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Crystal Setting by X-rays

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A review of published methods of crystal setting by X-rays and an analysis of the problem are given. A completely general setting method is developed which can be used on crystals that fail to give recognizable zero layer curves and which, in favourable cases, gives an accuracy of 0·05°. This method utilizes the Laue streak associated with a characteristic reflexion. Detailed instructions, an example and comparison with other methods are given. An appendix details hitherto unpublished methods of determining azimuthal orientation and arc adjustment using Laue photographs.

1. Introduction

The crystals which were the subject of the earlier investigations by X-rays could be set exactly by optical methods, but as soon as crystals without developed faces, such as metal crystals, began to be investigated, the problem of setting by means of X-rays arose.

The main problem can be defined as that of bringing a given reciprocal-lattice plane into the equatorial position relative to a rotation axis.

In practice research workers made use of various methods, but these remained unpublished, and Kratky & Krebs (1936) were the first to publish a paper giving details of a method of setting by X-rays, using the zero layer curve, which, with a mis-set crystal, replaces the straight zero layer line. Hendershot (1937) gave a rather more convenient formula, based on Kratky and Krebs' method, for calculating the arc corrections.

Recently, Weisz & Cole (1948) have given the version of Hendershot's method (using Laue instead of oscillation photographs) which is in use at the Cavendish Laboratory. Bairsto (1948) gives a method requiring three complete rotation photographs for the final setting of a crystal, which also depends on measurements of a zero layer curve.

All these methods are limited to small adjustments, and the formulae used are approximations valid only for such adjustments.

The main object of this paper is to give details of a setting method which utilizes the Laue streak associated with a characteristic reflexion. The principles of the method were suggested to the author by Prof. J. D. Bernal and are essentially those used by him in his early work. These principles have been taught at Cambridge and elsewhere, but each problem has been solved either from first principles by spherical trigonometry or by graphical methods. Both processes are unnecessarily long for routine setting purposes and with the latter it is difficult to get an accuracy greater than 0·5°. It is only the analytical form of the method described here which is thought to be new.

An appendix gives methods of determining the azimuthal orientation with respect to the X-ray beam and the adaptation of one such method to determining arc adjustments where a horizontal plane of Laue symmetry exists. These methods have been in use in various laboratories, but have also remained unpublished.

2. Statement of the problem

Setting problems can be divided into two main classes:

I. Those cases where a well-defined zero layer curve exists, and

II. Those cases where there are too few reflexions to define a zero layer curve.

Each of these classes can be subdivided again into

(*a*) those cases which can be set approximately by optical means, and

(*b*) those cases which cannot be orientated at all by optical means.

Rough adjustments from preliminary oscillation or Laue photographs (see Appendix II) can easily bring I (*b*) to the approximately set condition of I (*a*) and both categories can then be finally set by one of the methods using layer-line curves.

In the categories II (*a*) and II (*b*) it is necessary to work with individual reflexions to calculate the arc corrections, and here a further subdivision between crystals of known lattice and those of unknown lattice becomes important. The first task is to determine which reflexions on a preliminary photograph are to be brought into the equatorial plane and the second task is to calculate the arc adjustments necessary to do it. The first task will usually be much easier for II (*a*) than II (*b*) and both tasks will be considerably lightened if the crystal lattice is known. In both cases the task of setting can be accomplished only from a Laue photograph or from an oscillation photograph with a Laue streak associated with the characteristic reflexion. Since the reciprocal lattice is much easier to recognize in an oscillation photograph, the present method has been based on the use of such photographs.

3. Principles of the method

Two reciprocal-lattice vectors, whose associated reflexions have been obtained on a setting photograph, are selected to define the zero layer. Their azimuthal angles relative to the goniometer arcs are determined from the positions of the ends of the Laue streaks. The angle between each vector and the equatorial plane is obtained from Bernal's ζ, ξ values of the characteristic reflexion associated with each vector. By registering on the same film two oscillations 180° apart, two spots are obtained equally spaced above and below the equatorial plane. The ζ value is obtained accurately by calculation from the measured distance between these spots. The arc corrections necessary to bring these vectors into the equatorial plane are calculated from these four angles.

4. Theoretical development

(i) *Description*

The method aims at calculating the arc adjustments required to erect a crystal to the limit of accuracy of the goniometer arcs, normally 0·05°, from measurements on one compound oscillation photograph. It can be used for a crystal which is mis-set up to the limits of arc adjustment, even if the zero layer curve is difficult or impossible to recognize. Since the arcs may have been moved in taking earlier exploratory photographs, or for approximate setting by extinction direction or external form, the possibility of the bottom arc being initially off zero is taken into account. No particular relation of the arcs to lattice directions is assumed. The method can also be used for reorientating a set crystal, if the lattice constants are known and the angular adjustments required are within the limits of the arcs.

