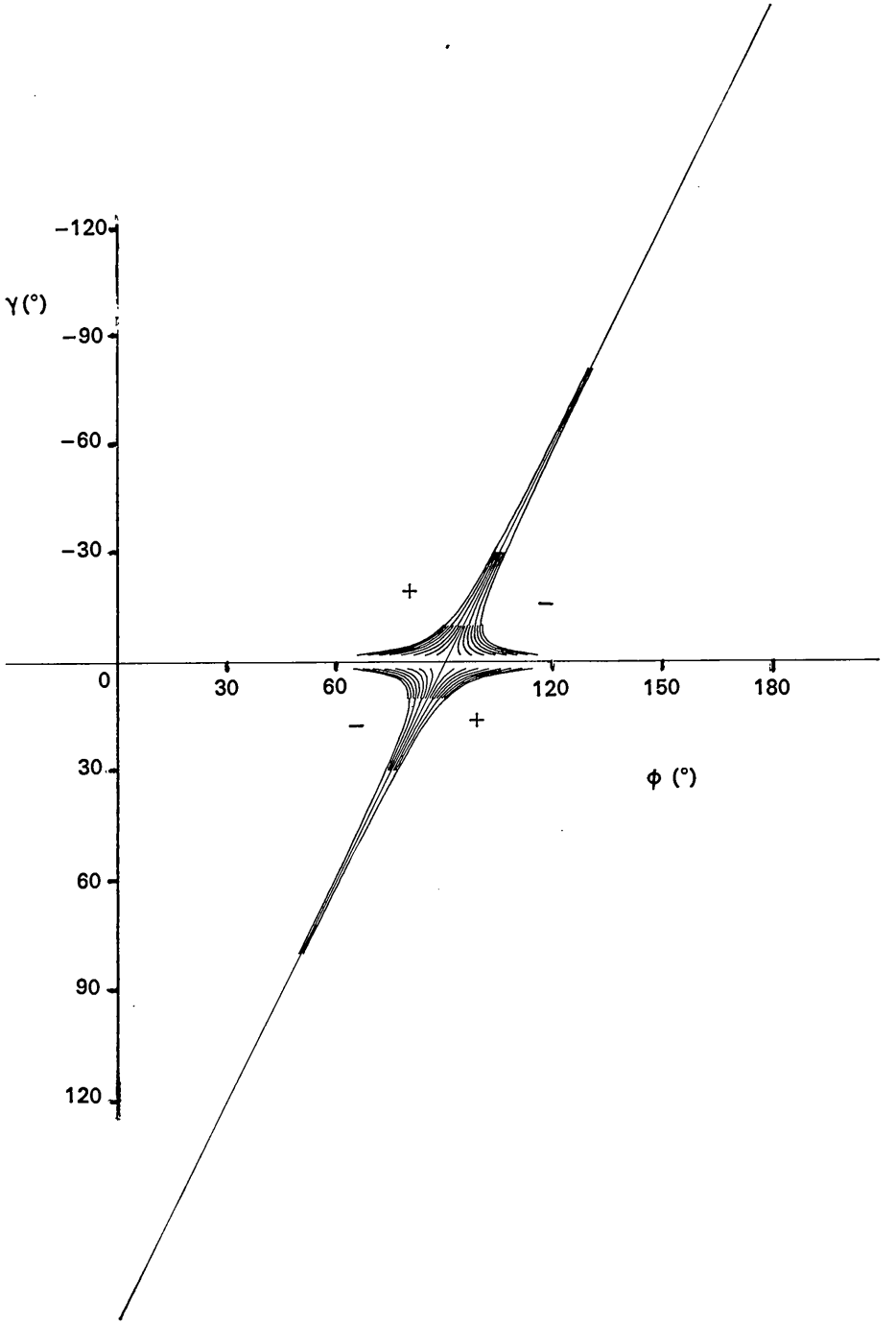

Fig. 3. Plot of γ *versus* φ for various values of the error factor δ/ϱ. The lines of equal δ/ϱ are in intervals of 0·002 for $2° \leq |\gamma| \leq 10°$, 0·005 for $10° \leq |\gamma| \leq 30°$, and 0·015 for $30° \leq |\gamma| \leq 80°$. The error factor is positive in the larger quadrants at the upper left and lower right, and negative in the remaining smaller ones. The scale is that for standard Weissenberg films (57·3 mm diameter and $2°\varphi$ per mm travel).

the edge of the triangle located opposite the particular corner. If the origin is within the triangle, the desired point is the intersection of the internal angle bisectors.

This procedure also picks the correct point if all of the $\delta/\varrho(n)$'s are negative. The remaining possibilities all involve one sign being different from the other two. If the terminal perpendicular of the odd δ/ϱ is the triangle edge adjacent to the region which includes the point that would be chosen if all the signs were the same, then the correct point is the one inside the triangle. If this terminal perpendicular forms another triangle edge, then the correct point is at the other end of the external angle bisector which goes through the initial point (chosen ignoring signs) and which does not intersect the perpendicular of the odd δ/ϱ between the two points.

