THE X-RAY DETERMINATION OF LATTICE CONSTANTS AND AXIAL RATIOS OF CRYSTALS BELONGING TO THE OBLIQUE SYSTEMS

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CONTENTS

Abstract . . . 416
Introduction . . . 417
Important Reciprocal Relations . . . 417
Relative Precision of X-Ray Determinations . . . 420
Determination of Linear Lattice Constants . . . 422
General Remarks . . . 422
Direct Determination of a, b, and c . . . 422
Direct Determination of a^*, b^*, and c^* . . . 424
Determination of Angular Lattice Constants . . . 425
Determination of α, β, and γ . . . 425
Method of Dome Offsets . . . 425
Monoclinic Case . . . 426
Triclinic Case . . . 428
Method of Triangulation . . . 431
Direct Determination of α^*, β^*, and γ^* . . . 431
Method of ω Separations . . . 431
Method of Triangulation . . . 431
The Determination of All Lattice Constants from One Crystal Setting . . . 432
Optimum Procedure Leading to Maximum Accuracy in Lattice Constants . . . 433

ABSTRACT

The determination of all the lattice constants of crystals belonging to the oblique systems has never received a systematic discussion, as a consequence of which the relative precisions of the several possible methods have not been treated, and certain possible methods have been neglected. A brief systematic discussion of the subject is given here. A distinction is made between determinations based upon chart measurements and those based upon steel scale and vernier measurements. The following new developments are included: (a) The attainment of precision in the determination of linear lattice constants with the rotating crystal technique. (b) The attainment of relative precision in the determination of angular lattice constants by the method of dome offsets. (c) The attainment of high precision in the determination of angular lattice constants by the method of triangulation.

The problem of the determination of all lattice constants with one crystal setting is discussed. This can be solved by Weissenberg methods without any plotting, with a precision comparable to that of optical goniometry. The determination of all lattice constants with extreme precision is also briefly considered, and it is shown that if the crystal can be oriented in three noncoplanar zones, these may be determined to about six significant figures, or with interaxial angles accurate to a few seconds of arc. The precision is independent of minor orientation errors and independent of minor crystal imperfections.

Introduction

The science of geometrical crystallography is primarily concerned with the study of the three-dimensional patterns of the repetitions of atoms in crystals. The motifs (the atom clusters themselves) repeated by the patterns are of no concern in this connection.

The sciences of descriptive geometrical crystallography, geometrical crystal classification, and geometrical crystal identification are based upon the possibility determinating the characteristic three-dimensional patterns of crystals. Patterns have two determinable fundamental aspects:

(a) A qualitative aspect—the determination of the pattern type. In crystals, this corresponds with the determination of the point-group symmetry (crystal class), the space lattice type, and the space group.

(b) A quantitative aspect—The determination of the magnitudes of the geometrical constants of the repeat periods. In crystals, this corresponds with a determination of the space lattice cell lengths, a, b, c, and interlinear angles, α, β, and γ.

The Weissenberg method (assisted by the simple rotating crystal method) is ideally suited to making both of these kinds of determinations.

The use of the Weissenberg method in the determination of the qualitative aspects (a) of the pattern has already been treated by the writer (1934, 1935, 1936A). The determination (b) of the lattice constants of crystals belonging to the orthogonal systems is relatively simple, and the methods are well known except in their precision aspects (Buerger, in press). The methods of arriving at the axial elements of crystals belonging to the oblique systems have received no systematic attention but have appeared from time to time in the form of incidental papers, appendanges and notes by Halla (1932, pp. 321–323), Tunell (1933), Barth & Tunnel (1933), Crowfoot (1935, pp. 218–222), Buerger (1936B, p. 580). As a result of this sporadic attention the comparative precisions of the several methods have been neglected, and several possible methods of determining important lattice elements have been overlooked. A brief systematic account of the determination of important linear and angular lattice constants of crystals belonging to the two oblique systems (monoclinic and triclinic) is given here.

Important Reciprocal Relations

Since each spot on a Weissenberg photograph corresponds with a point of the reciprocal lattice (Buerger, 1934, p. 357), many of the possible measurements made on a Weissenberg photograph have an immediate meaning in reciprocal space. Some of them, however, have an important meaning in direct space.