Two spots, P_1, P_2, which are to be brought into the equatorial plane, are chosen from preliminary photographs or direct from the setting photograph itself. The angle between the corresponding reciprocal-lattice vectors ($P_1'OP_2'$, Fig. 1, where O is the origin of the reciprocal lattice) should be, if possible, between 60° and 120°. If enough is known about the lattice to determine the angle between the vectors within half a degree, it is necessary to have only one spot with a pronounced Laue streak, but otherwise both spots must have recognizable Laue streaks associated with them.

An oscillation photograph* which will include P_1 and P_2 is taken with sufficient exposure to develop the necessary Laue streaks, and the crystal is stopped at one end of the oscillation for 15 min. to define sharply the ends of the streaks. The crystal is turned through 180° and a further oscillation photograph is registered on the same film, with, at most, half the exposure of the first.

The Laue streaks (or one Laue streak and the known angular relation of the lattice), with the aid of an α and ω chart, fix the azimuthal orientation of the reciprocal-lattice vectors with respect to the arcs (ϕ and ψ, Fig. 1, where YZ is the plane of the bottom arc, XZ that of the top arc when it is erect). The angles (α and β) between the lattice vectors, OP_1', OP_2', and the equatorial plane are given by the ζ, ξ values of the oscillation spots ($\tan\alpha = \zeta/\xi$).

* Usually a 15° oscillation will be best, but it may be preferable to take two 5° oscillations instead in order to obtain the most favourable reflexions, especially if the reciprocal lattice is known. Reflexions from two different films can be used, if necessary.

(ii) *Definitions*

The geometrical factors involved are defined as follows:

In Fig. 1, OXY is the equatorial plane and OZ the rotation axis, assumed vertical. OYZ is the plane of the bottom arc, which is fixed and whose axis is OX. OXZ is the plane of the top arc when it is erect. $ORLNM$ is the plane of the reciprocal lattice which is to be brought into the equatorial plane. OP_1' and OP_2' are the reciprocal-lattice vectors whose angles (α and β) above the equatorial plane, and azimuthal angles relative to

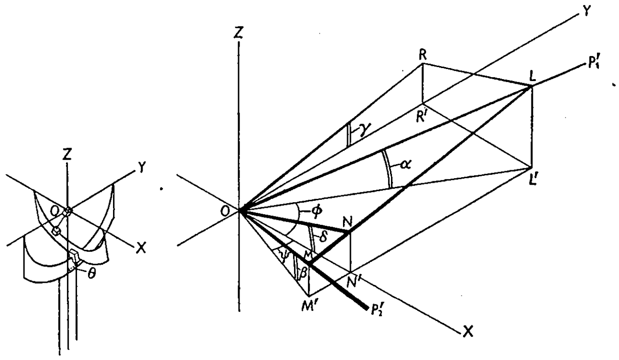

Fig. 1. Isometric diagram showing the geometrical relations of the reciprocal-lattice vectors OP_1', OP_2' to the goniometer arcs.

the arcs (ϕ and ψ) have been obtained from the setting photograph. $LNMM'N'L'$ is a vertical plane parallel to OY cutting OP_1' and OP_2' in L and M. ONN' is a vertical plane containing OX cutting LM in N. ORR' is a vertical plane containing OY and cutting the lattice plane in OR, so that the vertical plane $LL'R'R$ is parallel to OX. L', M', N', R' are the projections of L, M, N, R on the XY plane. The angular elevations of the reciprocal-lattice plane in the vertical planes OYZ, OXZ are ROR' (γ) and NON' (δ). α, β, γ, δ are measured positively upwards. The angles XOL' (ϕ) and XOM' (ψ) are measured positively as shown, anti-clockwise and clockwise from OX respectively.

(iii) *Method*

The problem can be divided into three parts: *

(a) To determine the angles between the equatorial and lattice planes parallel and perpendicular to the bottom arc, i.e. to calculate γ and δ.

* The problem could clearly be solved by spherical trigonometry, but involves the solution of a considerable number of spherical triangles and is unnecessarily elaborate compared with the solution given here.

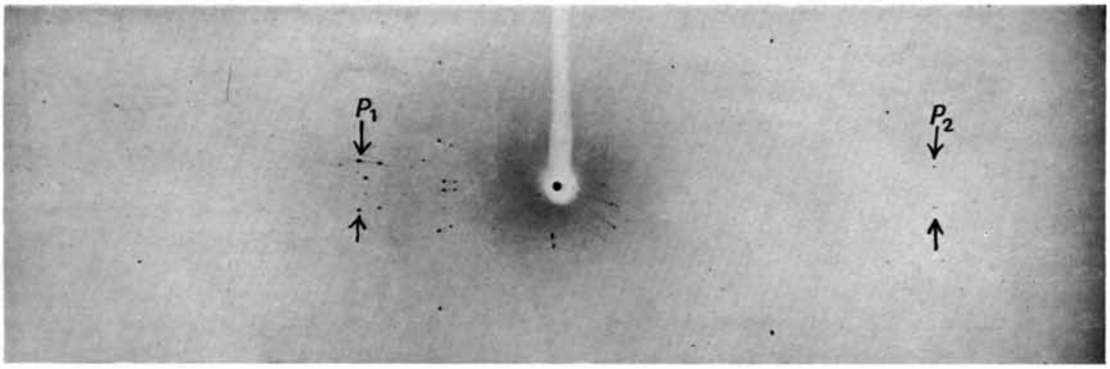

Fig. 2. The setting photograph from which the arc corrections were calculated.

