determination of the constant in equation (1) resulted in a value of $2{\cdot}48 \times 10^{-26}$ instead of $2{\cdot}64 \times 10^{-26}$. We also obtained a value of $\lambda^{2\cdot 8}$ instead of λ^3, the former being in qualitative agreement with Weiss (1966). It is interesting to note that on the Mo radiation curve the $(\mu/\varrho)A$ for Fe appears to be high even though Cooper's value is verified by Batterman, Chipman & DeMarco (1961).

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The Interpretation of X-ray Diffraction Photographs with the Use of Computers

BY W. A. WOOSTER

Brooklyn Crystallographic Laboratory, Bottisham, Cambridge, England

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The large number of reflexions which are recorded on diffraction photographs make it necessary to use automatic instruments for measuring the integrated intensity of reflexion. One class of such instruments requires the photographic film to be positioned automatically in the correct position for scanning over each spot in turn. The present paper sets out the way of computing the coordinates of spots on films so that a microdensitometer, with automatic setting along two mutually perpendicular directions, can set the film in the required positions. An alternative approach to this problem involves finding, instrumentally, the coordinates on the film of each spot and computing the indices of the reflecting plane. It is shown what programs are necessary to do this for oscillation, Weissenberg and precession photographs.

Introduction

The determination of the structure of a crystal frequently requires the measurement of the integrated reflexions of some thousands of spots on oscillation or Weissenberg or precession photographs. Eye estimation has been used extensively but it is tedious and not sufficiently accurate for many purposes. Efforts have therefore been made in recent years to develop automatic instruments capable of carrying out measurements, for each spot on a photograph, of its linear coordinates and its integrated intensity. The method described by Abrahamsson (1966) is very thorough. The intensity at every point on a 1/10th mm grid covering the whole film is registered, and the information stored magnetically. This means that some millions of measurements are made on each film. Subsequently this information must be sorted and the integrated intensities determined for each spot. A computer of considerable capacity is clearly required for this purpose. It seems likely that a more economical approach to the problem would involve calculating the position of each possible reflexion and using this information to examine and integrate the intensity in the region round this calculated position. This method has the merit that spurious 'reflexions' are not recorded along with the genuine ones. It also has the advantage over a method which depends on an automatic searching for the spots of intensity above a certain value, that no reflexion is too weak to be studied. The following paragraphs attempt to set out a method of calculating the position of spots on various types of photograph. The assumption is made that the cell dimensions and orientation of the edges of the unit cell relative to the photographic instrument are known.

Calculation of coordinates on the film of spots corresponding to given indices *hkl*

The unit-cell sides referred to Cartesian coordinates

Whatever the symmetry of the crystal and whatever the orientation of the unit cell with respect to the photographic instrument, it is always possible to write down the Cartesian coordinates of the axes, $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ of the reciprocal unit cell as follows:

$$\begin{matrix} p_{a^*} & q_{a^*} & r_{a^*} \\ p_{b^*} & q_{b^*} & r_{b^*} \\ p_{c^*} & q_{c^*} & r_{c^*} \end{matrix} \quad (1)$$

In many cases one crystallographic axis, say the c axis, will be arranged along the main axis of rotation of the goniometer. This may be called the Z axis. In this case $\mathbf{a}^*$ and $\mathbf{b}^*$ are perpendicular to $\mathbf{Z}$ and

$$r_{a^*}=r_{b^*}=0\ .$$

Other quantities in the matrix (1) may be zero depending on the crystal symmetry. Here we shall consider the general case in which none of them is zero.

Oscillation photograph

The Cartesian axes are defined as follows. The axis of rotation of the camera is taken as the Z axis and the positive direction is from the crystal away from the goniometer head. The positive direction of the X axis is from the crystal towards the X-ray tube. The Y axis forms with the other two axes a right-handed system. For a plane of indices (hkl) the reciprocal point, P, has coordinates $p_{d^*}, q_{d^*}, r_{d^*}$ given by

$$\begin{aligned} p_{d^*} &= hp_{a^*}+kp_{b^*}+lp_{c^*} \\ q_{d^*} &= hq_{a^*}+kq_{b^*}+lq_{c^*} \\ r_{d^*} &= hr_{a^*}+kr_{b^*}+lr_{c^*} \end{aligned} \qquad (2)$$

If this plane is in a reflecting position, intersecting the reflecting sphere at a distance ξ from the axis Z (Fig. 1) and at a height ζ above the equator, then we have

$$\begin{aligned} \xi &= \sqrt{(p^2_{d^*}+q^2_{d^*})} \\ \zeta &= r_{d^*}\ . \end{aligned}$$

If the angle $P'OY=\Phi$, where P' is the projection of P on the equatorial plane, then,

$$\tan\Phi = p_{d^*}/q_{d^*}\ . \qquad (3)$$

Also if the distance $OP=d^*$, then

$$d^* = \sqrt{(p^2_{d^*}+q^2_{d^*}+r^2_{d^*})}\ . \qquad (4)$$

We shall only consider a cylindrical camera.

