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Geometrical Properties of a Four-Circle Neutron Diffractometer for Measuring Intensities at an 'Optimum' Azimuth of the Reflecting Planes

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A procedure is described for calculating the setting angles of a four-circle neutron diffractometer for a single crystal of known lattice parameters. These angles are calculated as a function of the azimuth of the reflecting planes. In order to reduce the influence of the Renninger effect on the measured intensities, a method is proposed for computing an optimum value of the azimuth for each plane.

Introduction

In recent years it has been shown (Moon & Shull, 1961; Borgonovi & Caglioti, 1962; Willis & Valentine, 1962) that in many important cases the 'Renninger effect', or 'multiple Bragg scattering' (Renninger, 1937), has a significant influence on the measured intensities in neutron-diffraction work.

Because of this effect, the intensity reflected by a crystal plane undergoes considerable variations when the plane is rotated about the scattering vector (azimuthal rotation); such variations take place when the Bragg equation is simultaneously satisfied by other crystal planes.

It seems advisable, then, to measure the intensity of a reflexion at the values of the azimuth for which no multiple scattering occurs.

A four-circle diffractometer makes it possible to measure the intensities of all the reflexions from a single crystal* in the horizontal plane of the instrument and at any selected values of the azimuthal angle ψ.

Some of the geometrical properties of such an instrument have been described by Willis (1961, 1962), and Sabine (1963).

In the present paper we outline a method for calculating the four setting angles for any *hkl*, as a function of the lattice parameters and of the selected value of ψ; in addition, we propose a procedure for determining those values of ψ for which the Renninger effect is relatively less important or, in favorable cases, totally absent.

Reference systems and crystal orientation

The diffractometer comprises four circles designated Φ, χ, Ω and 2Θ. The Φ-circle axis rotates about the axis of the χ-circle; the Φ- and χ-circle axes are always perpendicular to each other. The Φ–χ-circle assembly rotates about the Ω-axis coincident with, but independent of the detector axis 2Θ, the 2Θ shaft being simply that about which the detector moves (Fig. 1).

To define the origins of the rotations and their positive directions, it is convenient to introduce a cartesian coordinate system attached to the laboratory in the following way:

(*a*) Z axis, perpendicular to the plane of the detector's circle;

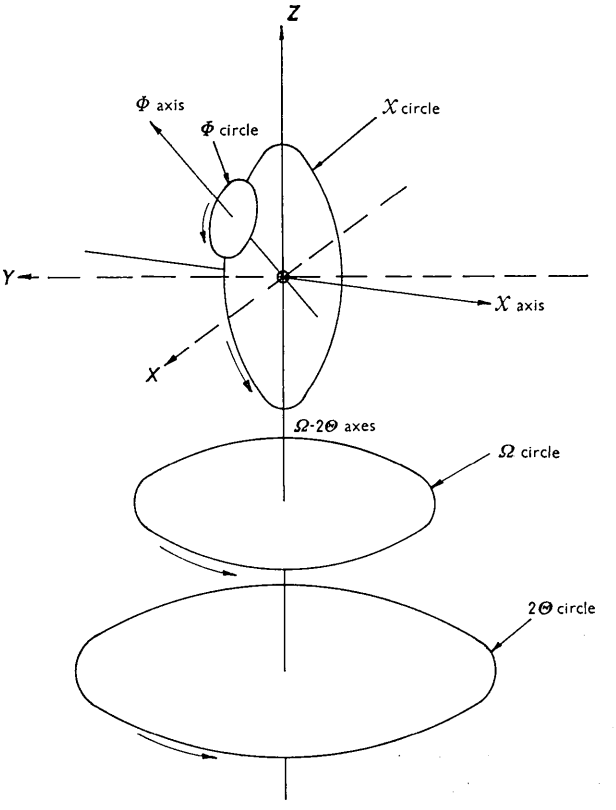

Fig. 1. Arrangement of the four circles of the diffractometer. The neutron detector is carried by the 2Θ circle.

* Actually, there is a small 'blind' region of the reciprocal space due to the finite dimensions of the diffractometer circles.

