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Automatic Cell-size Determination and Orientation of Single Crystals

By W. A. Wooster

Brooklyn Crystallographic Laboratory, Bottisham, Cambridge, England

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The object of this paper is to outline a means of avoiding the preliminary studies of cell size and shape, and the accurate orientation of single crystals, prior to the measurement by automatic diffractometers of a large number of intensities of reflexion. This is particularly important when spherical crystals are used. A universally applicable means of doing this photographically by Weissenberg, or rotation retigraph or precession techniques is described. Also the methods of using normal-beam and 4-circle diffractometers for this purpose are given. By all of these methods the positions in reciprocal space of the reflecting reciprocal points, for a crystal of arbitrary orientation, are determined.

The second part of the paper is concerned with the use of digital computers to evaluate the cell parameters and the angles defining the orientation of the unit cell. A method is indicated whereby the angular settings on the diffractometer for any reflecting plane can be found for the crystal of arbitrary orientation.

1. Introduction

The application of digital computers to crystallography has opened up many new ways of solving crystal structures. The first step in the investigation of crystal structures is the measurement of the intensity of reflexion of each lattice plane. Until now this has almost always required an accurate orientation of the crystallographic axes relative to the measuring instrument. A zone axis has usually been set parallel to the main axis of rotation of a Weissenberg or a precession instrument and in diffractometers a zone axis has been set parallel to the axis of rotation of the goniometer head on which the crystal is mounted. In order to avoid uncertain and difficult corrections on account of the absorption of X-rays in the specimen it is usual to grind the crystal into a spherical shape. In doing so all trace of the external faces is lost and the crystal must be set up on the goniometer head with an arbitrary orientation. Then follows a process of orientation which is difficult unless certain striking features of the diffraction pattern happen to be observed. Except in the simplest cases, it is necessary to know the cell dimensions and angles before the measurements can be used to orientate the crystal and identify the indices of the reflexions. This requires considerable knowledge of crystallographic theory and practice.

The present paper is concerned with ways of avoiding this prior determination of the cell size and shape and the present method makes no demands on the crystallographic knowledge of the operator. The problem has two aspects, one experimental and the other computational. The experimental problem is the determination of the directions in which the reflexions occur together with the corresponding settings of the crystal. This may be solved using either photographic goniometers (*e.g.* Weissenberg, rotation retigraph, precession) or diffractometers, either normal beam, equi-inclination or 4-circle instruments. Whichever experimental method is used the computational problem is the same. The angular measurements must be interpreted to give the cell size and shape and also the orientation of the cell edges with respect to the principal axes of the instrument used.

2. Experimental methods

2·1. *Weissenberg goniometers*

The instrument is used in the equi-inclination arrangement and all rays recorded on a given photograph make the same angle, denoted ν, with the axis of the goniometer head. The limiting screen is made narrow enough to admit rays which differ in their inclination to the main axis by a small angle. In this paper we shall take the range in ν-values passed by the screen in its equatorial setting to be $2\frac{1}{2}°$. The crystal sphere is set up on the goniometer head with an arbitrary orientation and the photograph is taken in the usual way. In general there will be only a small number of spots in the photograph. The coordinates in reciprocal space of each spot are measured on a Weissenberg chart and plotted on a diagram. In general this diagram is a section of reciprocal space parallel to the equatorial plane distant $2 \sin \nu$ from it. A general definition of the orientation of the reflecting plane, applicable to all such sections of reciprocal space, may be given as follows. Each reciprocal point is joined by a line (called the relvector) to the origin and the polar coordinates of this line are denoted ϱ and φ respectively. The angle ϱ is that between the relvector and the axis of rotation. The angle φ is that between two planes intersecting in the axis of rotation, one of which contains the relvector and the other is an

arbitrarily chosen reference plane. The length of the relvector is denoted d^*. On the diagram for the equatorial plane the values of d^* and φ may be read off directly from the plot of the reflecting points. For all points in the equatorial plane ϱ is equal to 90°.