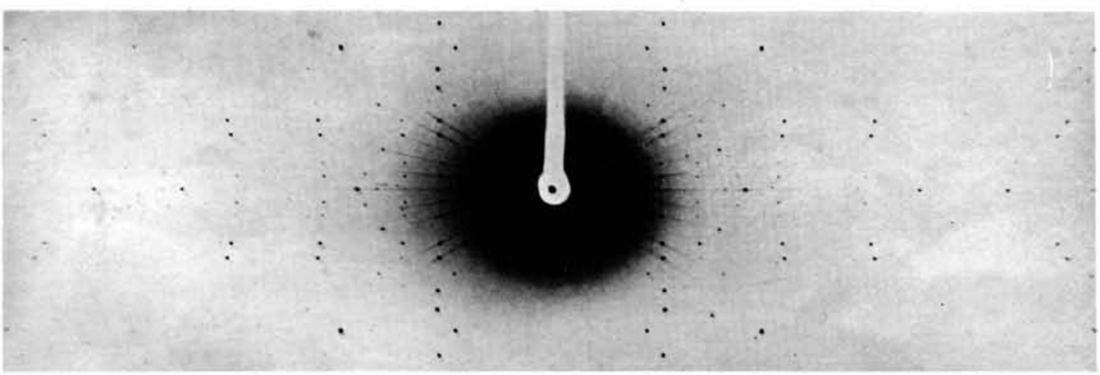

Fig. 3. The rotation photograph taken after applying the arc corrections calculated from Fig. 2.

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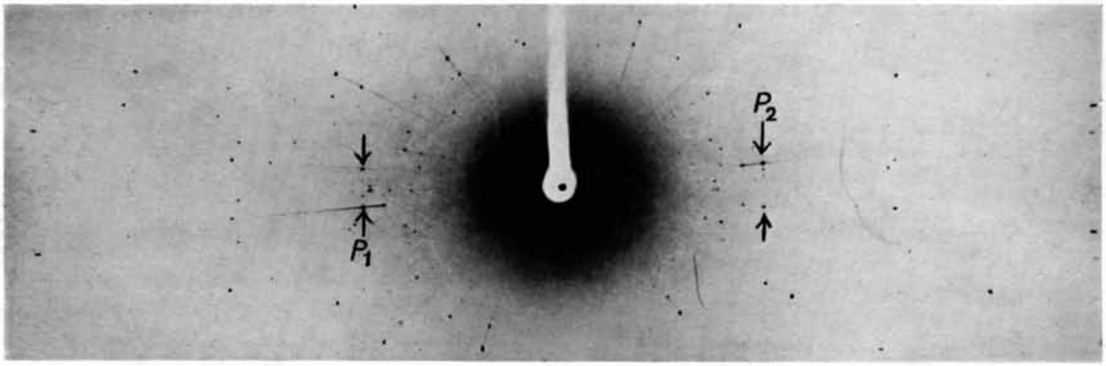

Fig. 4. The result of attempting to use Hendershot's method.

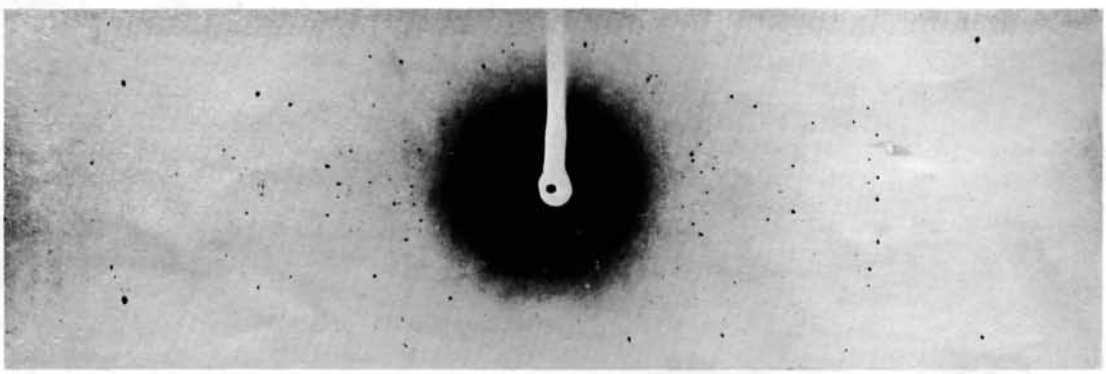

Fig. 5. The result of attempting to use Weisz and Cole's method.

(*b*) To bring the bottom arc to zero reading by adjustment through the known angle θ (i.e. to erect the top arc) and determine the alteration in γ and δ.

(*c*) To determine the arc corrections required to bring the plane into the equatorial position.