If the customary symbols,

	axial lengths	inter-axial angles	volume
direct lattice	$a,\ b,\ c$	$\alpha,\ \beta,\ \gamma$	v
reciprocal lattice	$a^*,\ b^*,\ c^*$	$\alpha^*,\ \beta^*,\ \gamma^*$	v^*

are adopted, then the important relations between direct and reciprocal lattice are as follows:

direct from reciprocal,

$$a=\frac{b^*c^* \sin \alpha^*}{v^*} \tag{1}$$

$$b=\frac{a^*c^* \sin \beta^*}{v^*} \tag{2}$$

$$c=\frac{a^*b^* \sin \gamma^*}{v^*} \tag{3}$$

reciprocal from direct,

$$a^*=\frac{bc \sin \alpha}{v} \tag{4}$$

$$b^*=\frac{ac \sin \beta}{v} \tag{5}$$

$$c^*=\frac{ab \sin \gamma}{v}. \tag{6}$$

The volume, v, of a triclinic parallelopiped may be expressed (Kraus & Mez, 1901, p. 390):

$$v=abc \sin \alpha \sin \beta \sin \gamma^* \tag{7}$$

$$=abc \sin \alpha \sin \beta^* \sin \gamma \tag{8}$$

$$=abc \sin \alpha^* \sin \beta \sin \gamma \tag{9}$$

$$v^*=a^*b^*c^* \sin \alpha^* \sin \beta^* \sin \gamma \tag{10}$$

$$=a^*b^*c^* \sin \alpha^* \sin \beta \sin \gamma^* \tag{11}$$

$$=a^*b^*c^* \sin \alpha \sin \beta^* \sin \gamma^*. \tag{12}$$

The volumes of the two cells are also reciprocal:

$$v=\frac{1}{v^*}. \tag{13}$$

Substitituting (7)–(12) in (1)–(6) gives the important relations:

$$a=\frac{1}{a^* \sin \beta^* \sin \gamma}=\frac{1}{a^* \sin \beta \sin \gamma^*} \tag{14}$$

$$b=\frac{1}{b^* \sin \gamma^* \sin \alpha}=\frac{1}{b^* \sin \gamma \sin \alpha^*} \tag{15}$$

$$c=\frac{1}{c^* \sin \alpha^* \sin \beta}=\frac{1}{c^* \sin \alpha \sin \beta^*} \tag{16}$$

$$a^*=\frac{1}{a \sin \beta \sin \gamma^*}=\frac{1}{a \sin \beta^* \sin \gamma} \tag{17}$$

$$b^*=\frac{1}{b \sin \alpha \sin \gamma^*}=\frac{1}{b \sin \alpha^* \sin \gamma} \tag{18}$$

$$c^*=\frac{1}{c \sin \alpha \sin \beta^*}=\frac{1}{c \sin \alpha^* \sin \beta}. \tag{19}$$

The polarform relation of Goldschmidt (1886, p. 14) also connects the direct and the reciprocal lattice:

$$a:b:c=\frac{\sin \alpha^*}{a^*}:\frac{\sin \beta^*}{b^*}:\frac{\sin \gamma^*}{c^*} \tag{20}$$

$$a^*:b^*:c^*=\frac{\sin \alpha}{a}:\frac{\sin \beta}{b}:\frac{\sin \gamma}{c}. \tag{21}$$

Goldschmidt's polarform relation, unfortunately, is of no use in the initial stages of a calculation, because solution of it for a direct lattice element from a reciprocal element, for example, requires a previous knowledge of one of the other two corresponding direct elements.

The direct and reciprocal angles are related to one another independent of the linear elements:

$$\alpha = 2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma^*}{2}\right)\sin\left(\frac{\Sigma^*}{2}-\alpha^*\right)}{\sin\beta^*\sin\gamma^*}} \tag{22}$$

$$\beta = 2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma^*}{2}\right)\sin\left(\frac{\Sigma^*}{2}-\beta^*\right)}{\sin\alpha^*\sin\gamma^*}} \tag{23}$$

$$\gamma = 2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma^*}{2}\right)\sin\left(\frac{\Sigma^*}{2}-\gamma^*\right)}{\sin\alpha^*\sin\beta^*}} \tag{24}$$

$$\alpha^* = 2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma}{2}\right)\sin\left(\frac{\Sigma}{2}-\alpha\right)}{\sin\beta\sin\gamma}} \tag{25}$$

$$\beta^* = 2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma}{2}\right)\sin\left(\frac{\Sigma}{2}-\beta\right)}{\sin\alpha\sin\gamma}} \tag{26}$$

$$\gamma^* = 2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma}{2}\right)\sin\left(\frac{\Sigma}{2}-\gamma\right)}{\sin\alpha\sin\beta}}. \tag{27}$$

The Relative Precision of X-Ray Determinations

The Weissenberg film is a two dimensional sheet and consequently two coördinates completely specify one of its points. The position of a reflection on the film is fixed in space while the film is a cylindrical surface in the camera, by two coplanar angles: ϕ, the reflection angle, and ω, the azimuthal orientation of the crystal at the time of reflection. The actual corresponding measurements made on the film to determine these are linear ones, and designated x and η respectively (Fig. 1). Now, from the point of view of precision, it is important to observe that the original equatorial reflections are focussed with respect to the circumference of the camera but not with respect to the axis of the camera. Unless a tiny crystal is used, therefore, each reflection on an equatorial photograph will be narrow along the $x(\phi)$ axis, but drawn out normal to the $\eta(\omega)$ axis. Determinations of the former may therefore be accurately made, while determinations of the latter cannot. The corresponding relations for n-layer photographs are somewhat more complicated.