(*b*) Y axis, coincident with the neutron monochromatic beam;
(*c*) X axis, perpendicular to the YZ plane and oriented so that the scattering vectors have their x components positive.

The Z axis is oriented so that left-handed coordinates result for diffractometers with counterclockwise θ-motion, as seen from the top of the instrument, and right-handed coordinates for the others.

This criterion, together with the proper choice of the rotations on the four circles, makes it possible to obtain equations for the setting angles which apply to both cases.

The four-circle assembly is oriented with respect to the reference system so that the 2Θ and Ω axes are always coincident with the Z axis; therefore the Φ-circle axis always lies in a plane perpendicular to the XY plane and the χ-circle axis is always parallel to the XY plane.

We define a 'standard orientation' of the diffractometer as follows:

(*a*) The 2Θ, Ω and Φ axes point in the same direction as the Z axis;
(*b*) The χ-axis points in the direction opposite to the Y axis.

The origins for the rotations are defined so that $\omega=2\theta=\chi=0$, when the diffractometer is in its standard orientation, with the counter in position to pick up the primary beam and the crystal located between the Φ and 2Θ circles. The origin of φ is arbitrary.

The crystal is mounted on the goniometer arcs attached to the Φ circle of the diffractometer, kept in its standard setting, and has to be oriented, by means of the goniometer head arcs, so that:

(*a*) A rational line of known indices comes to point in the same direction as the Z axis; this line and its reciprocal will be indicated by **V** and **V***, respectively.
(*b*) A reciprocal vector becomes coincident with the X axis. This vector and its correspondent direct element will be indicated by **P*** and **P**, respectively.
(*c*) A reciprocal vector comes to lie in the XY plane, with positive y-component; this vector and its corresponding direct element will be indicated by **T*** and **T**, respectively.

The indices of a reciprocal point referred to these new axes will be named p, t, v.

In the calculation of the setting angles we will use, as unit cell of the crystal, the cell with the edges P, T, V. The procedure for computing the direct and reciprocal elements of this 'orientation' cell from the standard lattice parameters, a, b, c, α, β, γ, is based on the determination of the transformation matrix from particular index transformations (Buerger, 1942). A pair of planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ defining the vertical zone-axis are first identified; the zone symbol $[HKL]$ is then calculated and a third plane with indices $(h_3k_3l_3)$ equal to the zone symbol is selected. Assigning the new indices (100), (010) and (001) respectively to these planes, the elements of the transformation matrix and the elements of the orientation cell are calculated.

Finally we adopt as positive the rotations given by the right-handed screw rule if the left-handed reference system is used, and by the left-handed screw rule if the right-handed reference system is used.

It is worth noting that the same setting angles can be used independently of whether $+\mathbf{V}$ or $-\mathbf{V}$ points away from the goniometer head, if the screw rule is reversed in the two cases.

Setting angles

Let us suppose that, initially, the diffractometer is in its standard orientation.

To bring a reciprocal point into the reflecting position in the horizontal plane of the diffractometer at an azimuth ψ, one has to rotate the crystal through an angle φ about the Z axis, through an angle χ about the Y axis and through an angle $\theta+\omega$ about the Z axis. (Fig. 2).

The simplest way to relate the azimuth ψ with the setting angles is to divide the φ rotation into two parts φ_L and φ', where φ' is a simple function of ψ, and φ_L is the rotation which brings the reciprocal point onto the χ-circle plane.

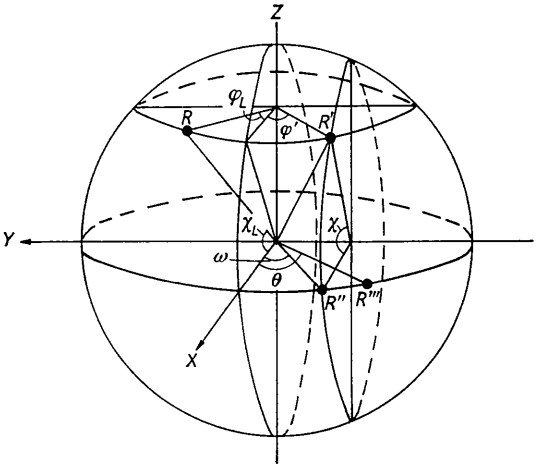

Fig. 2. Diagram showing the rotations required to bring into reflecting position (R''') a reciprocal point (R). R' and R'' are the positions of the reciprocal point after the rotations $\varphi_L+\varphi'$ and χ respectively.