The solutions to (*a*), (*b*) and (*c*) are given below and the proofs will be found in Appendix I.

$$(a)\quad \gamma=\tan^{-1}\frac{\tan\alpha\cos\psi-\tan\beta\cos\phi}{\sin(\phi+\psi)},$$

$$\delta=\tan^{-1}\frac{\tan\alpha\sin\psi+\tan\beta\sin\phi}{\sin(\phi+\psi)}.$$

(*b*) Let θ be the reading of the bottom arc, positive in the direction OY (i.e. θ is positive when the axis of the top arc is tilted upwards in the direction OY).

On erecting the top arc γ is changed to γ' and δ is changed to δ':

$$\gamma'=\gamma-\theta;\quad \delta'=\tan^{-1}\frac{\tan\delta\cos\gamma}{\cos(\gamma-\theta)}.$$

(*c*) *Top arc.* δ' is the correction to be applied to the top arc so that a point on OX is brought downward if δ' is positive, upward if it is negative.

Bottom arc. $\gamma''=\tan^{-1}\tan\gamma'\cos\delta'$ is the correction, *from zero*, to be applied to the bottom arc so that a point on OY is brought downward if γ'' is positive, upward if it is negative.

It is clear from the character of the trigonometrical functions that, providing the sign conventions are observed and α and β are associated with ϕ and ψ respectively, these expressions will hold whatever the orientation of P_1' and P_2' with respect to the arcs.

(iv) *Summary*

The process can be summarized as follows:

(1) A double-oscillation setting photograph is taken, either at random or to bring in zero-layer reflexions selected from earlier photographs. One oscillation must have sufficient exposure to develop the necessary Laue streaks and the other should have less than half that exposure. The crystal should be held stationary at one end of the first oscillation for about 15 min.

(2) The two pairs of spots to be brought on to the equatorial plane are marked on the photograph and their vertical separations, x_1 and x_2 mm., are measured. The stronger spot of each pair will normally be taken as the basis for the calculation and x_1, x_2 will be positive if this spot is above the equatorial plane, negative if below it.

(3) The ξ values of the marked spots are read off from the Bernal chart.

(4) The ω readings of the marked ends of the Laue streaks are obtained by means of an α and ω chart, and are combined with the goniometer readings (*a*) where the crystal was held stationary, and (*b*) where the bottom arc is parallel to the X-ray beam,* to give ϕ and ψ. (In some cases measurements will be necessary only on one streak, the second angle being obtained from the known reciprocal-lattice angles).

(5) The goniometer is set approximately to the reading 4(*b*), and θ, the reading of the bottom arc, is noted together with its sign (positive if the reading is towards the collimator, negative if in the opposite direction).

(6) The ζ values for a camera of radius r mm. are obtained from the formula

$$\zeta=\frac{x/2r}{\sqrt{[1+(x/2r)^2]}},$$

and $\tan\alpha=\zeta_1/\xi_1$ and $\tan\beta=\zeta_2/\xi_2$ are calculated.

(7) Table 1, which summarizes the procedure for calculating δ' and γ'' from the observed α, β, ϕ, ψ, θ, is completed and the arc corrections are applied according to (*c*) above, care being taken to measure γ'' *from zero* and not from the previous reading of the bottom arc, if that was different from zero. (The figures in Table 1 refer to a numerical example considered in § 5 (i) below.)

Table 1. *Procedure for calculating δ' and γ''*

$\tan\alpha$	$\tan\beta$	ϕ	ψ	θ	$\tan\delta=\frac{\tan\alpha\sin\psi+\tan\beta\sin\phi}{\sin(\phi+\psi)}$	$\gamma=\tan^{-1}\frac{\tan\alpha\cos\psi-\tan\beta\cos\phi}{\sin(\phi+\psi)}$	$\delta'=\tan^{-1}\frac{\tan\delta\cos\gamma}{\cos(\gamma-\theta)}$	$\gamma''=\tan^{-1}\tan(\gamma-\theta)\cos\delta'$
0·1279	0·0632	78·7°	11·8°	−9·65°	0·0882	6·4°	5·2°	16·0°

The crystal should now be set, except for lateral adjustment.

(v) *Errors.*

Since ξ is about 1·0 and ζ will not usually be much more than 0·1, the accuracy of $\tan\alpha$ (or $\tan\beta$) depends mainly on the ζ value. For small values of x (*c.* 6 mm.)

$$\max.\ \Delta\zeta=\frac{dx}{2r}-\frac{xdr}{2r^2}=\frac{0{\cdot}05}{60}+\frac{0{\cdot}1\times 6}{2\times 30^2}=0{\cdot}0011,$$

if the error in the measurement of x is 0·05 mm. (this is possible with a small crystal giving sharp reflexions), the error in the radius is 0·1 mm., and $r=30$ mm.

If ξ (measured with the Bernal chart) $=1{\cdot}0\pm0{\cdot}005$, $\alpha=\beta=30°$, and $\phi=\psi=45\pm0{\cdot}5°$, the maximum final error in the calculated arc corrections is about 1·0°, but if $\alpha=\beta=1{\cdot}0°$ and $\phi=\psi=45\pm0{\cdot}5°$, the maximum final error is 0·08° and the probable error will be less than 0·05°. In the most difficult case two applications of the method will therefore produce the desired accuracy.

