

A TWO-DIMENSIONAL REFINEMENT OF THE
CRYSTAL STRUCTURE OF SILLIMANITE

by

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ABSTRACT

The crystal structure of sillimanite has been refined by 2-dimensional Fourier syntheses. The specimen used throughout this investigation was from Willimantic, Connecticut, U.S.A.

Accurate unit cell dimensions were measured by the method of C. L. Christ (1956) using a conventional Weissenberg camera with an internal standard. The values obtained were $a_0 = 7.476 \pm .003 \text{ \AA}$, $b_0 = 7.666 \pm .005 \text{ \AA}$, $c_0 = 5.763 \pm .003 \text{ \AA}$. The specific gravity was measured on a Berman microbalance and was found to be $3.240 \text{ gm. cm.}^{-3}$. From the volume of the unit cell and the measured density, the number of formula units in the unit cell of sillimanite was thus $4 (\text{Al}_2\text{SiO}_5)$. The presence of a centre of symmetry was indicated by a statistical analysis of the hkl data and the space group was confirmed to be Pbnm .

Two-dimensional intensity data were collected from Weissenberg photographs using a triple film pack and molybdenum X-radiation. The intensities were measured by visual comparison with a standard intensity scale and the structure amplitudes derived by applying the Lorentz-polarization factor to each reflection. The observed structure factors were placed on an absolute scale by comparison with structure factor data calculated from previously published atomic parameters of sillimanite.

Using the atomic parameters of Taylor (1928) and of Hey and Taylor (1931) as starting points, refinement of the structure was made by seven successive F_0 and $F_0 - F_c$ syntheses along all three of the principal axes; the final R factors for 148 $hk0$, 57 $h0l$ and 63 $0kl$ reflections being 18.9%, 12.8% and 12.9% respectively. The mean Si-O

bond distance is $1.630 \pm 0.014 \text{ \AA}$, the mean tetrahedral Al-O bond distance is $1.742 \pm 0.014 \text{ \AA}$ and the mean octahedral Al-O bond distance is $1.916 \pm 0.013 \text{ \AA}$. Temperature factors are given for each atom in each projection.

A comparison is made with the results recently published by Burnham (1963), and possible electrostatic charge distributions within the structure are discussed. The tetrahedral site sizes indicate that the structure is ordered with respect to silicon and aluminum.

A programme for the computation of 2-dimensional structure factors for sillimanite on the I.B.M. "1620" is included in an Appendix of this dissertation.

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CHAPTER I

INTRODUCTION

This project was undertaken for the purpose of instructing the author in the methods of crystal structure analysis by doing a refinement of a relatively simple structure. The experimental work was done in the X-Ray Diffraction Laboratory of the Geology Department of the University of Manitoba, and it was thus appropriate to choose a mineral which fell into the general programme of research in that Laboratory. The mineral chosen was sillimanite, an aluminosilicate of the ideal formula Al_2SiO_5 . It was felt that this mineral would yield valuable information about the silicon-aluminum "ordering" in this mineral and about the bonding in silicates.

In the determination of a completely unknown crystal structure it is necessary to solve the structure with no previous knowledge of the atomic positions. However, in a refinement approximate atomic positions have to have been determined beforehand, and during the refinement the atoms are located more accurately in the unit cell. For the above reasons, an unknown structure determination is more difficult and requires more time to complete than a refinement. By its nature an unknown structure determination is uncertain in its outcome, while a refinement of this complexity may be expected to reach completion in one year.

The original derivation of the crystal structure of sillimanite was done by W. H. Taylor (1928), and later, J. S. Hey and W. H. Taylor (1931) published a revision of the original structure which was more accurate, but which still required refinement by modern Fourier methods. A search of the literature to June 1962, revealed that no

refinement had been published so the author began work on this structure at that time. However, in November of 1962, while this work was in progress, an abstract of a refinement of the sillimanite structure was published by C. W. Burnham (1962a). In view of the fact that the present refinement had already included the accurate determination of cell dimensions, the collection of all the intensity data for a two-dimensional refinement, and a number of the computations, the decision was made to continue this work and so produce a completely independent refinement. Furthermore, it appeared unlikely that Burnham's full paper would be published before the present refinement would be completed.