The cartesian coordinates x, y, z, of a reciprocal point ptv are given by:

$$x=pP^*+tT^*\cos\widehat{P^*T^*}+vV^*\cos\widehat{P^*V^*}$$
$$y=tT^*\sin\widehat{P^*T^*}-vV^*\cos\widehat{TV}\sin\widehat{P^*V^*}$$
$$z=vV^*\sin\widehat{TV}\sin\widehat{P^*V^*} \qquad (1)$$

where P, T, V, *etc.* are the elements of the orientation cell (Appendix I).

In order to bring a point x, y, z into reflecting position one has to rotate the crystal through the angles $\varphi=\varphi_L+\varphi'$, χ, $\theta+\omega$ where (Appendix II):

$$\tan\varphi_L=y/x \tag{2}$$

$$\tan\varphi'=-\frac{d^*}{z}\tan\psi \tag{3}$$

$$\tan\chi=\frac{n|(z^2+d^{*2}\tan^2\psi)^{\frac{1}{2}}|}{x_p} \tag{4}$$

$$\sin\omega=-\frac{x_p}{d^*}\sin\varphi' \tag{5}$$

$$\sin\theta=d^*/2 \tag{6}$$

In the above equations x_p is the first coordinate of the reciprocal point after the φ_L rotation, *i.e.*

$$x_p=x\cos\varphi_L+y\sin\varphi_L$$

d^* is the reciprocal vector length, and:

$$n=\begin{cases}+1, & \text{if } z>0\\ -1, & \text{if } z<0\end{cases} \text{ and for } z=0: n=\begin{cases}+1, & \text{if } \tan\psi\geq 0\\ -1, & \text{if } \tan\psi<0\end{cases}$$

We shall see later that in order to find an 'optimum' value of the azimuth it is sufficient to consider only a part of the full range of 360°; to save computing time it is convenient to limit the angular range of ψ, and therefore of φ', χ and ω, between $-90°$ and $+90°$.

There are cases in which such angular limitations are imposed by mechanical restraints mainly depending on how the Φ circle is mounted on the χ circle.

The setting equations show that for $z=0$ (equatorial reflexions) the φ' rotation brings the reciprocal vector perpendicular to the χ-circle plane, so that (see equation 4) the variation of the azimuth is provided by the rotation about the χ axis.

If $z=d^*$ (*i.e.* $x_p=0$; reciprocal point on the vertical axis) $\chi=90°$ and $\tan\varphi'=-\tan\psi$. In this case the ψ-rotation is provided by the rotation about the Φ axis.

For $\psi=0$ the above equations become:

$$\tan\varphi_L=y/x;\ \tan\chi_L=z/x_p;\ \tan\varphi'=0;\quad \sin\omega=0;\ \sin\theta=d^*/2\,. \tag{7}$$

Equations (7) are used for calculating the setting angles of a three-circle diffractometer in which the scattering vectors always lie in the χ plane (Levy & Busing, 1962; Furnas & Harker, 1955). If in addition $z=0$ (two-circle diffractometer; Prince & Abrahams, 1959), only φ_L and θ have to be calculated; in this case only one plane in the reciprocal space can be investigated for a given mounting of the crystal.

Geometrical conditions for simultaneous reflexion

For computing purposes it is convenient to suppose that a reciprocal point *ptv* ('primary' reflexion) is brought into the reflecting position, at an arbitrary azimuth ψ, through the rotations φ_L about Z, χ_L about Y, ψ about X, and θ about Z. The angles φ_L, χ_L, and θ are easily calculated, using equations (1) and (7) from the indices *ptv* and from the elements of the orientation cell.