* This camera constant can usually be obtained by cutting a microscope slide lengthwise and fixing the two halves to the two sides of the bottom arc with plasticene. The tops of the glass slips will then be in the field of view of the camera microscope and can be lined up parallel to its axis. If this fails, a simple jig can be made to fasten to the bottom arc for the same purpose.

For $\alpha=\beta=5°$ and $\phi=\psi=45\pm0{\cdot}5°$ the maximum error (arising from four errors of measurement) is less than $0{\cdot}2°$; it is thus unlikely that an error greater than $0{\cdot}1°$ will remain after one application of the method for this degree of mis-setting.

The error gets less as ϕ, ψ approach 0° and 90°.

5. Example and comparison with other methods

The necessity for the method and its practical application can probably best be understood by means of an example, and by a comparison with attempts to set a crystal of tricalcium silicate (*c.* $0{\cdot}1\times0{\cdot}1\times0{\cdot}05$ mm.) by other methods.

(i) *Example*

An exploratory oscillation photograph taking 2 hr., together with a knowledge of the reciprocal lattice, enabled the setting photograph to be planned.

Two 5° oscillation photographs were taken on the same film, with settings which gave two intense reflexions with reciprocal-lattice vectors 90° apart, together with the photographs at 180° to the first two. Exposure times, as detailed below, totalled 2 hr. 15 min. Fig. 2 was the result.

The measurement of the film and calculation of the arc corrections took half an hour. The arcs were reset, a check double oscillation taking 45 min. showed that there were no mistakes in the setting, and the rotation photograph (Fig. 3) was taken with filtered radiation and a 48 hr. exposure.

The arc corrections were calculated from Fig. 2 using the following data:

Oscillation No.	Oscillation Goniometer readings	Exposure time (min.)	Reflexion produced
1	$304{\cdot}0+5°$	60	P_1 (stronger)
2	$321{\cdot}0+5°$	30	P_2 (stronger)
3	$124{\cdot}0+5°$	15	P_1 (weaker)
4	$141{\cdot}0+5°$	15	P_2 (weaker)

The crystal was kept stationary at $304{\cdot}0°$ for 15 min.

The goniometer readings increase with clockwise rotation, viewed from above.

The bottom arc is in the plane of the X-ray beam and the rotation axis (i.e. OY and the X-ray beam coincide) when the goniometer reads $21{\cdot}8°$ (or $201{\cdot}8°$).

At $21{\cdot}8°$ the reading of the bottom arc was $9{\cdot}65°$ away from the collimator, i.e. $\theta=-9{\cdot}65°$.

The angle between the reciprocal-lattice vectors, OP'_1 and OP'_2 is 90°.

Oscillations (1) and (2) were used as the basis for the calculations, since both the stronger spots of the two pairs are above the equatorial plane, and the following measurements were made on the film.

The distance between the L.H. pair of spots $=x_1=+6{\cdot}8$ mm.

The distance between the R.H. pair of spots $=x_2=+5{\cdot}75$ mm.

The ξ reading of P_1 $=\xi_1=0{\cdot}88$

The ξ reading of P_2 $=\xi_2=1{\cdot}51$

The ω reading of the inner end of the Laue streak associated with P_1 (corresponding to the goniometer reading 304°) $=\omega_1=66{\cdot}5°$

From §4(iv) (6), for $r=30$ mm.

$$\zeta_1=\frac{0{\cdot}1133}{1{\cdot}007}=0{\cdot}1127,\quad \tan\alpha=\zeta_1/\xi_1=0{\cdot}1279,\quad \therefore\ \alpha=7{\cdot}3°,$$

$$\zeta_2=\frac{0{\cdot}0958}{1{\cdot}004}=0{\cdot}0954,\quad \tan\beta=\zeta_2/\xi_2=0{\cdot}0632,\quad \therefore\ \beta=3{\cdot}6°.$$

The angular relations when the goniometer reading is $304{\cdot}0°$ are shown in Fig. 6, where P''_1, P''_2 are the projections of P'_1, P'_2 on the equatorial plane.

As no observable Laue streak is associated with P_2, ω_2 must be calculated from the known lattice angle $P'_1OP'_2$. Fig. 7 is a stereogram showing the relation between the lattice angle $P'_1OP'_2$ (Υ) and the projected angle $P''_1OP''_2$ ($\omega_1+\omega_2=\phi+\psi$). Q_1 and Q_2 are the points in which OP'_1, OP'_2 cut the sphere of projection.

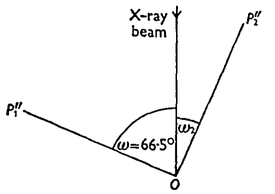

Fig. 6

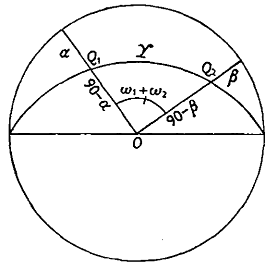

Fig. 7

Fig. 6. Angular relations at goniometer reading 304°.