All of the X-ray data that would be required for the refinement were collected on single-crystal Weissenberg photographs. Most of the computations were done on an I.B.M. "650" computer at Great West Life Assurance Company, Winnipeg.

CHAPTER II

DESCRIPTION OF THE SILLIMANITE SPECIMEN

Sillimanite is a polymorph in the aluminosilicate group of minerals of ideal formula Al_2SiO_5 . The other two members of this group are kyanite and andalusite. The temperature-pressure relationships between sillimanite, kyanite and andalusite have not been completely determined, but sillimanite is known to be the high-temperature polymorph and is characteristic of high-temperature and high-pressure metamorphic rocks.

A Locality

The sillimanite specimen used in this investigation was taken from the mineral museum at the Geology Department of the University of Manitoba (Museum Number 399-3). The rock containing the sillimanite was found in Willimantic, Connecticut, U.S.A. The sillimanite occurs as large (up to 3 cm.), elongated, transparent amber crystals in a sillimanite gneiss with quartz, feldspar, biotite and muscovite. A suitable crystal of sillimanite was broken off the large specimen and used to provide material for the investigation.

B Chemical Analysis

A chemical analysis of the specimen was done on the X-ray fluorescence spectrometer in the Geology Department of the University of Manitoba by Mr. K. Ramlal. The specimen was prepared by crushing about 0.5 grams of sillimanite to a moderately fine size, and then visible impurities removed under the binocular microscope. The results of the analysis are shown in Table I. The low total for the analysis may be due to absorbed water which was not analysed for but which may

TABLE I

CHEMICAL ANALYSIS OF THE SILLIMANITE SPECIMEN

	Theoretical Al_2SiO_5 Weight %	Weight %*	Willimantic, Conn. Weight % Recalculated to 100	Number of Metal Atoms per 5 Oxygen Atoms
SiO_2	37.07	36.10	37.25	Si 1.011
Al_2O_3	62.93	58.60	60.48	Al 1.935
Fe_2O_3		1.58	1.63	Fe 0.033
MgO		0.57	0.59	Mg 0.024
CaO		0.01		
K_2O		0.05	0.05	
				1.992
Total	100.00	96.91	100.00	

*Done on the X-ray Fluorescence Spectrometer in the Geology Department of the University of Manitoba, by K. Ramlal.

have been present because the finely powdered specimen was possibly hygroscopic. The small amount of potassium and correspondingly small amounts of magnesium and iron in the sample may be due to small amounts of biotite still present in the handpicked sample. However since the potassium analysis is so low this will not explain the large amounts for Fe_2O_3 and MgO . It has been assumed in Table I in the calculation of the number of metal atoms per five oxygen atoms that the magnesia and ferric oxide are present in the sillimanite, while that present as biotite has been neglected. It is unlikely, from this analysis compared to analyses in Deer, Howie and Zussman (1962, Vol. I), that anything is unusual about the composition of this sillimanite.

C Density and Cell Content (Z)

The specific gravities of three small fragments were determined with the aid of the Berman specific gravity balance, using toluene at an average temperature of 24°C . The values found for each were, 3.234, 3.245 and 3.241 gm/cm^3 . The average specific gravity of these fragments is 3.240 gm/cm^3 which lies within the range listed in Deer, Howie and Zussman (1962, Vol. I) of $3.23\text{--}3.27 \text{ gm/cm}^3$.

From the measured density $d \text{ (gm/cm}^3\text{)}$, the volume of the unit cell $V \text{ (cm}^3\text{)}$, Avogadro's number N , and the molecular weight, $M \text{ (gm/mole)}$, the number of formula units (Z) in the unit cell may be calculated using the formula
$$Z = \frac{V \times d \times N}{M} .$$

The volume of the unit cell in the orthorhombic system is simply the product of the three cell edges, a , b and c . The determination of these values is described in Chapter V, but they are used here to calculate the volume, which is $330.28 \text{ \AA}^3$.