The coordinates x_i, y_i, z_i, of any other reciprocal point $p_it_iv_i$, are transformed by each of the four rotations, in accordance with the following transformation matrices:

$$A=\begin{pmatrix} g & h & 0\\ -h & g & 0\\ 0 & 0 & 1\end{pmatrix};\ B=\begin{pmatrix} e & 0 & f\\ 0 & 1 & 0\\ -f & 0 & e\end{pmatrix};$$

$$C=\begin{pmatrix}1 & 0 & 0\\ 0 & c & -d\\ 0 & d & c\end{pmatrix};\ D=\begin{pmatrix} a & b & 0\\ -b & a & 0\\ 0 & 0 & 1\end{pmatrix}$$

where:

$$a=\cos\theta;\ c=\cos\psi;\ e=\cos\chi_L;\ g=\cos\varphi_L$$
$$b=\sin\theta;\ d=\sin\psi;\ f=\sin\chi_L;\ h=\sin\varphi_L$$

The resultant transformation is given by:

$$\mathbf{R}=\begin{pmatrix}\{(ae+fbd)g-bch\} & \{(ae+fbd)h+bcg\} & \{af-bde\}\\ \{(-be+fda)g-ach\} & \{(-be+fda)h+acg\} & \{-bf-dae\}\\ \{-cfg-hd\} & \{-cfh+dg\} & \{ce\}\end{pmatrix} \tag{8}$$

Using matrix (8) we are able to calculate the final coordinates x_f, y_f and z_f of every reciprocal point after the point *ptv* under examination has been brought into the reflecting position.

Simultaneous reflexion takes place if, in addition to *ptv*, other reciprocal points $p_it_iv_i$ lie on the reflexion sphere ('secondary' reflexions).

If the centre of this sphere has coordinates $x=0$, $y=-1$, $z=0$, the condition for reflexion is:

$$x_f^2+(y_f+1)^2+z_f^2=1$$

i.e.

$$d_i^{*2}=-2y_f \tag{9}$$

From (9) it is evident that the solution is real for $y_f\leq 0$.

Expressing y_f as a function of ψ and θ, from (8) we get:

$$y_f=L\cos\theta\sin\psi-M\cos\theta\cos\psi-N\sin\theta \tag{10}$$

where:

$$L=(x_ig+y_ih)f-z_ie;\ M=x_ih-y_ig;\quad N=(x_ig+y_ih)e+z_if\,.$$

A possible procedure for checking for simultaneous reflexion is as follows:

(*a*) The rotations φ_L, χ_L, and θ are calculated for the reflexion to be measured;

(*b*) An arbitrary value for ψ is selected;

(*c*) Using equation (10) the y_f's for all the reciprocal points within the limiting sphere are calculated;

(*d*) If no reciprocal point satisfies equation (9), no simultaneous reflexion for the selected value of ψ occurs.

Such a value of ψ is not necessarily suitable for intensity measurements because of the finite width of the Renninger peaks.

Computation of the 'optimum' value of ψ

It seems proper to consider a value of ψ eligible for an intensity measurement when no simultaneous reflexions occur in the interval $\psi-\varepsilon$, $\psi+\varepsilon$, where ε is related to the width of the Renninger peaks.

Accordingly, each reciprocal point $p_it_iv_i$ covers an interval of y_f's as the crystal is supposed to rotate from $\psi-\varepsilon$ to $\psi+\varepsilon$ about the scattering vector corresponding to the point *ptv* under examination.

In Appendix III, the limits R_i, and S_i of the interval of y are calculated; for a given *ptv*, R_i and S_i depend on $p_it_iv_i$, ψ and ε.

Therefore, a point $p_it_iv_i$ is simultaneously reflected in the interval $\psi-\varepsilon$, $\psi+\varepsilon$ if:

$$R_i \leq -d_i^{*2}/2 \leq S_i\,. \qquad (11)$$

The width of the Renninger peaks is, in general, unknown so that any *a priori* evaluation of ε is not possible.