Fig. 7. Stereographic projection showing the relation between the reciprocal-lattice and azimuthal angles.

Solving the triangle OQ_1Q_2, we have

$$\cos(\omega_1+\omega_2)=\frac{\cos\Upsilon}{\cos\alpha\cos\beta}-\tan\alpha\tan\beta.$$

In this case $\Upsilon=90°$,

$$\therefore\quad \cos(\omega_1+\omega_2)=-0{\cdot}1279\times0{\cdot}0632=-0{\cdot}0081.$$

$$\therefore\quad \omega_1+\omega_2=90{\cdot}5°.$$

For α, β equal to 5° or less the projected angle can be taken as equal to the lattice angle.

The orientation with respect to the arcs can be obtained from a third, known, lattice point, if that is more convenient, but if α or β is greater than 5° this involves the solution of a further spherical triangle.

By reorientating Fig. 6 about O, through

$$360-304+21{\cdot}8=77{\cdot}8°,$$

so that the plane of the bottom arc is parallel to the X-ray beam, and putting in the value of $\omega_1+\omega_2$ given above, we obtain Fig. 8.

The figures given in Table 1 can now be inserted and the arcs adjusted. Fig. 3 was taken after this adjustment had been made.

(ii) *Comparison*

In the case of this crystal the setting by Bairsto's procedure, even if possible, would have taken at least three days and was not attempted.

Hendershot's method was tried (Fig. 4) with an overnight exposure of 12 hr. followed by an exposure of 2 hr. with a setting at 180° from the first, using 15° oscillations. It is impossible to trace the zero-layer curve.

A 12 hr. Laue exposure followed by 2 hr. in the 180° position (as in Weisz and Cole's method) also failed to produce a recognizable zero-layer curve (Fig. 5).

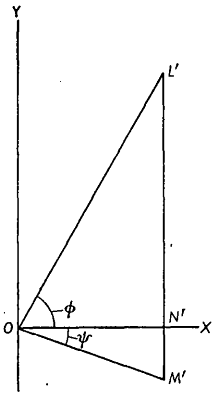

Fig. 9

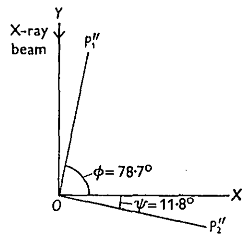

Fig. 8.

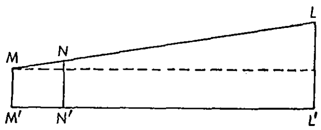

Fig. 10

Fig. 8. Angular relations when goniometer reading is 21·8°.

Fig. 9. Projection on the XY plane.

Fig. 10. Section parallel to OZ through LMN.

Fig. 4 could, however, be used as a setting photograph for the method described here, using the marked spots, and since these both have associated Laue streaks no knowledge of the reciprocal-lattice angles would be necessary, nor would any extra calculations be required to find ϕ and ψ. This is the simplest case of the use of the method and the normal one for a crystal with unknown lattice, but for the marked spots on Fig. 4 $\omega_1+\omega_2=120°$, which is rather too large for the most accurate setting.

It is thus possible to use the present method when others fail and that, together with its accuracy, constitutes its main justification.

I wish to thank Prof. J. D. Bernal for his encouragement and advice during the preparation of this paper.

This work was carried out as part of a program of research on the mechanism of volume and other changes in building materials, due to moisture changes, undertaken on behalf of the Department of Scientific and Industrial Research.

APPENDIX I

Proofs of the relations given in § 4 (iii)

(*a*) In Figs. 1, 9 and 10

$$OM'=\frac{ON'}{\cos\psi},\quad OL'=\frac{ON'}{\cos\phi},$$

$$LL'=\frac{ON'\tan\alpha}{\cos\phi},\quad MM'=\frac{ON'\tan\beta}{\cos\psi},$$

$$N'M'=ON'\tan\psi,\quad L'N'=ON'\tan\phi,$$

$$\begin{aligned}NN'&=MM'+\frac{(LL'-MM')\,N'M'}{L'N'+N'M'}\\&=\frac{MM'(L'N'+N'M')+(LL'-MM')\,N'M'}{L'N'+N'M'}\\&=\frac{MM'\times L'N'+N'M'\times LL'}{L'N'+N'M'}.\end{aligned}$$

$$\begin{aligned}\therefore \tan\delta=\frac{NN'}{ON'}&=\frac{\dfrac{\tan\beta}{\cos\psi}\times\tan\phi+\tan\psi\times\dfrac{\tan\alpha}{\cos\phi}}{\tan\phi+\tan\psi}\\&=\frac{\tan\beta\sin\phi+\tan\alpha\sin\psi}{\sin\phi\cos\psi+\cos\phi\sin\psi}\\&=\frac{\tan\beta\sin\phi+\tan\alpha\sin\psi}{\sin(\phi+\psi)}.\end{aligned}$$

Similarly, by substituting $\phi-90°$ and $\psi+90°$ for ϕ and ψ, we have

$$\tan\gamma=\frac{\tan\alpha\cos\psi-\tan\beta\cos\phi}{\sin(\phi+\psi)}.$$

(*b*) In Fig. 11, NS is the position of the line in which the lattice plane cuts the section before alteration of the bottom arc, N_1S_1 the position after bringing the reading to zero. $N'T$ is constructed at the angle θ with NN' to cut NS in T. T_1 is the new position of T.