Another source of error inherent in x-ray determinations depends upon the fact that while x coördinates are ordinarily rather reliable due to focussing, they cannot be depended upon for small values of x. This is because the absorption and thickness of the specimen tend to shift the center of the spot (Hadding, 1921) to a higher value of x. While this effect is a continuous function of x, the displacement is most important for spots near the center line of the film.

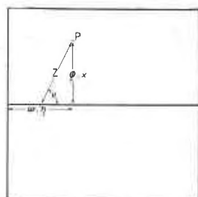

FIG. 1

A third source of error is due to the initial error in orienting the axis of the crystal parallel with the rotation axis. This sort of an error leads to only a negligible error in the x coördinate of a reflection, but causes an important error in η of approximately

$$\Delta\eta_{max} = r \tan (2e) \tag{28}$$

were e = the original angular orientation error. The resulting error in calculated ω angles thus amounts to

$$\Delta\omega_{max} = \frac{\Delta\eta_{max}}{K} = \frac{r \tan (2e)}{K} \tag{29}$$

where K = the coupling constant of the instrument, i.e., the number of millimeters translation of the camera per degree of crystal rotation. This error is serious. It can be reduced to some extent experimentally by using a narrow layer line screen slit (which will prevent recording if the orientation error, e, is high) and also by increasing the coupling constant, K. There is a physical limit to K if one wishes to keep the size of the Weissenberg instrument down to practical size.

Because of the first and last sources of error discussed, truly precise determinations of crystallographic constants cannot be based upon any methods involving measurements of η, but can only be based upon methods involving the measurement of x only. In other words, any precision determinations of lattice constants must be based upon measurements of reciprocal cell translations, which correspond with direct cell interplanar spacings.

In most cases the measurements mentioned above can be made against a steel millimeter scale (Tunell, 1933, p. 183; Buerger, *in press*, fig. 9) or with a vernier caliper.[1] If measurements are made with the aid of charts, however, such as d-charts, Z-charts, or ξ-charts, several additional sources of inaccuracy appear. In the first place, inaccuracies in the charts themselves reduce the precision of the measurement. Second, since non-uniform scales are inherent in charts, a vernier cannot be used in subdividing the chart graduations. The use of charts therefore reduces the precision of the results still further and determinations based upon chart measurements can only be considered rough determinations.

Determination of Linear Lattice Constants

General Remarks

The linear lattice constants of crystals may be derived by making measurements leading either directly to a, b and c or by making measurements leading directly to a^*, b^* and c^*. The latter scheme, at present the most accurate, is extremely tedious and roundabout for the oblique systems, since the final desired result (the direct lattice constants) can only be derived after a further knowledge of the angular lattice constants is gained (see equations (14)–(16)). If the latter can be only inaccurately determined, the calculated linear lattice constants must also remain inaccurately known.

Direct Determination of a, b, and c.

It is well known that the layer line spacings of a rotating crystal photograph lead directly to the identity period of the axis of rotation. The measurement method ordinarily employed for this purpose consists of (or is the equivalent of) laying the film directly on a Bernal (1926) chart which has been reduced to scale for the camera diameter used, and reading off the ζ coördinates of the layer lines directly. The identity period along the rotation axis is then

$$T = \frac{n\lambda}{\zeta} \tag{30}$$

n = layer number

λ = x-ray wavelength

ζ = reciprocal lattice coördinate of the layer line as read on the Bernal chart.

This method leads to very inaccurate estimates of the crystallographic axes because,

(a) charts are used, a source of inaccuracy previously discussed,
(b) the reflections are, in general, unfocussed normal to the ζ film coördinate,
(c) the apparent ζ coördinate increases as ζ decreases, due to absorption and thickness of the specimen, as already discussed, and
(d) orientation inaccuracies result in multiple, or broadened, layer lines.

This method can be made to yield greatly more accurate values of the identity period sought by eliminating or minimizing inaccuracies (a), (b), (c) and (d) in several ways:

(I) Inaccuracy source (a) can be eliminated by the direct measurement of the Bernal coördinate, y, instead of ζ. This enables one to use a scale and vernier. Suitable instruments for this purpose are indicated elsewhere. The appropriate relation corresponding to (30) for computation purposes is then

$$T=\frac{n\lambda}{\sin\ \tan^{-1}\left(\frac{y}{r}\right)} \tag{31}$$

where y = the height of the nth layer line measured from the zero layer line
r = the radius of the camera

(II) Inaccuracy source (c) may be minimized by measuring only spots of large x coördinates.