In order to overcome this difficulty the following procedure can be proposed:

First an $\varepsilon_{\min}$ and an $\varepsilon_{\max}$ are selected in a reasonable way; for example $\varepsilon_{\min}$=half-maximum width of the reflexion under examination, and $\varepsilon_{\max}=n\varepsilon_{\min}$ (n is about 5 or more). Next, for a given ψ, the limits R_i and S_i are calculated for every reciprocal point $p_it_iv_i$ within the limiting sphere, using the value $\varepsilon_{\max}$. If relation (11) is satisfied by no $p_it_iv_i$'s, the chosen ψ can be used to calculate the setting angles. If this is not the case, the angle $\varepsilon_{\max}$ is decreased by a proper amount and the whole procedure is repeated with the new $\varepsilon<\varepsilon_{\max}$.

Two cases are possible:

(i) In reducing ε the value of $\varepsilon_{\min}$ is reached and the corresponding interval $\psi-\varepsilon_{\min}$, $\psi+\varepsilon_{\min}$ is not free from Renninger peaks. In this case the selected ψ is excluded from any further consideration.

(ii) An $\varepsilon \geq \varepsilon_{\min}$ is found such that the interval $\psi-\varepsilon$, $\psi+\varepsilon$ is free from Renninger peaks. In this case the selected ψ is one of the eligible azimuths for the intensity measurement. By repetition of this procedure for values of ψ taken in regular steps, a list of ψ's and corresponding ε's is obtained.

It can be assumed that the 'optimum' value of ψ is the one in the list corresponding to the largest value of ε. This is the value of ψ we propose to use in calculating the setting angles.

If finally, none of the ψ's are eligible, we have to assume an arbitrary value of ψ (for example $\psi=0°$) as the azimuth of the measurement.

In general, the azimuth of a given reflecting plane *ptv* cannot be changed over the full range of 360° because of the physical dimensions of the χ and Φ circles, and those of the neutron beam.

In fact, for certain values of the angle $\theta+\omega$ the metal ring of the χ circle obstructs the neutron beam; as ω is a function of ψ this has the effect of limiting the angular range of ψ. As a consequence some of the eligible azimuths have to be excluded form the list $\psi(\varepsilon)$.

In addition to the above limitations on ψ, others are sometimes imposed by the construction features of the circles; for example full 360° rotation of χ may not be possible, the range of ψ being thus limited similarly.

It does not seem that the restrictions on the azimuth discussed above have any important effects on the possibility of finding an optimum value of ψ, provided that the azimuth is scanned in sufficiently small steps in the permissible range.

In the case of a large unit cell the probability of finding an azimuth with a reasonably large value of ε is very small; to overcome this difficulty one has to reduce the value $\varepsilon_{\min}$, or increase the wavelength, or both.

Conclusions

In this paper a method has been described for measuring the intensities of reflexions from single crystals with a four-circle diffractometer. With such an instrument it is possible to change the azimuth of the reflecting planes and, for this reason, to reduce the influence of the Renninger effect on the measured intensities.

A method for computing an optimum value of the azimuth has been proposed. This method makes it possible to measure the intensity of a reflexion only once with an accuracy which is probably the same as or better than the one obtainable by measuring the same reflexion at different values of the azimuth.

It is not possible to predict with certainty whether the Renninger effect is important in a particular case. A systematic effort to determine the importance of such effect in a number of different experimental conditions will be undertaken with the automatic four-circle diffractometer — based on the principles here described — now under construction. A computer program for calculating the setting angles for such a diffractometer has been written in FORTRAN and tested in a few experimental cases. In all the considered cases (cubic crystals of different reciprocal parameters), the program takes a few seconds per reflexion on the IBM 7090 computer, for a given value of ε.

For all the reflexions the program computes an azimuth free from Renninger peaks for the selected value of ε.

We think, therefore, that the computation of the setting angles for a crystal can be carried out routinely by the program also in more complicated cases.

The program will be described in a subsequent paper.