We have

$$\tan\delta=\frac{NN'}{ON'},\quad \tan\delta'=\frac{N'T_1}{ON'}.$$

In triangle $N'TN$, angle $TNN'=90°-\gamma$, angle $NTN'=90°+(\gamma-\theta)$,

$$\frac{N'T}{\sin TNN'}=\frac{NN'}{\sin NTN'},\quad \therefore N'T=N'T_1=\frac{NN'\cos\gamma}{\cos(\gamma-\theta)}.$$

$$\therefore \tan\delta'=\frac{NN'\cos\gamma}{ON'\cos(\gamma-\theta)}=\frac{\tan\delta\cos\gamma}{\cos(\gamma-\theta)}.$$

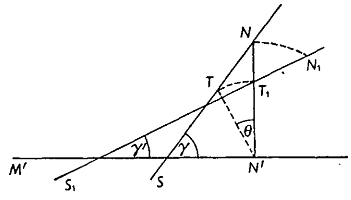

Fig. 11. Section parallel to YOZ through N'.

(c) In Fig. 12, R_1U_1 is the line in which the given plane cuts the section before the movement of the top arc, and R_2U_2 after the alteration

$$R'U_2 = R'U_1 = R_1R'\cos\delta',$$

$$\tan\gamma'' = \frac{R'U_2}{OR'}, \quad \tan\gamma' = \frac{R_1R'}{OR'}.$$

$$\therefore \tan\gamma'' = \tan\gamma'\cos\delta'.$$

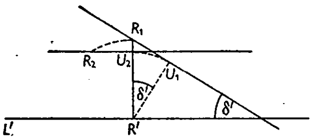

Fig. 12. Section parallel to XOZ through R' after the reading of the bottom arc has been brought to zero.

APPENDIX II

Azimuthal orientation with respect to the X-ray beam and arc adjustment using a horizontal plane or vertical axis of symmetry.

(i) *Azimuthal orientation*

(a) The azimuthal orientation with respect to the X-ray beam is given, before adjustment, by Fig. 8. It is accurate only to the nearest 0·5° at best, and the angles are altered by the adjustment. However, if the adjustments are not too large, this alteration can be neglected for most purposes.

If the adjustments are large, the simplest way to find the altered orientation is:

(a) to calculate angle

$$ROL \text{ (Fig. 1)} = \cos^{-1}(\sin\gamma\sin\alpha + \cos\gamma\cos\alpha\sin\phi)$$

(from the straightforward solution of a spherical triangle, similar to that of Fig. 7);

(b) to calculate angle $R'OR_3 = YOR_3$, where OR_3 is the final direction of OR.

In Fig. 12 the final adjustment brings R_2U_2 down to the equatorial plane. Therefore angle $R'OR_3 = R_2OU_2$:

$$\sin R'OR_3 = \frac{R_2U_2}{OR_2} = \frac{R_1R'\sin\delta'}{OR_1} = \sin\gamma'\sin\delta'.$$

Therefore, after adjustment, angle

$$YOP_1' = R'OR_3 + ROL = \sin^{-1}\sin(\gamma-\theta)\sin\delta' + \cos^{-1}(\sin\gamma\sin\alpha + \cos\gamma\cos\alpha\sin\phi).$$

(b) If the azimuthal orientation after erection is required to the nearest 0·1°, it is necessary to take a Laue photograph at a distance of at least 4 cm. on a plate camera. Since the approximate orientation is known, the crystal can be set to give an equatorial Laue spot at a convenient angle and the angle can be calculated accurately from the measured distances, crystal to plate (Y cm.) and central spot to Laue spot (X cm.).

Then $\tan 2\theta = X/Y$ and $\omega = 90° - \theta$ (where θ is the Bragg angle).

Differentiating, we have

$$\Delta 2\theta = \frac{YdX - XdY}{X^2 + Y^2}.$$

If

$X = 4$ cm., $Y = 4$ cm., $dX = 0{\cdot}005$ cm., $dY = -0{\cdot}01$ cm., then

$$\text{max. } \Delta\omega = \text{max. } \Delta\theta = \frac{1}{2}\left(\frac{4\times0{\cdot}005 + 4\times0{\cdot}01}{4^2+4^2}\right) = 0{\cdot}001 \text{ rad.} = 0{\cdot}06°.$$

If Y is increased to 8 cm., the same final accuracy will be produced with $dX = 0{\cdot}01$ cm. and $dY = 0{\cdot}02$ cm.