Using this value for the volume V , the above value of the measured density, and the molecular weight of ideal Al_2SiO_5 of 162.00 gms/mole, the cell content of sillimanite calculates to be,

$$Z = \frac{330.28 \times 10^{-24} \times 3.240 \times 6.023 \times 10^{23}}{162.00} = 3.98$$

Since the unit cell must contain an integral number of molecules or formula units, the ideal cell content of sillimanite must be 4 (Al_2SiO_5). With this value for the cell content (4), the ideal density as determined by X-ray methods is 3.258 gm/cm^3 .

CHAPTER III

SOME BASIC X-RAY DIFFRACTION THEORY

A crystalline substance may be defined as one that is a regular arrangement of atoms in space repeated throughout the volume of the crystal. X-radiation is an electromagnetic phenomenon like visible light but of short wave-length ($0.6 - 2.5 \text{ \AA}$). If X-rays are directed at any crystalline substance they are diffracted just as visible light is diffracted by an optical grating. The interaction of the electric field of the X-radiation with the electrons of the atoms produces this diffraction. The electric field sets the electrons into forced vibrations making them secondary emitters of the radiation. This interaction of the incident radiation and the electrons causes them to scatter the original X-ray wave.

There are two general techniques used in examining crystals by X-ray diffraction. The first is X-ray powder photography which is concerned mainly with the study of crystalline compounds for the purpose of identification and, in favourable cases, quantitative analysis of mixtures although some simple crystal structures have been solved by the use of powder photographs. The second includes single crystal methods which are used mainly for complete structure determinations. The single crystal methods are used for structural analyses because they yield more information about the crystal than do powder photographs. There are several different types of single crystal methods that have been used to advantage. These include oscillation, rotation, Weissenberg and precession methods. This report describes the interpretation of only oscillation, rotation and Weissenberg photographs because they are the only ones used in this investigation.

X-ray diffraction by a crystal can be thought of as reflection by sets of parallel lattice planes in a crystal (Buerger, 1942, p. 43). From a consideration of the positions of these reflections from different sets of lattice planes in the crystal one is able to determine the geometrical nature of the lattice and the size of the unit cell. From the systematic absences of reflections one is able to determine, sometimes uniquely, the space group for that crystal. Finally from chemical analysis and specific gravity measurements, the kinds and numbers of atoms that are contained in a unit cell can be determined.

Measurements of the intensities of these reflections afford much of the information required to determine the atomic positions in the unit cell. However, associated with these reflections there is not only the magnitude of the intensity but also a phase angle and this is in general, unobservable. Therefore, in order to fully define the nature of the waves producing the reflections, one must calculate the phase angles from a structure that is essentially correct. It is this "phase problem" which makes the derivation of a crystal structure so uncertain but at the same time so challenging.

The discovery of the diffraction of X-rays by crystals took place in 1912 when M. von Laue suggested that the wave-length of X-radiation was likely of the order of 10^{-8} cm. Thus a natural crystalline substance would serve as a three-dimensional diffraction grating for X-rays. Laue set down the conditions for the diffraction of X-rays by a three-dimensional crystal lattice in three equations, which require that the path difference between waves scattered from successive lattice points be equal to a whole number of wave-lengths n :

$$a (\cos \alpha_0 - \cos \alpha) = n_1 \lambda$$

$$b (\cos \beta_0 - \cos \beta) = n_2 \lambda$$

$$c (\cos \gamma_0 - \cos \gamma) = n_3 \lambda$$

In these three equations α_0 , β_0 , γ_0 are the angles which the incident beam makes with the three principal axes, a , b and c in the crystal lattice. The direction of the diffracted beam is defined by the angles α , β and γ , and the set of integers, n_1 , n_2 and n_3 denotes the order of the reflection. A formal proof of these relationships which must be satisfied in order that diffraction will occur, is given in Buerger, (1942, Chapter 3). Also in this reference it is shown that these three conditions for diffraction are geometrically equivalent to a reflection of the X-ray beam by the lattice plane, whose intercepts on the three principal axes would be a/n_1 , b/n_2 and c/n_3 .