The axes of reference on the film when laid flat will be denoted S and T. T is a line parallel to the axis of the camera which passes through the point on the film where the direct beam of X-rays would strike it. S is a line perpendicular to T and also passing through the line of the incident X-ray beam. The positive direction of T is upwards and that of S is to the right, the origin being at the point where the X-rays pass through the film. The centre of the reflecting sphere is denoted C. The inclination of the reflected rays, CP, to the equatorial plane is denoted χ and we have

$$r_{d^*} = \sin\chi\ . \qquad (5)$$

The coordinates on the film are denoted s and t. From equation (5) we can obtain t since

$$t = R\tan\chi \qquad (6)$$

where R is the radius of the cylindrical camera.

The s coordinate is given by the relation

$$s = RY \qquad (7)$$

where $Y=\angle P'CO$.

The angle Y can be obtained from the three sides of triangle OCP' namely $OC=1$, $OP'=\xi$, $CP'=\sqrt{1-\zeta^2}$, all of which are known in terms of the coordinates of the point P.

The result is

$$\cos Y = (2-d^{*2})/2\sqrt{1-r^2_{d^*}}\ . \qquad (8)$$

Thus, given the indices of the reflecting plane and the coordinates of the ends of the vectors $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ the position on the film of the corresponding reflexion can be obtained.

It is, of course, necessary to limit the values of hkl used to those which correspond to reciprocal points lying between the extreme positions of the sphere of reflexion during the oscillation. The condition that the point P' should lie on the circle of radius $\sqrt{1-\zeta^2}$ about C is given by the equation

$$(p_{d^*}-1)^2+q^2_{d^*}-(1-r^2_{d^*})=0\ . \qquad (10)$$

If the oscillation is through 15° the coordinates of the centre of the reflexion sphere at the other extremity of the oscillation will be (cos 15°, sin 15°, 0). The condition that the reflecting reciprocal point shall lie on this reflecting circle is given by the equation

$$(p_{d^*}-\cos 15°)^2+(q_{d^*}-\sin 15°)^2-(1-r^2_{d^*})=0\ . \qquad (11)$$

For reciprocal points lying between the extreme positions of the reflecting sphere the left-hand side of equation (10) will have a different sign from that of equation (11). The computer must be programmed to select those values of hkl for which this condition is valid. The values of r_{d^*} and d^* are calculated, and using equations (5) and (6) the film-coordinates t, s are determined.

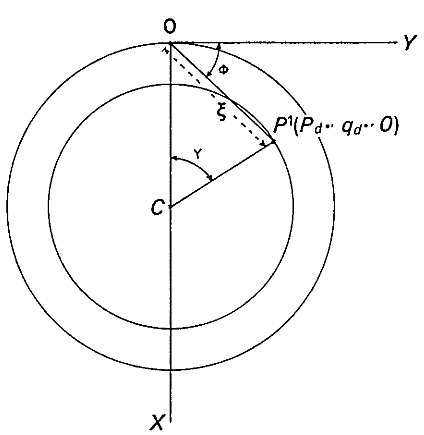

Fig. 1. A projection on to the equatorial plane of the reflecting reciprocal point P'. O is the origin of the reciprocal lattice and OX and OY the orthogonal axes of reference.

Weissenberg photograph

The Z axis is taken parallel to the main axis of rotation of the goniometer and its positive direction is from the crystal away from the goniometer head. The X axis is perpendicular to the Z axis and lies in the plane containing Z and the incident X-ray beam. The positive direction of the X axis is from the crystal towards the X-ray tube. The Y axis completes a right-handed Cartesian system.

We shall suppose the photograph to be taken in the equi-inclination setting with a tilt of the main axis of rotation through an angle μ away from the normal (equatorial setting).

All reflecting planes lying in the plane IQ (Fig. 2) perpendicular to the axis of rotation CT have a constant value of r_{d^*}, where

$$\sin \mu = r_{d^*}/2 \,. \qquad (12)$$

The computer is therefore given the task of finding all values of hkl for which r_{d^*} has the value given by equation (12) and for which ξ is less than $2\sqrt{1-r_{d^*}^2/4}$. The values of p_{d^*} and q_{d^*} are calculated for each of the possible reflexions. We obtain from equation (4), d^*, and from equation (3), Φ.