The limiting screen is now moved along the axis of rotation so that the previous range of reflected rays is just excluded. In the equatorial photograph the ν-values at the edges of the screen were $90° \pm 1\frac{1}{4}°$. In the second they are $90° - 3\frac{3}{4}°$ and $90° - 1\frac{1}{4}°$. The base of the instrument is rotated $2\frac{1}{2}°$ to correspond to the equi-inclination arrangement. The camera is also moved relative to its carriage so as to ensure that $\varphi = 0°$ corresponds to the same position on the film as in the previous photographs. The coordinates of the spots are read off as before, but to get the true values these must be multiplied by $\cos \nu$ to allow for the smaller radius of the reflecting circle when the equi-inclination angle is ν. The distance, f, of a reciprocal point from the centre of the plot of reciprocal points is $(d^{*2} - 4 \sin^2 \nu)^{\frac{1}{2}}$ further, $\sin \varrho = f/d^*$. The φ-value for each reflexion may be read off as for the equatorial photograph. Thus for this photograph d^*, ϱ, and φ-values can be assigned to each spot.

This process may be repeated as many times as may be required. If the cell size is large there will be many spots on each photograph and few photographs will be necessary. It is, of course, not necessary to take all the settings contiguous with one another. It would be advantageous to take at least one with as high an inclination angle as possible.

Other types of photographic goniometer, such as the rotation retigraph and the precession instruments, could be used to find the same experimental data as can be obtained with a Weissenberg goniometer.

2·2. *Diffractometers*

2·2·1. *Normal-beam type.* — In the normal-beam type of diffractometer the X-ray beam is perpendicular to the axis of rotation of the crystal. This axis, denoted φ, also coincides with the axis about which the detector arm can rotate. The zero setting of the detector is that in which the direct beam enters it. The angle of rotation of the detector arm from this position is denoted Υ. When the detector lies in the equatorial plane $\Upsilon = 2\theta$. The detector may be rotated about an axis lying in the equatorial plane and the angle of tilt relative to this plane is denoted ν.

The survey of all possible reflexions is carried out as follows. The detector is set with $\Upsilon = 3°$ and $\nu = 0°$ and the crystal is rotated from $\varphi = 0°$ to 180° at such a speed that a moderately strong reflexion can produce a registration of its effect. Usually the crystal will stop when a reflexion is detected, retreat, say, 2° and then traverse the reflexion slowly so as to obtain an accurate measure of its intensity. The finite size of the aperture in front of the detector causes the volume of reciprocal space surveyed by the rotation of the crystal to be half of a tore round the φ axis of mean radius $2\sin 3°$. If the angular divergence, in the equatorial plane, of the rays entering the counter is, say, 2°, the counter is now set to $\Upsilon = 5°$, $\nu = 0°$ and the crystal rotated through half a turn as before. Again the settings for reflexions are registered. This process is repeated up to, say, $\Upsilon = 30°$. The detector is now rotated so that it is tilted with respect to the equatorial plane by 2°, assuming this to be the angular divergence of the rays entering the counter in a plane perpendicular to the equator. A survey from $\Upsilon = 0$–30° is made as before. Each rotation of the crystal permits the examination of the reflexions lying in a tore which is parallel to the equatorial plane at a height $\sin \nu$ above it. If a reflexion occurs with settings Υ, ν, φ the coordinates in reciprocal space of the reflecting reciprocal point may be obtained as follows. In Fig. 1 the incident X-rays are represented on the stereogram by point I and the reflected rays by R. The normal to the reflecting planes is given by N. From the geometry of the figure we have

$$\cos 2\theta = \cos \Upsilon \cos \nu \tag{1}$$

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

$$\sin y = \sin \nu / (2 \sin \theta) . \tag{3}$$

The three quantities required to define the position of the reflecting reciprocal points are d^*, ϱ, φ_0. We obtain d^* from equation (2); ϱ is the angle between the normal N and the φ axis, *i.e.* $\frac{1}{2}\pi - y$, and is given by equation (3); φ_0 is the angle between the plane containing N and the φ axis and an arbitrarily chosen reference plane projecting in Fig. 1 as the line CA. Thus by the survey described above all three quantities can be obtained for each reflexion.