Shortly after the discovery of the diffraction of X-rays by crystals by von Laue, W. L. Bragg in 1913 suggested a simpler interpretation of this phenomenon which he expressed in the now well known Bragg Law, $n\lambda = 2d \sin \Theta$. This equation arose from the fact that Bragg considered the scattered radiation to be "reflected" from lattice planes within the crystal. Reinforcement of one wave by another reflected from a parallel neighbouring plane at a distance d will occur when the path difference between these two waves is equal to a whole number of wave-lengths, i.e., when $n\lambda = 2d \sin \Theta$ where λ is the wave-length in $\text{\AA}$, d the interplanar spacing in $\text{\AA}$, and Θ is the angle in degrees between the crystal plane and the incident X-ray beam. Thus Bragg showed that the concept of the crystal lattice as a set of parallel planes through lattice points is extremely useful in explaining the theory of diffraction.

Coupled with this concept of the direct lattice, there is also the concept of a "reciprocal lattice" without which the interpretation of single-crystal photographs would be very difficult. The idea of a reciprocal lattice was introduced by Ewald in 1921. It has no physical reality and is used only in the interpretation of the diffraction of X-rays by crystals. However, the direct or space lattice does have reality for it describes the manner in which groups of atoms are repeated in space. The reciprocal lattice is similar in many respects to the gnomonic projection used in the morphological description of crystal faces.

In crystallographic problems it is convenient to represent sets of lattice planes by their normals rather than by the sets of planes themselves. In this way the task of interpreting single-crystal photographs is greatly simplified. The reciprocal lattice closely corresponds to a single-crystal photograph in that both are characterized by points or spots which represent sets of parallel lattice planes. In order to construct the reciprocal lattice corresponding to a direct or space lattice, consider a two dimensional projection of a primitive monoclinic space lattice along the y axis shown in Fig. 1. Each interplanar spacing d_{h0l} is then considered. For example, d_{001} is the perpendicular distance from the origin to the (001) plane. A vector σ_{h0l} is plotted parallel to the interplanar spacing d_{h0l} and its length is made proportional to the reciprocal of d_{h0l} , i.e., equal to $\frac{k}{d_{h0l}}$ where k is a constant of proportionality. When this construction is made for each plane of the direct lattice, the resulting array of points, one at the end of each vector σ_{h0l} , constitutes the reciprocal lattice.