(III) Inaccuracy source (d) may be minimized, if recognized, by the following means: Each plane reflects to four spots on a rotation film, the spots having coördinates $x, y; x, -y; -x, y; -x, -y$. If an orientation error exists, the y coördinates of the first two and the second two pairs of spots will be displaced in the same direction by approximately the same amounts. If, therefore, the difference between the $+y$ and $-y$ coördinates of these spot pairs is measured, half of this difference is nearly the correct value of y to substitute in (31). If the form whose reflection is under consideration contains more than one centrosymmetrical pair of planes, as it does in the monoclinic system (but not in the triclinic system), then each of the spots in the above $+y$, $-y$ pair will be doubled. The upward shifted pair and the downward shifted pair should be considered separately for this measurement method.

This method can be carried out with the usual rotation photograph, provided the camera not only has a high x (ξ) range, but also provided that the film lies accurately along the camera circumference in this region. More appropriate photographs for this purpose, however, may be made by a back reflection method, since in this type of photograph the ξ range then becomes the maximum possible. Such photographs are

required for the increase in accuracy due to focussing, next mentioned:

(IV) Focussing in the y direction may be realized along the line $\xi = $ a maximum, i.e., along the line $x = \pi r$. This line is unattainable in ordinary rotation films because the film ends are placed in this region. If a back reflection photograph is used, however, this region is in the middle of the film.

Ordinarily, spots will not fortuitously appear having exactly the x coördinates of this line. If the rough value of the identity period, t, is known, however, polychromatic radiation may be employed (as from an alloy target, for example) and multiple layer lines may be produced. Spots having x fortuitously on or very near this line will then have their y coördinates focussed, and accurate values of y may be obtained. It should be observed that the geometrical aspects of this back reflection method are analogous to the flat-film, back reflection powder method of Sachs & Weerts (1930). Therefore, further accuracy is attainable by plotting the values of the lattice constant so obtained from several layer lines, against Sachs and Weerts' function

$$\text{ctg}\, \theta \cdot \sin 4\theta. \tag{32}$$

Extrapolation of the graph to $\theta = 90°$ gives a refined value of the identity period.

Direct Determination of a^*, b^*, and c^*

Rough determinations of the linear reciprocal lattice constants may be made with the aid of the Z scale using the relation

$$a^*, b^*, c^* = \frac{Z}{n\lambda} \cdot \tag{33A}$$

A more exact determination of these constants is identical with an exact determination of the interplanar spacings $d_{(100)}$, $d_{(010)}$, and $d_{(001)}$. This is easily accomplished from Weissenberg photographs (Buerger, 1935, p. 281) by measurements of the x coördinates of the appropriate reflections. The computation in this case is

$$d = \frac{n\lambda}{2 \sin\left(\dfrac{x}{2} \cdot \dfrac{360}{2\pi r_F}\right)} \cdot \tag{33B}$$

The precision of d can be greatly increased with the aid of an extrapolation method developed by Bradley and Jay (1932). In this method

the values of d as computed from measurements of different spots of different reflection order, n, are plotted against $\cos^2\theta$. The extrapolation of the curve (which is a straight line for high values of θ) so obtained, to $\theta=90°$ leads to the correct value of d. From this the correct value of a^*, b^*, or c^* can be obtained by taking the reciprocal of the appropriate multiple of d.

This important method of attaining precision in a^*, b^* and c^* is of the greatest value in attaining maximum precision in other crystallographic constants. A complete treatment of the subject will appear elsewhere (Buerger, *in press*).

Determination of Angular Lattice Constants

Determination of α, β and γ

Method of Dome Offsets. The n-layer reflections from the orthodomes of monoclinic crystals, and from macrodomes, brachydomes, and prisms of triclinic crystals, correspond with non-central reciprocal lattice lines (Buerger, 1934, p. 375). The amount of offset or departure, d, from a central lattice line can be measured in the equi-inclination method with the aid of an equi-inclination lattice line template. This offset, d, is a function of the reciprocal lattice level height, ζ, and the direct lattice angle α, β, or γ, as graphically shown in Figs. 2 and 4. From these figures it is evident that in either the monoclinic or triclinic system, the angular offset of the nth reciprocal lattice line of points is the direct crystallographic angle β. A measure of β may evidently be obtained with the aid of the following relation:

$$\tan\beta=\frac{\zeta}{d}. \qquad (34)$$

For chart determinations, ζ may be derived from the rotation photograph with the aid of the Bernal chart, and d may be derived from the n layer Weissenberg film by fitting the d interval template over the film and reading $d/\cos\mu$ directly from the template. This method of assigning values to oblique angles has been suggested by Miss Crowfoot (1935, p. 220).

A great gain in accuracy may be obtained in this method by avoiding the use of the chart and substituting a steel scale measurement of d. Because of symmetry, a direct measure of d may be obtained in the monoclinic system by measuring the x coördinate of the orthodome reflection nearest the center of the film (Fig. 3). If x_d is the cördinate of 011, then

$$d = 2 \cos \mu \sin \left(\frac{x_d}{2} \cdot \frac{360}{2\pi r} \right). \tag{34A}$$

This method is not of general application and cannot be applied in the triclinic system where symmetry is lacking. A still better way of determining d, however, is through the angular lag in the reflection of the dome series behind the pinacoid series, due to d. This angular lag, ψ, is a very sensitive measure of d for reciprocal lattice points near the origin, i.e., for dome reflections near the center of the film. The strategy of determinating d varies in monoclinic and triclinic cases.