A similar analysis may be carried out with the equi-inclination type of diffractometer for which the

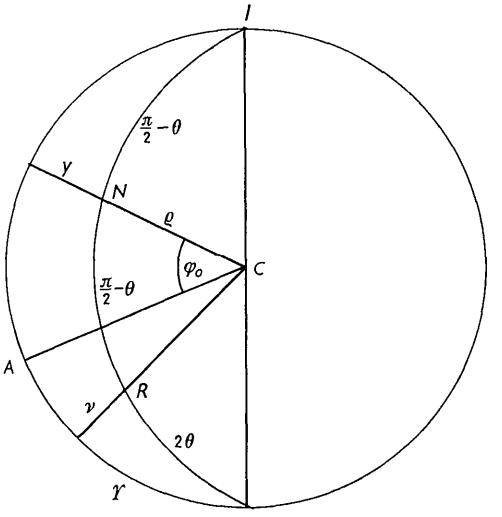

Fig. 1. Stereogram giving the angles defining the incident beam., I, the normal to the reflecting plane, N, and the direction of the reflected rays, R.

relevant equations corresponding to (1), (2) and (3) are a little different.

2·2·2. *4-circle diffractometer.* — The 4-circle diffractometer is derived from the normal-beam diffractometer by giving the φ axis a rotation about an axis, denoted χ, which is perpendicular to the 2θ axis of the detector (Wooster, 1962). Thus the φ axis is parallel to a radius of the χ circle and the φ, χ and 2θ axes all meet at a point where the crystal is placed. The $\chi-\varphi$ assembly is carried on a spindle coaxial with the 2θ axis, and rotation about this spindle is denoted ω. In the present discussion the symmetrical setting will be used for which $\omega=\theta$ and the χ axis is the internal bisector of the angle between the incident and reflected beams. The detector is always in the equatorial plane.

The starting setting is that in which the φ, $\omega(2\theta)$ axes coincide and for this $\chi=0$. When the crystal is rotated about the φ axis conditions are just the same as in the normal-beam diffractometer for the equatorial setting. When χ is given any other value, the ϱ-value of the reflecting points is fixed at a value $\frac{1}{2}\pi-\chi$. Thus, if a rotation about the φ axis is made, a tore is described in reciprocal space of mean radius $d^*=2\sin\theta\sin\varrho$, and lying in a plane perpendicular to the φ axis. Thus the values of d^*, ϱ and φ can be directly obtained from the 2θ, χ and φ settings. A systematic survey is carried out in a similar manner to that described for the normal-beam diffractometer. The crystal is oscillated continuously between $\varphi=0°$ and 180°, the χ-value is changed by, say, $2\frac{1}{2}°$ at the end of each oscillation, and at the end of a cycle of $\chi-\varphi$ changes the value of 2θ is changed by, say, $2\frac{1}{2}°$ and the cycle repeated. The time required for such a survey would depend on the strength of the incident beam, the reflecting power of the crystal and the number of sections of reciprocal space studied. In general a number of sections close to the origin would be followed by a few at much greater distances from the origin so as to obtain more accurate values of the cell dimensions.

3. Computations

3·1. *The reciprocal vector defining the unit cell*

Any two reflexions $h_1k_1l_1$, $h_2k_2l_2$ are defined by $|d_1^*|$, ϱ_1, φ_1 and $|d_2^*|$, ϱ_2, φ_2 respectively. If the sides and angles of the reciprocal unit cell are $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, α^*, β^*, γ^* then, (Azaroff & Buerger, 1958; Buerger, 1956; *International Tables for X-ray Crystallography*, 1959):

$$\mathbf{d}_1^*=h_1\mathbf{a}^*+k_1\mathbf{b}^*+l_1\mathbf{c}^*$$
$$\mathbf{d}_2^*=h_2\mathbf{a}^*+k_2\mathbf{b}^*+l_2\mathbf{c}^*\,.$$

The angle, σ, between the two reciprocal vectors is obtained from $\varrho_1\varphi_1$, $\varrho_2\varphi_2$ by the equation

$$\cos\sigma=\cos\varrho_1\cos\varrho_2+\sin\varrho_1\sin\varrho_2\cos(\varphi_1-\varphi_2). \quad (4)$$

The lengths of the reciprocal vectors are related to the unit-cell dimensions by the equations

$$\begin{aligned}d_1^{*2} &= \mathbf{d}_1^*.\mathbf{d}_1^*\\ &= h_1^2a^{*2}+k_1^2b^{*2}+l_1^2c^{*2}+2k_1l_1|b^*||c^*|\cos\alpha^*\\ &\quad +2l_1h_1|c^*||a^*|\cos\beta^*+2h_1k_1|a^*||b^*|\cos\gamma^*\ \textit{etc.}\end{aligned} \quad (5)$$