The relation giving Y is

$$\sin \frac{Y}{2} = \frac{1}{2} \sqrt{\frac{p_{d^*}^2 + q_{d^*}^2}{1 - r_{d^*}/4}} \,.$$

The Cartesian coordinates measured along and perpendicular to the central line of the Weissenberg film may be denoted u, v (Fig. 3).

Then we have

$$u = k\Phi + \frac{R}{2} Y$$

$$v = RY \,, \qquad (13)$$

provided the slope of the line corresponding to a central row line such as MN is $\tan^{-1}2$. The value of k is the translation–rotation constant of the goniometer. Thus the position on the film at which each reflexion should occur can be obtained from equations (13).

Precession photograph

The Cartesian axes of reference are chosen so that if the angle of the precession cone is reduced to zero, then the Z axis is parallel to the incident X-ray beam and its positive direction is from the crystal towards the X-ray tube. The X axis is then horizontal and the Y axis vertical. We shall suppose that the annular limiting aperture is set to transmit only reflexions having a given value of r_{d^*}. The computer is programmed to sort out all the values of hkl having this value of r_{d^*} and a value of d^* less than about unity (depending on the settings used). If D is the distance between the crystal and the point about which the film rocks, the coordinates of the spots on the film are Dp_{d^*} and Dq_{d^*} respectively for each of the possible values of hkl.

Calculations of the indices h, k, l using the coordinates measured on the film

Oscillation photograph

In the following it is assumed that the cell dimensions and orientation of the unit cell, with respect to a chosen set of Cartesian axes, are known, *i.e.* all the components $p_{a^*} - r_{c^*}$ are known. The s, t coordinates of a spot on an oscillation photograph are measured and we require to find the corresponding indices h, k, l of the reflecting plane. There are three conditions which the reflecting reciprocal point must satisfy, namely (*a*) it must lie on a plane parallel to the equator and distant from it by r_{d^*}, (*b*) it must lie on a cylinder of radius ξ, described about the axis of the camera and (*c*) it must lie between two reflecting spheres corresponding to the extremities of the oscillation.

From the t coordinate we obtain χ from equation (6) and r_{d^*} from equation (5). Now

$$r_{d^*} = hr_{a^*} + kr_{b^*} + lr_{c^*} \qquad (14)$$

and the computer can be set to sort out and store all values of h, k, l which satisfy this relation. It will thus determine all reciprocal points lying in the plane of the reciprocal lattice at a height ζ above the equator.

From the s coordinate and equation (7) we obtain Y (expressed in radians). From Fig. 1 we see that

$$\xi^2 = 2 - r_{d^*}^2 - 2\sqrt{1 - r_{d^*}^2} \cos Y \,, \qquad (15)$$

so that ξ may be obtained from r_{d^*} and Y.

Further we have

$$\begin{aligned}\xi^2 = p_{d^*}^2 + q_{d^*}^2 &= h^2(p_{a^*}^2 + q_{a^*}^2) + k^2(p_{b^*}^2 + q_{b^*}^2) \\ &+ l^2(p_{c^*}^2 + q_{c^*}^2) + 2hk(p_{a^*}p_{b^*} + q_{a^*}q_{b^*}) \\ &+ 2kl(p_{b^*}p_{c^*} + q_{b^*}q_{c^*}) + 2lh(p_{c^*}p_{a^*} \\ &+ q_{c^*}q_{a^*}) \,. \qquad (16)\end{aligned}$$

The values of h, k, l which satisfy equation (14) and are stored in the computer are now applied to equation (16) and only those values which give the correct value of ξ are retained in the computer store. In this way the reciprocal points which lie on the circle passing through P (projected as P' in Fig. 1) are determined.

The conditions (*c*) may be inserted in the following way. The centre of the reflecting circle may be supposed to lie on a line through O making an angle δ with the line OX, Fig. 1. The coordinates of the centre of this

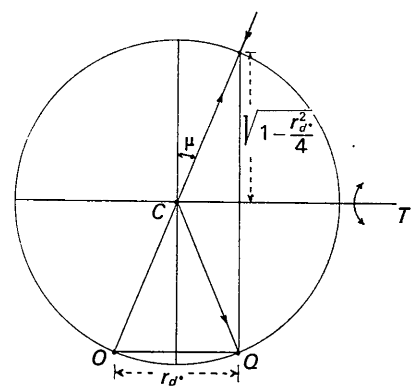

Fig. 2. A projection on to the plane containing the principal axis of rotation in the Weissenberg goniometer, CT, and the direction of the incident X-rays, IC. The reflected cone of rays cuts the reflecting circle in a plane which projects as IQ.