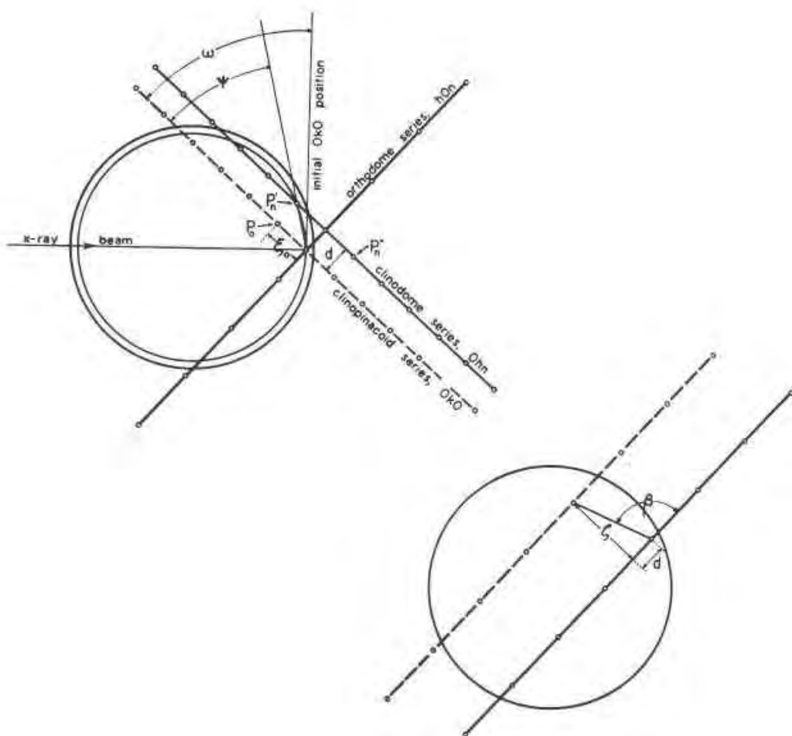

Fig. 2

Monoclinic Case. The following discussion applies to a monoclinic crystal rotated about the c-axis, but by interchange of notation, applies also to rotation about the a-axis. The upper part of Fig. 2 shows the important aspects of the plan of the first (or any n-) level of the reciprocal lattice. The beaded lines are the orthodome and clinodome series of reciprocal lattice points on this level. The latter is displaced a distance,

d, behind the corresponding clinopinacoid line (dashed) on the zero level; consequently a lattice point, P_n', of radial coördinate ξ_n from the rotation axis, reflects later than an imaginary lattice point of the same ξ_n coördinate on the zero level. The amount of this angular lag, ψ, is given by

$$\tan\psi = \frac{d}{\xi_0} \tag{35}$$

where ξ_0 is the radial coördinate of P_0, the pinacoid reflection on the zero level corresponding with dome reflection, P_n', on the nth level. Combining (35) with (34) gives

$$\beta = \tan^{-1} \frac{\zeta}{\xi_0 \tan \psi}. \tag{36}$$

Now the point, P_n, occurs in pairs symmetrically located on each side of the clinodome series. If the film coördinates of these two reflections are η' and η'' (Fig. 3), then the distance between these spots on the film

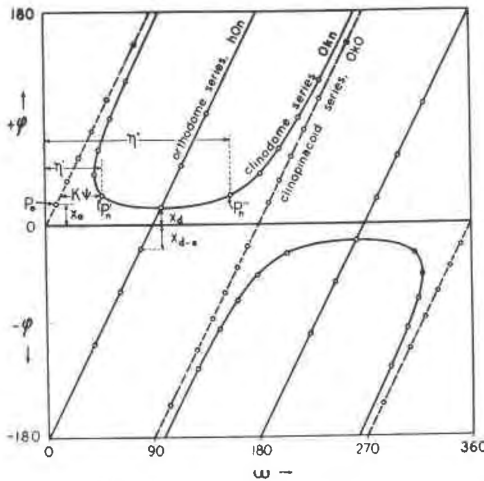

FIG. 3

$\eta''-\eta'$, is the film representation of the angular distance between these lattice points

$$\eta''-\eta' = K(180-2\psi) \tag{37}$$

or

$$\psi = 90 - \frac{\eta''-\eta'}{2K}. \tag{38}$$

Combining (36) with (38) gives

$$\beta=\tan^{-1}\left(\frac{\zeta}{\xi_0}\tan\frac{\eta''-\eta'}{2K}\right). \tag{39}$$