3·2. *Determination of* $|a^*|$, $|b^*|$ *and* $|c^*|$

The first part of the computer program involves determining $|(\mathbf{d}_2^*-\mathbf{d}_1^*)|$ for every pair of reflexions. The value of σ is computed by equation (3) from $\varrho_1\varphi_1$ and $\varrho_2\varphi_2$ and then we have

$$(\mathbf{d}_2^*-\mathbf{d}_1^*)^2=d_1^{*2}+d_2^{*2}-2|d_1^*||d_2^*|\cos\sigma\,.$$

The values of $|d^*|$ and the lengths of all vectors such as $(\mathbf{d}_2^*-\mathbf{d}_1^*)$ are sorted. The smallest values will probably give $|a^*|$, $|b^*|$ and $|c^*|$ but in the case when $|c^*|$ is much longer than $|a^*|$ and $|b^*|$ it is possible that $|(\mathbf{a}^*+\mathbf{b}^*)|$ or some other combination of $\mathbf{a}^*$ and $\mathbf{b}^*$ may be less than $|\mathbf{c}^*|$. To obviate this possibility a test must be applied to see if the three shortest vectors obtained by sorting are coplanar. The direction cosines of $\mathbf{d}_1^*$ with respect to the χ, R and φ axes are $\sin\varrho_1\sin\varphi_1$, $\sin\varrho_1\cos\varphi_1$ and $\cos\varrho_1$, (Fig. 2) so that the test for coplanar character of the three vectors denoted by subscripts 1, 2, 3 is that equation (6) shall be satisfied

$$\begin{vmatrix}\sin\varrho_1\sin\varphi_1 & \sin\varrho_1\cos\varphi_1 & \cos\varrho_1\\ \sin\varrho_2\sin\varphi_2 & \sin\varrho_2\cos\varphi_2 & \cos\varrho_2\\ \sin\varrho_3\sin\varphi_3 & \sin\varrho_3\cos\varphi_3 & \cos\varrho_3\end{vmatrix}=0\,. \quad (6)$$

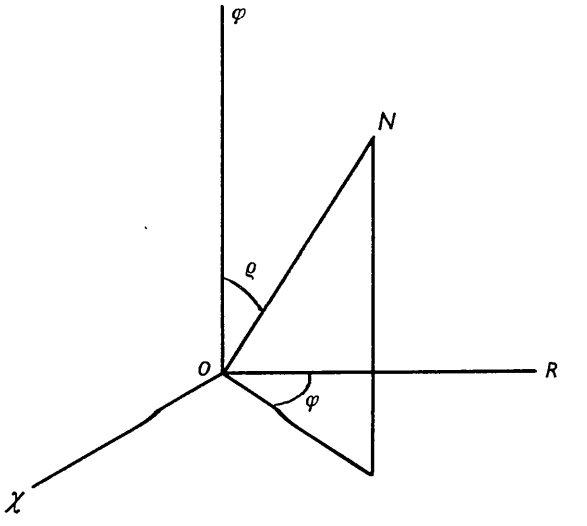

Fig. 2. Diagram showing the instrumental $\chi R\varphi$ axial system and the angles defining the normal to the reflecting plane, ON.

In applying this criterion allowance must be made for the errors in measuring the angles ϱ and φ. These errors would make the determinant depart slightly from zero even when the vectors are coplanar. The

three shortest non-coplanar reciprocal vectors are taken to define the unit cell. The values of a^*, b^* and c^* may be refined by a least-squares computer program, giving the best fit between calculated and observed d^*-values.