An interesting special case occurs when two of the three measurements are made 180° apart (on the same reciprocal lattice line). In this case, one triangle apex is at infinity, and the two solution points that exist at angle bisectors lie on the line half-way between the two parallel δ/ϱ perpendiculars. An arbitrary choice of which side of the perpendicular to the third δ/ϱ in the space between the first two is to be considered the 'inside', followed by the general rules above will choose correctly between these points (as long as one does not worry about temporary points at infinity).

Working through an example

As an illustration of this method, the second upper-layer zone of a monoclinic diphenyl-Δ^2-pyrazoline derivative along its b axis is shown in Fig. 4, where a film, taken when the camera and crystal were somewhat misaligned, is superimposed upon a film of weaker intensity taken under fairly good alignment conditions. The steps taken to find the corrections to achieve this alignment improvement will now be outlined.

In this zone there are seven reciprocal-lattice lines represented by reflexions with $|\gamma| < 15°$ (a convenient

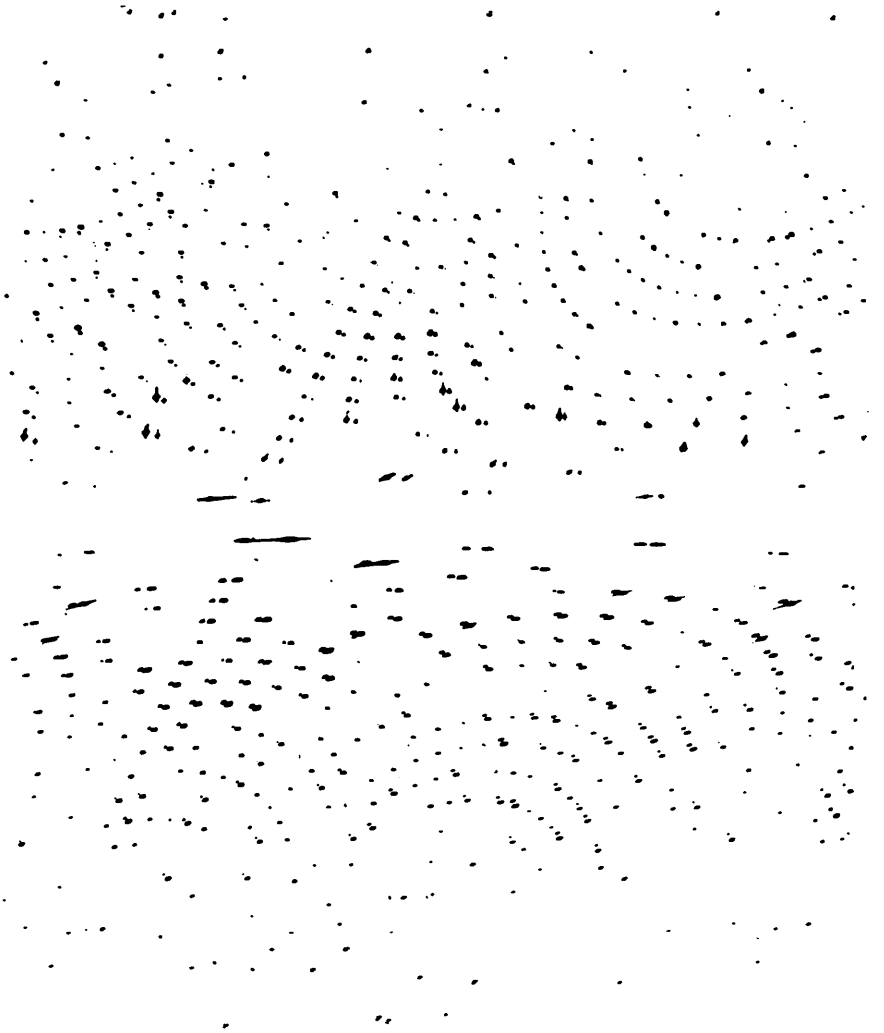

Fig. 4. Superimposition of upper-layer Weissenberg photographs taken under normal (errors $< 0{\cdot}5°$) and improved (errors $< 0{\cdot}05°$) alignment conditions.