In this equation, ζ, the reciprocal lattice layer height, is determined from the rotation photograph and may have a value refined as demonstrated on page 424, and ξ_0 has a value determined from the x coördinate of the spot P_0' on the zero layer with the aid of the relation given by Buerger (1934, p. 362, equations 10 or 11).

$$\xi_0=2\sin\left(\frac{x}{2}\cdot\frac{360}{2\pi r}\right). \tag{40}$$

A considerably more accurate estimate of ξ_0 may be had, however, by computing spacing, $d_{(010)}$, from a number of ξ_0 measurements of the $(0k0)$ series, and determining a refined value of $d_{(010)}$ by the method of Bradley and Jay (1932). ξ_0 is derived by the reciprocal relation:

$$\xi_0=\frac{\lambda}{d_{(0k0)}}. \tag{41}$$

Returning to equation (39), it may be said that, of the variables indicated there, ξ_0 can be determined with relatively great precision. ζ can also be determined with considerable precision by the methods outlined on page 424. The angular difference represented by $\eta''-\eta'$ is subject to the main lack of precision. This includes the matters mentioned on page 421, as well as the error of setting the equi-inclination angle (Buerger, 1936, p. 96). An error in this setting, however, can be detected, if present, by a lack of straightness of the orthodome series of reflections.

Triclinic case. In Figs. 4 and 5 the triclinic case corresponding with the monoclinic case of Figs. 2 and 3 is shown. The triclinic case offers a more complicated situation and the lack of specialization makes new measurement strategies necessary.

The value of ξ_0 can no longer be used in computing d. Instead, the relation

$$\sin\psi=\frac{d}{\xi_n} \tag{42}$$

must be used. Furthermore, the reflection P_n no longer has a symmetrical companion, so some other method must be devised for the measurement of the film equivalent of ψ. The difficulty here is that there is no zero on the n layer film from which to measure ψ intervals. The difficulty can

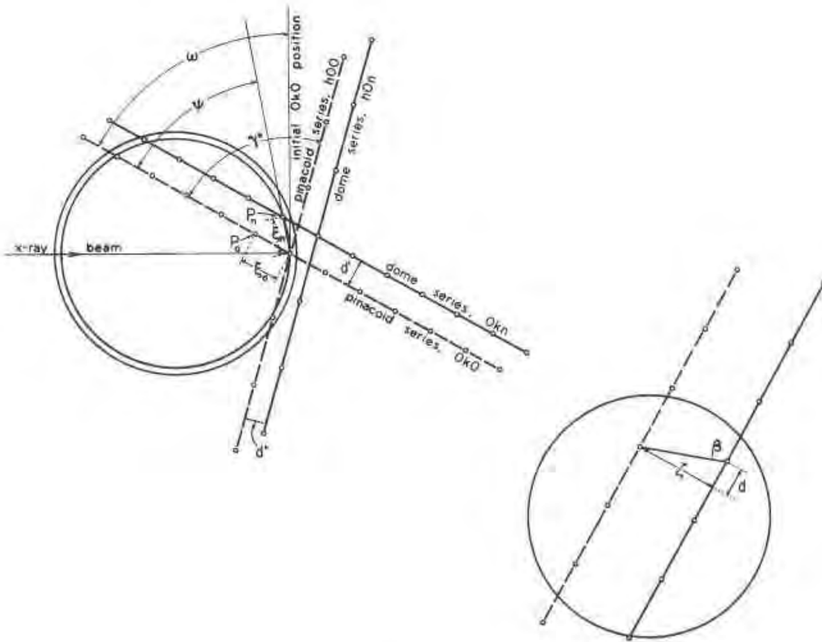

FIG. 4

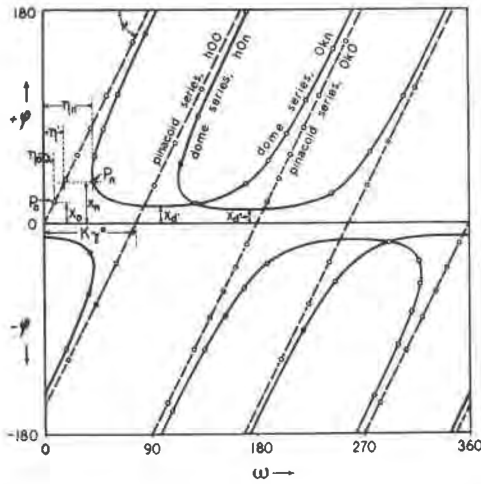

FIG. 5

be overcome if some equivalent fiducial mark can be made both on the zero and n layer films. This can be accomplished in either of two ways:

(a) The direct beam may be recorded on each film when the crystal rotation spindle has identical settings. The fiducial mark of the n layer film is then at $-2s$ compared

with that on the equator film, where s is given by (43) below. This method requires a very accurate crystal rotation spindle setting, which is not very easily accomplished, and also records the fiducial mark in the form of a shadow, instead of a reflection.