3·3. *Determination of the ϱ, φ values for* **a***, **b*** *and* **c***

The components of the vector joining the ends of $\mathbf{d}_2^*$ and $\mathbf{d}_1^*$ are

$$\begin{aligned} |d_2^*| \sin \varrho_2 \sin \varphi_2 - |d_1^*| \sin \varrho_1 \sin \varphi_1 &= p \\ |d_2^*| \sin \varrho_2 \cos \varphi_2 - |d_1^*| \sin \varrho_1 \cos \varphi_1 &= q \\ |d_2^*| \cos \varrho_2 - |d_1^*| \cos \varrho_1 &= r \,. \end{aligned}$$

The direction cosines of the vector $(\mathbf{d}_2^* - \mathbf{d}_1^*)$ are therefore,

$$\frac{p}{|(\mathbf{d}_2^* - \mathbf{d}_1^*)|} = s, \quad \frac{q}{|(\mathbf{d}_2^* - \mathbf{d}_1^*)|} = t, \quad \frac{r}{|(\mathbf{d}_2^* - \mathbf{d}_1^*)|} = u$$

which can be computed.

If by the sorting for the shortest lattice vectors, we find $\mathbf{a}^*$ lies along $(\mathbf{d}_2^* - \mathbf{d}_1^*)$ its ϱ, φ values are given by

$$\begin{aligned} \cos \varrho &= u \\ \cos \varphi &= t/\sin \varrho \,. \end{aligned}$$

Thus three vectors have been selected as **a***, **b***, **c*** and their ϱ, φ values can be obtained.

The values of α^*, β^*, γ^* are given by equation (7), namely,

$$\cos \alpha^* = \cos \varrho_{b^*} \cos \varrho_{c^*} + \sin \varrho_{b^*} \sin \varrho_{c^*} \cos (\varphi_{b^*} - \varphi_{c^*}) \quad (7)$$

and similar expressions yield $\cos \beta^*$ and $\cos \gamma^*$.

These values are also computed and stored.

4. The computation of the settings for all possible reflexions

At this point we have available the information

$$|a^*|, \ \varrho_{a^*}, \ \varphi_{a^*}, \ \alpha^*, \ u_{a^*} v_{a^*} w_{a^*}$$

and similar data for **b*** and **c***. The uvw's are direction cosines of the cell edges referred to the χ, R, φ axial system.

From these values we may calculate α, β, γ for the Bravais cell by the formulae

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*} \quad etc.$$

Also we need the angle ε (Wooster, 1962) given by

$$\cos \varepsilon = \sin \alpha^* \sin \beta \,.$$

Integral values are assigned to hkl and are used to calculate d_{hkl}^* from the expression (5). From this $2\theta_{hkl}$ may be obtained since

$$d_{hkl}^* = 2 \sin \theta_{hkl} \,.$$

We now require to calculate ϱ and φ for any given hkl. This cannot be done directly but first we calculate the ϱ_z, φ_{y^*} values relative to an orthogonal system which is illustrated in Fig. 3. The following relations hold (Wooster, 1962):

$$\cos \varrho_z = \frac{l|c^*|}{d^*} \cos \varepsilon$$

$$\cos \varphi_{y^*} = \frac{ha^* \cos \gamma^* + kb^* + lc^* \cos \alpha^*}{(h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} \sin^2 \varepsilon + 2klb^* c^* \cos \alpha^* + 2lhc^* a^* \cos \beta^* + 2hka^* b^* \cos \gamma^*)^{\frac{1}{2}}} \,.$$

It is possible to transform to the χ, R, φ axial system since the direction cosines of z and y^* relative to that system can be found.

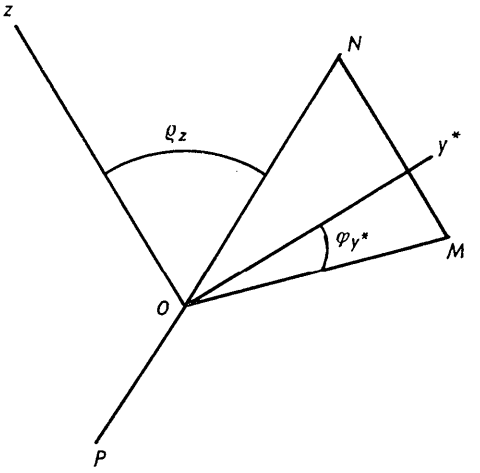

Fig. 3. Diagram showing the crystallographic Py^*z axial system and the angles defining the normal to the reflecting plane, ON.

The axis z is perpendicular to **a*** and **b***. We denote the direction cosines of z as u_z, v_z, w_z. Then

$$u_z = v_{b^*} w_{a^*} - v_{a^*} w_{b^*}$$

and similar expressions for v_z and w_z.