APPENDIX I

Calculation of the cartesian coordinates of a reciprocal point

From Fig. 3 we have:

$$\begin{aligned} x &= OC' = OA + AE + EC' \\ &= pP^* + tT^* \cos \widehat{P^*T^*} + vV^* \cos\mu \cos\nu \\ y &= CC' = CD + DC' \\ &= vV^* \cos\mu \sin\nu + tT^* \sin \widehat{P^*T^*} \\ z &= RC = vV^* \sin\mu \,. \end{aligned} \tag{12}$$

From the Napierian triangle FHL represented in the stereogram of the reciprocal cell vectors (Fig. 4) we have:

$$\cos\mu \cos\nu = \cos \widehat{P^*V^*} \tag{13}$$

and:

$$\tan\nu = -\cos \widehat{TV} \tan \widehat{P^*V^*} \,. \tag{14}$$

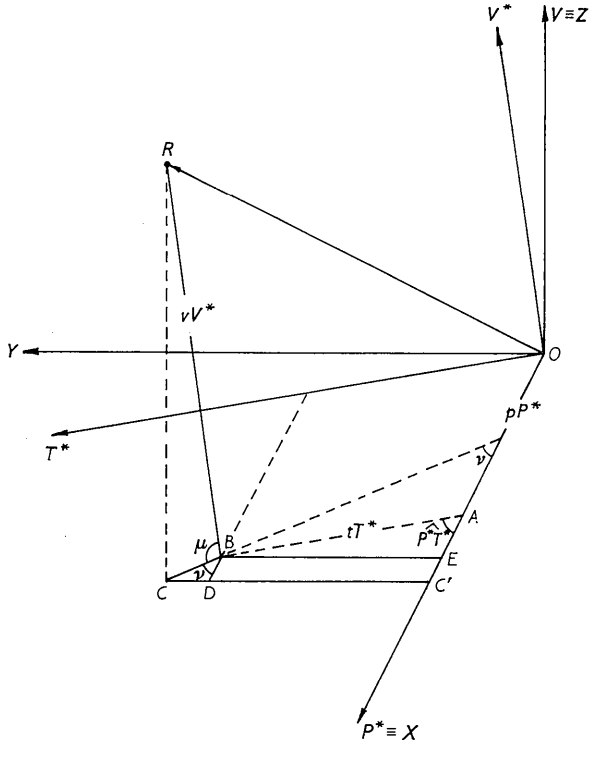

Fig. 3. Perspective view of the linear and angular elements involved in the determination of the setting angles.

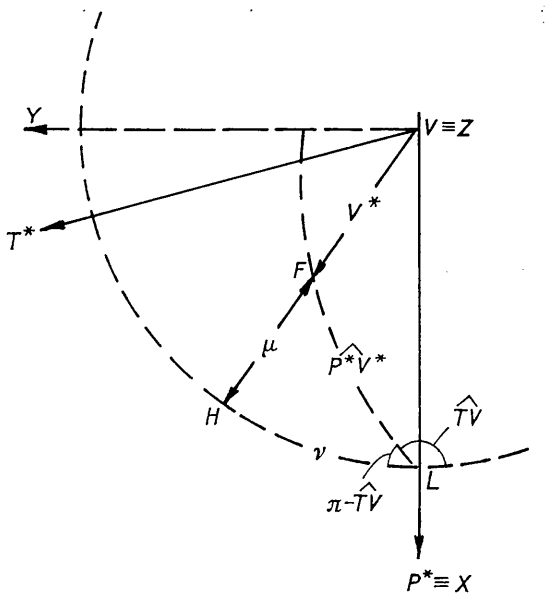

Fig. 4. Stereogram of the reciprocal cell vectors.

By combining (13) and (14) we obtain:

$$\sin\nu \cos\mu = -\cos \widehat{TV} \sin \widehat{P^*V^*} \,. \tag{15}$$

From the same triangle we get, finally:

$$\sin\mu = \sin \widehat{TV} \sin \widehat{P^*V^*} \,. \tag{16}$$

By substituting (13), (15) and (16) into (12), equations (1) are obtained.

APPENDIX II

Calculation of the setting angles

The cartesian coordinates x_p, y_p, z_p of a reciprocal point x, y, z, after the rotation φ_L are given by:

$$\begin{aligned} x_p &= x \cos\varphi_L + y \sin\varphi_L \\ y_p &= -x \sin\varphi_L + y \cos\varphi_L = 0 \\ z_p &= z \,. \end{aligned} \tag{17}$$

From the second equation of (17), equation (2) is obtained.