(b) The recommended method is to record both zero and n-layer on the same film without any experimental changes except the change in equi-inclination setting, and the corresponding changes in camera settings (Buerger, 1936, p. 94).

The latter change must be exact for this purpose, and is possible with the instrument designed by the writer (1936). If the camera is set on its carriage with the camera scale reading zero for the zero layer, the setting, s, for the nth layer is

$$s = r_F \tan \beta \tag{43}$$

where r_F = the effective film radius

β = the equi-inclination setting

With the zero and n layers recorded on the same film, the angle of lag, ψ, of the dome reflections behind the pinacoid reflections can be measured (Fig. 5). For a definite reference point in the pinacoid reflection line, select a pinacoid reflection preferably with an x coördinate near to the corresponding coördinate of the dome reflection P_n. If now, the coördinates of the several important points on the film are:

η_n, x_n = the film coördinates of the dome reflection P_n

η_0, x_0 = the film coördinates of a pinacoid reflection P_0

η', x_n = the film coördinates of a point on the P_0 reflection series

then,
$$K\psi = (\eta_n - \eta_0) - (\eta' - \eta_0) \tag{44}$$

and since $\tan \nu = \dfrac{x}{\eta}$, (Buerger, 1934, p. 366), (45)

$$K\psi = (\eta_n - \eta_0) - \frac{(x_n - x_0)}{\tan \nu}. \tag{46}$$

Substituting (46) in (42) gives:

$$d = \xi_n \sin \left\{ \frac{1}{K} \left[(\eta_n - \eta_0) - \frac{(x_n - x_0)}{\tan \nu} \right] \right\}. \tag{47}$$

In the triclinic case, β (or α, by using the second set of dome offsets) is determinable by (34). The value of d may be crudely obtained for this equation by fitting the equi-inclination chart to the spots on the film. It may be obtained much more accurately directly from steel scale and vernier film measurements by combining (47) and (34) which gives:

$$\beta = \tan^{-1} \frac{\zeta}{\xi_n \sin\left\{\frac{1}{K}\left[(\eta_n - \eta_0) - \frac{(x_n - x_0)}{\tan \nu}\right]\right\}}. \tag{48}$$

The sources of error in the solution of (48) are similar to those encountered in the monoclinic case, and there are two additional sources of possible inaccuracy: a possible inaccuracy in the camera setting, s, for the nth layer, and the inferior accuracy of the determination of ξ_n as compared with ξ_0.

Method of triangulation. The identity periods of a crystal along a, c, and [101] may be obtained from rotation photographs about these three directions. These three identity periods form a triangle whose obtuse angle is the crystallographic angle β. Since the three sides of the triangle are known, the angle may be calculated. All three angles of a triclinic crystal may be calculated from a knowledge of the six identity periods a, [110], b, [011], c, and [101], and these data may be obtained from the six corresponding rotation photographs.

This method of calculating interaxial angles is not ordinarily of much practical importance since, if the crystal is sufficiently well developed to permit orientations of the rotation axes parallel with these zones, the reciprocal interaxial angles may be measured with an optical goniometer and the direct interaxial angles calculated from them.

Direct Determination of α^*, β^*, and γ^*

Method of ω separations. If the b axis zero layer Weissenberg film is placed on the coördinate measuring device so that the measuring line is parallel with the Z lines of reflection orders, then the film measurement between the reflection orders of (100) and (001) is

$$m = K\beta^* \sin \nu. \tag{49}$$

The easiest method of arriving at any crystallographic angle is thus this measurement of interplanar angles on equatorial Weissenberg films. Unfortunately it is also quite inaccurate for reasons stated on page 424.

Method of triangulation. The reciprocal lattice vectors a^*, c^*, $[10\bar{1}]^*$ form a triangle which includes the reciprocal lattice angle β^*. These three linear elements may be very accurately determined, hence β^* can be very accurately computed. Similarly α^* can be computed from b^*, c^*, $[011]^*$, and γ^* can be very accurately computed from a^*, b^*, $[1\bar{1}0]^*$. This method is the most accurate one for determining any crystallographic angles because the angles depend upon spacing measurements, which can be very accurately made.

The Determination of All Lattice Constants from One Crystal Setting

An important problem which occasionally arises is the determination of all the lattice constants of a crystal which is only sufficiently well developed to permit orientation about one zone. A small acicular crystal without terminations presents a case in point. This problem cannot be solved by optical goniometric methods.

Barth and Tunell (1933) have discussed the graphical solution of this problem using the normal beam technique, and as applied to the determination of the lattice constants of chalcanthite. The problem may be more accurately solved without any plotting whatever using the equi-inclination technique, and making only steel scale and vernier measurements. Three films are required: a rotation photograph, a Weissenberg equator photograph, and an equi-inclination Weissenberg n-layer photograph. If the symmetry of the latter proves the crystal to be triclinic, it is desirable, for maximum accuracy, to have, in addition, another single film combining the equator and equi-inclination Weissenberg n-layer recording.