The axis **y*** has direction cosines $u_{y^*} v_{y^*} w_{y^*}$, which are already known. Finally, the axis P, perpendicular to z and y^*, has direction cosines given by

$$u_P = v_z w_{b^*} - v_{b^*} w_z \quad etc.$$

The matrix for conversion from the Py^*z to the χ, R, φ system is

	χ	R	φ
P	u_P	v_P	w_P
y^*	u_{b^*}	v_{b^*}	w_{b^*}
z	u_z	v_z	w_z

The direction cosines of **d*** relative to the Py^*z axes are obtained from ϱ_z, φ_{y^*} and by the above matrix the corresponding direction cosines relative to the χ, R, φ axial system may be obtained. The ϱ, φ values are obtained as before from the relation

$$\cos \varrho = w_{d^*}$$
$$\cos \varphi = v_{d^*}/\sin \varrho \, .$$

Thus the 2θ, ϱ and φ values for any value of hkl can be obtained and used to set the crystal to enable any desired reflexion to be studied.

5. Conclusions

The procedure described here will lead to an unambiguous result but the cell determined by this procedure need not be the one usually employed. For instance a face-centred cubic Bravais lattice has a reciprocal counterpart in which the three shortest vectors define a rhombohedral cell of side equal to $\sqrt{3}a^*$ and $\alpha^* = 110°$. A body-centred cubic Bravais lattice would likewise be represented in reciprocal space by a rhombohedral cell the sides of which are $\sqrt{2}a^*$ in length and the angle $\alpha^* = 60°$. There are other possible instances where the unit cell chosen by this method would have a lower symmetry than that of the usually accepted cell or lack its orthogonality. The indices determined by the present procedure could be readily transformed to those usually accepted after the measurements of the intensity of reflexion had been made.

Buerger (1942) discusses the relation between the reduced reciprocal lattice, derived by the procedure described here, and the corresponding Bravais lattice. Usually the reduced reciprocal lattice leads to the reduced Bravais lattice by the usual transformations. In a few cases, however, Buerger points out that other conditions must be applied to determine the true reduced Bravais lattice.

Another feature of this method which should be mentioned is the fact that the low-angle reflexions are very convenient for determining the approximate size and shape of the reciprocal unit cell while the high-angle reflexions are best for finding accurate values of these dimensions. It would be necessary to design the program of computation so that after finding the approximate values of a^*, b^*, c^*, α^*, β^*, γ^* these were automatically refined by taking into account the high-angle reflexions. The final values of the cell parameters would have to be based on the high-angle reflexions so that the calculated settings of the circles were correctly determined for these reflexions.

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The Crystal Structure of Diammonium Dihydrogen Hypophosphate $(NH_4)_2H_2P_2O_6$

BY A. WILSON AND H. MCD. MCGEACHIN

Albright and Wilson (Mfg) Ltd., Oldbury, Birmingham, England

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The crystal structure of diammonium dihydrogen hypophosphate has been solved by trial and error and refined in three dimensions. The bond lengths are P–P 2·17, P–O(H) 1·57, and P–O 1·50 Å (twice). The hypophosphate ion has twofold symmetry and adopts a staggered configuration with symmetry approaching $\bar{3}m$.

Introduction

Speculation on the structure of the hypophosphate ion $[P_2O_6]^{4-}$ has a long history, chronicled by Van Wazer (1958). No complete structure determination of a hypophosphate has been reported, however.

Crystal data

$(NH_4)_2H_2P_2O_6$, M.W. 196·1, orthorhombic, $a = 7{\cdot}240$, $b = 11{\cdot}465$, $c = 9{\cdot}350$ Å (all $\pm 0{\cdot}005$), observed density 1·679, four molecules per unit cell. Space group *Pccn* (D_{2h}^{10}, No. 56), implied symmetry of the hypophosphate ion $\bar{1}$ or 2.

Crystals of good quality with a typical dimension of 0·15 mm were kindly supplied by D. R. Peck of this laboratory.

Structure determination

The unit cell and space group were reported by Raistrick & Hobbs (1949), who from the space group and density deduced that the hypophosphate ions existed in the symmetrical form. The resemblance