(c) If the Laue symmetry of the crystal includes a vertical reflexion plane, this plane can be set approximately parallel to the X-ray beam and measurements can be made on a Laue photograph, as above, for corresponding equatorial spots on each side of the centre. If δ is the angle between the symmetry plane and the X-ray beam, we have

$$\tan 2(\theta+\delta) = X_1/Y, \quad \tan 2(\theta-\delta) = X_2/Y;$$

$$\therefore \delta = \frac{1}{4}\left\{\tan^{-1}\frac{X_1}{Y} - \tan^{-1}\frac{X_2}{Y}\right\},$$

where θ is the Bragg angle when the symmetry plane is parallel to the beam.

For similar values of X and Y, this method has a smaller probable error but the same maximum error. However, if the plate is near enough (normally at 4 cm. or less), a number of major zones make identification of corresponding spots easier than the identification of a single spot in the previous method, and this usually more than compensates for some increase in the maximum error.

If suitable equatorial reflexions are not available, spots a few degrees above or below the equatorial plane can be used without introducing appreciable error.

(ii) *Arc adjustment*

(a) The method (i) (c) can be used for calculating small adjustments about a horizontal axis which is perpendicular to the beam (i.e. the axis of an arc whose plane is parallel to the beam), providing a horizontal plane of Laue symmetry is present. Two photographs are required, preferably on flat film, for the two arc adjustments, and the measurements are made on corresponding spots above and below the centre.

Since the arc corrections are approximations in this case (the effect on the correction for one arc of missetting on the other, and the possible tilt of the axis of the top arc, being neglected) it may be necessary to repeat the process before satisfactory adjustment is obtained.

(b) If the arc corrections required are large, preliminary adjustments must be made on the arc whose *axis* is parallel to the beam, equal to the angle (measured with a protractor) between the zero-layer curve and the equatorial plane at the central spot. In this case the method is further limited to class I crystals. For such preliminary adjustments either Laue or symmetrical oscillation photographs can be used.

(*c*) Lonsdale (1947) has suggested the use of a flat film perpendicular to the rotation axis for determining small arc corrections from a Laue photograph when a symmetry axis is being adjusted parallel to the rotation axis. The same method of calculation can be used, taking reflexions related by a diad axis of symmetry instead of by a plane. The main difficulties lie in determining the point where the rotation axis cuts the film, and the crystal–film distance. A trial-and-error process may have to be resorted to, using estimated instead of calculated adjustments.

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Crystal Symmetry and Physical Properties: Application of Group Theory

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The paper gives a brief account of group-theoretical methods of studying the effect of symmetry on all possible physical properties (known and already measured or not known) which depend on crystal symmetry; based on the fact that all such properties represent the relation between two quantities each of which may be a scalar, a vector, or a tensor. Tables are given showing the character of the transformation matrices for each possible combination of the above quantities, the number of independent constants needed to describe the corresponding phenomenon in each of the 32 classes, and actual examples (where known) of physical properties corresponding to the different possible combinations. The 32 crystal classes are reduced to 11 in all cases where centro-symmetrical properties are dealt with. When comparison is made with results of other methods of considering the same problems, discrepancies are found in the case of the photo-elastic coefficients and the third-order elastic coefficients.

All the properties considered above are such as will remain invariant under a transformation of axes according to any symmetry operation. There are other properties, such as enantiomorphism and optical activity, which change sign for an operation of rotation reflexion. The numbers of independent constants in each of the 32 classes are deduced for these properties also.

1. Introduction

Physical properties of substances generally express the relation between two quantities. These may be scalars, vectors, second- or higher-order tensors, all differing from one another by their transformation properties. Voigt made the transformation properties of the quantities involved in a physical relation the basis for the classification of crystal properties, thus distinguishing scalar–scalar relations (density), scalar–vector relations (pyro-electricity), vector–vector relations (dielectric polarization), tensor–tensor relations (elasticity), and so on. Each of these relations requires a number of independent coefficients connecting the components of the quantities involved, and, without assuming any symmetry of the crystal, the number of independent coefficients in the case of linear relations is the product of the numbers of independent components of the quantities being related. In crystals with symmetry elements, this maximum number of coefficients will be reduced. In order to find the reduction, produced by a symmetry element, Voigt transforms the axes of reference according to the symmetry element and demands that this transformation have no influence on the values of the coefficients expressing the relation of the physical quantities. It follows by this direct method of transformation that a number of coefficients must be zero, while others are equal. The systems of non-vanishing as well as of independent constants for various properties were thus derived in considerable detail by Voigt (1910) and by Pockels (1906). Love (1928), Wooster (1938), Cady (1946), Mason (1947) and others have subsequently dealt with the subject.

The fact that the symmetry operations of a crystal form a group allows the application of group theory to the study of the effect of symmetry on the physical properties of crystals. This very powerful method can be used as a valuable check on the direct process of deriving the non-vanishing constants in each of the 32 crystal classes. Thus Jahn (1937) made use of group theory for deducing the number of independent parameters and the non-vanishing elastic constants of