Suppose that the crystal is undescribed. The needle axis (or zone sufficiently well developed for orientation) may be chosen as the c-axis. The status of information determinable from the photographs is then as follows:

Computable from film measurements discussed:	a^*,	b^*,	c,	α,	β,	γ^*
Remaining direct lattice constants to be found:	a,	b,				γ

Of the remaining direct lattice elements, a may be computed from the upper list with the aid of (14) and b with the aid of (15). With these direct elements known, γ may be computed from Goldschmidt's polar-form relation (21). The appropriate equations to use for the computation of the several lattice constants for different rotation axes is indicated in table 1.

It follows from the above discussion that a single setting of a crystal permits the preparation of x-ray films from which all lattice constants can be computed. No graphical interpretation or construction is required, and the results have an accuracy comparable with those obtainable from surface morphological studies of a well developed crystal made with an optical goniometer, provided the precautions discussed above are observed. The results are distinctly inferior to those obtained by optical goniometry if chart measurements are used for computations.

Optimum Procedure Leading to Maximum Accuracy in Lattice Constants

It has been pointed out that measurements of η (ω) are subject to maximum errors and that therefore computations based upon these measurements are least reliable, while measurements of x (ϕ) are made with great accuracy. Add to this the fact that the latter measurements are transposable without error into interplanar spacing values, $d_{(hkl)}$, which can be refined by Bradley and Jay's method, and it is apparent that crystal lattice constants which can be expressed as functions of x measurements alone can be determined with the greatest precision.

Now, all lattice constants can be expressed in terms of such measurements, provided only that a crystal is available which is sufficiently well developed to permit orientations for rotations about any three non-coplanar axes. Suppose that these axes are chosen as the three crystallographic axes. Then, with the aid of three equatorial Weissenberg photographs, the data given in column II below can be directly determined.

I	II	III
rotation axis	precisely determinable constants	additional contants precisely computable from values in column II
a	b^*, $[01\bar{1}]^*$, c^*	α^*
b	a^*, $[10\bar{1}]^*$, c^*	β^*
c	b^*, $[1\bar{1}0]^*$, a^*	γ^*

From the six distinct linear reciprocal values in column II, the reciprocal lattice angles in column III can be precisely computed by the method of triangulation. From these reciprocal angles, the direct lattice angles may be computed with the aid of (22), (23), and (24). With the values of a^*, b^*, c^*; α^*, β^*, γ^*; α, β, and γ, which are then available, the values of a, b, and c may be precisély computed with the aids of equations (14), (15) and (16).

All these values rest solely upon refined spacing measurements. The results are easily comparable, if not superior, to those computed from interfacial angle measurements made with an optical goniometer, and this accuracy is obtainable without much precaution. The method is of such obvious promise that the writer (1936 C) has developed a special back-reflection Weissenberg instrument for taking full advantage of it.

The instrument, and method of attaining extreme precision in the determination of all lattice constants with its aid, will be described elsewhere (Buerger, *in press*). It may be mentioned that, by the methods there outlined, linear lattice constants can be determined with a precision of about six significant figures (Axial ratios are now customarily quoted to four significant figures.) Since this precision pervades the entire work, the angular lattice constants can be determined with an accuracy of a few seconds of arc. This represents a great improvement in crystal goniometry, and it may be mentioned that the method is almost independent of crystal imperfections which, in ordinary optical goniometric work, prevent the attainment of even the angular measuring accuracy possible in the instrument.

TABLE 1. TABULATION OF COMPUTATIONAL FORMULAE NECESSARY IN THE DETERMINATION OF ALL LATTICE CONSTANTS FROM ONE CRYSTAL SETTING. M, CORRECT FORMULA FOR MONOCLINIC CRYSTAL; T, FOR TRICLINIC CRYSTAL.

I rotation axis	II constants directly computable	III formula for rough computation from chart measurements	IV formula for accurate computation from steel scale measurements	V constants indirectly computable	VI formula for computation of values of V from values of II
	a	(30)	(31)		
	b^*	(33A)	(33B)	b	(15)
a	c^*	(33A)	(33B)	c	(16)
	α^*	(49)	triangulation	α	(21)
	β	(34)	(39M) (48T)		
	γ	(34)	(48)		
	a^*	(33A)	(33B)	a	(14)
	b	(30)	(31)		
b	c^*	(33A)	(33B)	c	(16)
	α	(34)	(48)		
	β^*	(49)	triangulation	β	(21)
	γ	(34)	(48)		
	a^*	(33A)	(33B)	a	(14)
	b^*	(33A)	(33B)	b	(15)
	c	(30)	(31)		
c	α	(34)	(48)		
	β	(34)	(39M) (48T)		
	γ^*	(49)	triangulation	γ	(21)

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