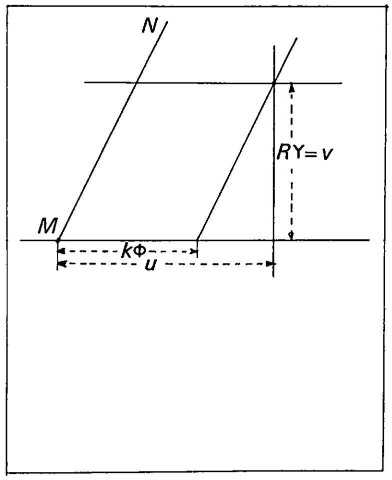

Fig. 3. Diagram showing the relation between the coordinates u, v on the film and the angles Φ and Υ.

circle are then $\cos\delta$, $\sin\delta$ and δ lies between 0 and 15°, if the angle of oscillation is 15°. The condition that a point must lie on a circle of radius $\sqrt{1-r_{d*}^2}$ having a centre at $(\cos\delta, \sin\delta)$ is

$$(p_{d*}-\cos\delta)^2+(q_{d*}-\sin\delta)^2=1-r_{d*}^2\,. \quad (17)$$

Since δ is less than 15° (0·26 rad) we may reduce this expression to

$$p_{d*}+q_{d*}\delta=\tfrac{1}{2}(\xi^2+r_{d*}^2)=\tfrac{1}{2}d^{*2}. \quad (18)$$

This gives values for δ

$$\delta=\frac{\tfrac{1}{2}d^{*2}-(hp_{a*}+kp_{b*}+lp_{c*})}{hq_{a*}+kq_{b*}+lq_{c*}}\,. \quad (19)$$

The value of δ must lie between 0 and 0·26 if the angle of oscillation is 15°. The values of h,k,l already stored in the computer are applied in turn to equation (19) and only those which give a value of δ lying between the prescribed limits are retained. There may be one or more sets of h,k,l values which satisfy equation (19), but this is due to the inevitable ambiguity of the oscillation method.

It should be noted that no particular orientation of the crystal is required for this method of analysis. It is, however, necessary to know the precise orientation of the crystal relative to the goniometer at the end of the oscillation. The computer program requires the following steps.

1. Evaluate r_{d*} from coordinate t.
2. Sort out all values of h,k,l which give this value of r_{d*}.
3. Evaluate ξ from the coordinate s.
4. Select those h,k,l values which give this value of ξ.
5. Again sort the value of h,k,l using equation (19) and retain only those giving δ lying between the limits set by the oscillation.

Weissenberg photograph

The measured Cartesian coordinates u,v of any spot on the film can be converted into the angles Υ,Φ (Fig. 3) by using equation (13) written in the form

$$\Upsilon=v/R$$
$$\Phi=(u-v/2)/k\,. \quad (20)$$

The radius of the reflecting circle is $(1-r_{d*}^2/4)^{\frac{1}{2}}$ (Fig. 2) and the distance, ξ, of the reciprocal point from the origin is given by

$$\xi/2=\sin\frac{\Upsilon}{2}\left(1-\frac{r_{d*}^2}{4}\right)^{\frac{1}{2}}. \quad (21)$$

Now $\quad p_{d*}=\xi\cos\Phi,\ q_{d*}=\xi\sin\Phi \quad (22)$

and $\quad r_{d*}=2\sin\mu\,.$

Thus the coordinates of the reciprocal point corresponding to the spot on the film are determined.

Now from equation (2) we have

$$h=\begin{vmatrix} p_{d*} & p_{b*} & p_{c*}\\ q_{d*} & q_{b*} & q_{c*}\\ r_{d*} & r_{b*} & r_{c*}\end{vmatrix}\Bigg/\begin{vmatrix} p_{a*} & p_{b*} & p_{c*}\\ q_{a*} & q_{b*} & q_{c*}\\ r_{a*} & r_{b*} & r_{c*}\end{vmatrix} \quad (23)$$

and similar expressions for k and l.

Thus the indices of the reflecting plane may be directly determined from the measured coordinates and the equi-inclination angle μ.

Precession photograph

The Cartesian coordinates of each spot on the film are Dp_{d*} and Dq_{d*} and the setting of the limiting aperture determines r_{d*}. Thus the expression (23) can be used to obtain the h,k,l values. It should be noted that it is not assumed that any particular orientation of the crystal is chosen. It is only necessary that this orientation should be defined by the nine components given in expression (1).

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