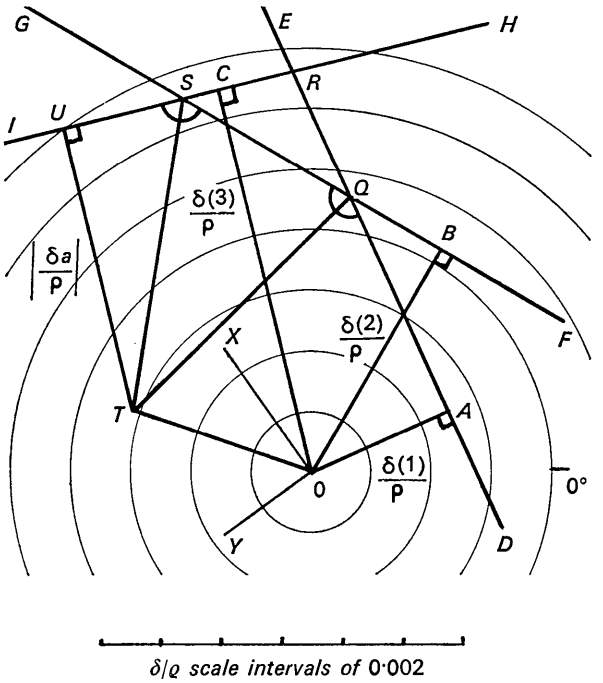

Fig. 5. Construction for finding inclination-angle and goniometer arc error factors in given example.

range within which accuracy is high). The three on the right have δ/ϱ greater than the range covered in Fig. 3 so that, though they can easily be estimated by extrapolation, and though final accuracy would be improved by covering a larger range of φ's with our three chosen lines, we can still afford to ignore them. The three chosen for this example are the first, second and fourth counting from the left. By superimposition of Fig. 3 onto the original pattern, it is estimated that the error factors $\delta/\varrho(n)$ for these three are respectively +0·005, +0·0085 and +0·013. The angles $\varphi_s(n)$ are measured along the central axis of the film, and each is taken to be twice the distance in millimeters between the left edge of the film and the centre of symmetry of that particular reciprocal-lattice line curve. For the above three lines, these values are 24, 59 and 103° respectively. On Fig. 5, these three $\delta/\varrho(n)$'s are plotted at these $\varphi_s(n)$'s and are shown as OA, OB and OC respectively. The terminal perpendiculars DE, FG and HI are constructed, forming triangle QRS. It is noticed that the origin is in an external region that shares an edge (QS) of the triangle, so the initial angle bisector intersection point to consider is in the same region as the origin O. This point is the desired one since all of the $\delta/\varrho(n)$'s are of the same sign. The external angle bisectors at Q and S are then drawn and they intersect at point T.

The perpendicular distance from point T to any of the terminal perpendiculars (*e.g.* TU) is δ_a/ϱ, the error factor for the inclination angle. Its value is 0·0047, and it is positive since all of the $\delta/\varrho(n)$'s would have to shrink uniformly for all the terminal perpendiculars to intersect at T. Since $\mu = 16{\cdot}0°$ for this upper-layer zone, we find from Fig. 2 that the inclination-angle error $\Delta = +28$ minutes of arc.

The vector OT is the error factor δ_0/ϱ which is associated with the total goniometer arc error. This vector must be resolved along the directions along which each goniometer arc is horizontal. These components are OX and OY, the latter being negative with respect to the direction for the angle in the range concerned at which the second arc is horizontal. The goniometer arc error factors δ/ϱ's are 0·0025 and −0·0018, resulting in errors (Δ's) of +16 and −10 minutes of arc respectively.

Conclusion

Since quite adequate Weissenberg data have been collected for many years with goniometer-setting and inclination angle errors of $\pm\frac{1}{2}°$, one might question the value of a technique for achieving greater but unnecessary accuracy. Nevertheless, the increased accuracy may be quite useful. For instance, if intensity data on the reflexions close to the central axis of the Weissenberg pattern are available only from this pattern, quite small setting errors can give rather large differences between the real Lorentz factor and the standard calculated one (Sayre, 1954; MacGillavry, 1965), resulting in considerable error in corrected intensity. Also, with a well calibrated inclination scale, the more accurately measured inclination angle than that derived from the rotation diagram provides a more accurate value of the unit-cell periodicity along the rotation axis. We have also found that difficulties in indexing upper layer patterns by superimposing them onto zero layer ones dissolved when this technique was used to achieve critical alignment.

The graphical technique for finding the errors is quite rapid and is surprisingly insensitive to small errors in reading off δ/ϱ from a superimposition of the Weissenberg pattern with Fig. 3. The rules for deciding which intersection of angle bisectors provides the correct solution admittedly seem complex. They need only be used as a check when there may be some confusion in choosing the point towards which all of the δ/ϱ perpendicular intersections converge when the δ/ϱ's all simultaneously increase or decrease. This graphical solution involving just ruler and compass with polar coordinate paper would apply to any relationship of the form $Y = A\sin(X-B)+C$ where we know the Y's for three X's and we want to find A, B and C.

The primary difficulties we have experienced with this technique are lack of facility for fine enough adjustment on our goniometer heads and their instability.

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