The rotations φ', χ and ω transform x_p, y_p, and z_p in the following way:

$$\begin{aligned} x' &= x_p \cos\varphi' \\ y' &= -x_p \sin\varphi' \\ z' &= z \end{aligned} \tag{18}$$

$$\begin{aligned} x'' &= x' \cos\chi + z' \sin\chi \\ y'' &= y' \\ z'' &= -x' \sin\chi + z' \cos\chi = 0 \end{aligned} \tag{19}$$

$$\begin{aligned} x''' &= x'' \cos\omega + y'' \sin\omega = d^* \\ y''' &= -x'' \sin\omega + y'' \cos\omega = 0 \\ z''' &= 0 \,. \end{aligned} \tag{20}$$

From equations (19) and (20) we obtain:

$$\tan\chi = \frac{z'}{x'} = \frac{z}{x_p\cos\varphi'} = \frac{n\sqrt{(z^2+z^2\tan^2\varphi')}}{x_p} \quad (21)$$

$$\sin\omega = \frac{y''}{d^*} = -\frac{x_p}{d^*}\sin\varphi' \quad (22)$$

where $n = \pm 1$ as explained in the text.

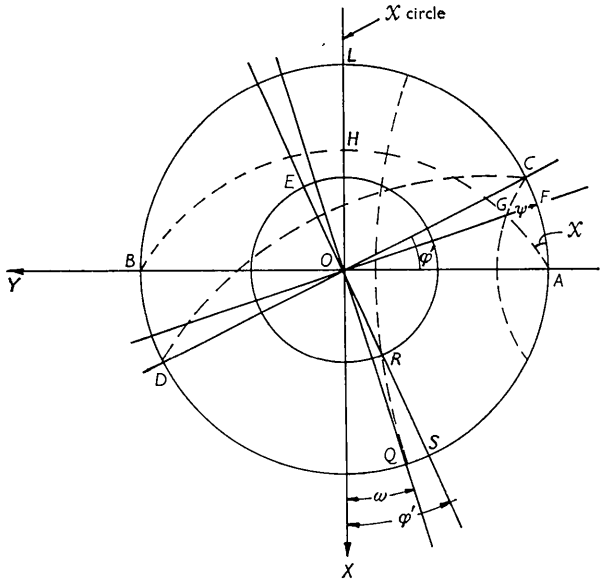

Fig. 5. Stereogram showing the change of the azimuth of a reflecting plane. R is the pole of the plane before the χ rotation and Q is the same pole after this rotation. The corresponding change in the azimuth is given by the angle FG. (After Willis, 1961.)

According to Willis (1961), from the Napierian triangle AFG (Fig. 5) we obtain:

$$\tan\psi = \sin\omega\tan\chi .$$

We can express now φ' as function of ψ:

$$\tan\varphi' = -\frac{d^*}{z}\tan\psi . \quad (23)$$

By substitution of this in equation (21), equation (4) is obtained.

APPENDIX III

Calculation of the interval limits R_i and S_i

If the z coordinates of the reciprocal point $p_it_iv_i$ corresponding to the interval limits $\psi-\varepsilon$, $\psi+\varepsilon$ have the same sign, the limits of the y interval are:

$$y_f^- = L\cos\theta\sin(\psi-\varepsilon) - M\cos\theta\cos(\psi-\varepsilon) - N\sin\theta = (\varrho L-\eta M)\cos\theta\sin\psi - (\eta L+\varrho M)\cos\theta\cos\psi - N\sin\theta \quad (24)$$

and similarly:

$$y_f^+ = (\varrho L+\eta M)\cos\theta\sin\psi + (\eta L-\varrho M)\cos\theta\cos\psi - N\sin\theta \quad (25)$$

where $\varrho = \cos\varepsilon$; $\eta = \sin\varepsilon$.

If the z coordinates have not the same sign, the limits of the y interval are given by y_f^- or y_f^+ and

$$y_f' = L\cos\theta\sin\psi' - M\cos\theta\cos\psi' - N\sin\theta$$

where ψ', the value of ψ in the interval $\psi-\varepsilon$, $\psi+\varepsilon$ for which $z_f=0$, is given by:

$$\tan\psi' = -L/M .$$

In both cases R_i and S_i are the lower and upper limits of this y interval respectively.

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