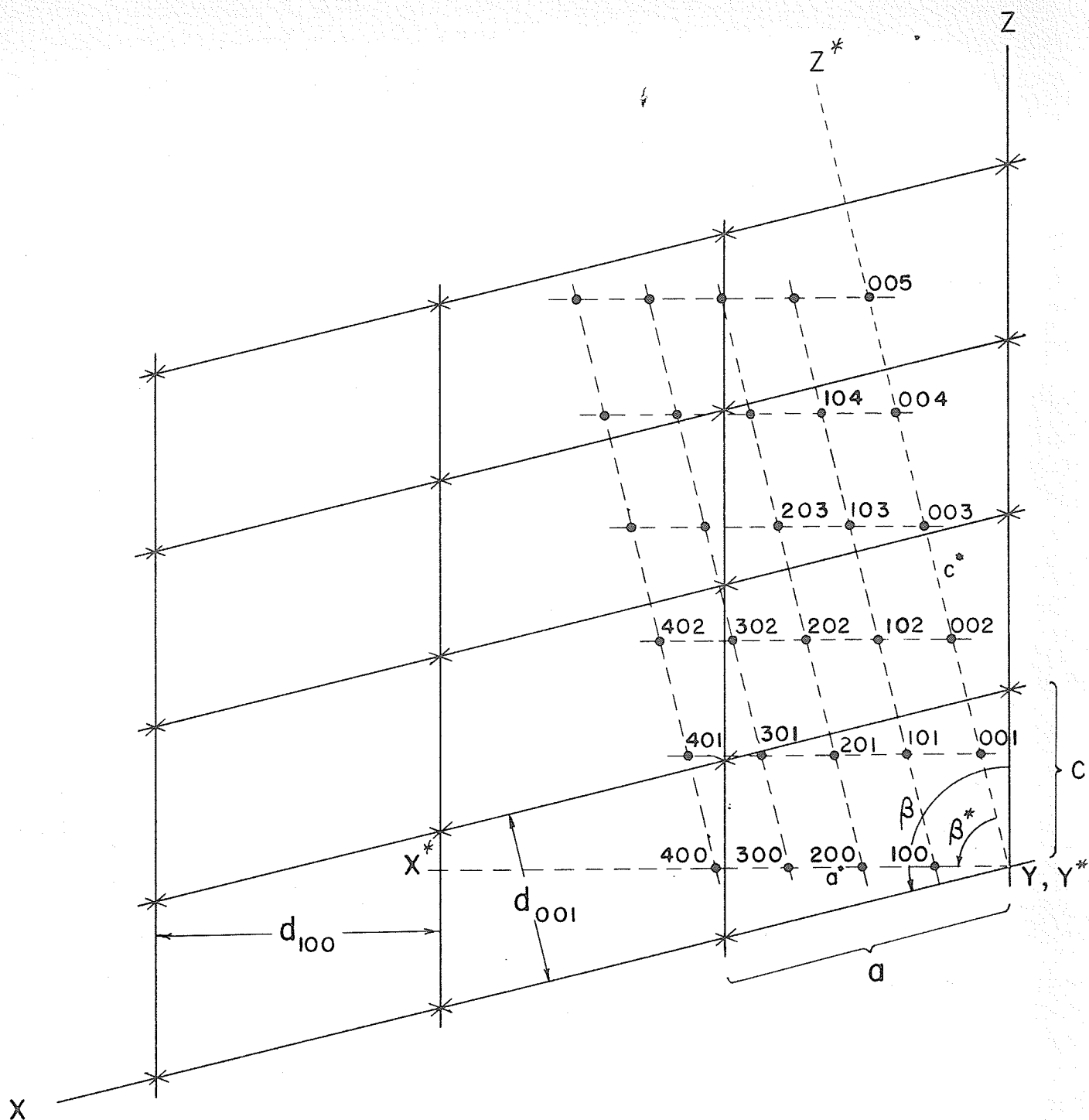


Fig. 1. Construction of the reciprocal lattice of a primitive monoclinic space lattice projected along the y axis. Solid lines represent the direct lattice; dashed lines represent the reciprocal lattice.

In Fig. 1 the direct lattice points are represented by crosses and the reciprocal lattice points by closed circles. The principal axes of the reciprocal lattice x^* , y^* and z^* are the directions from the origin normal to the three principal planes of the direct unit cell (100), (010), and (001). The unit lengths of the reciprocal axes a^* , b^* and c^* are defined as equal to k/d_{100} , k/d_{010} and k/d_{001} respectively. Reciprocal lattice elements are thus denoted by the same letters as used for the direct lattice elements with the addition of asterisks.

Direct elements	$x, y, z, a, b, c, \alpha, \beta, \gamma.$
Reciprocal elements	$x^*, y^*, z^*, a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*.$

The scale of any given reciprocal lattice is determined by the constant of proportionality k . For a reason that will be developed shortly, the constant k in all X-ray work is taken as λ , the wave-length of the X-radiation.

With this concept of the reciprocal lattice it is now possible to consider a geometrical interpretation of Bragg's Law and the conditions necessary for reflection by a real lattice. The concept of reflection by the reciprocal lattice results in a "sphere of reflection" which is shown diagrammatically in Fig. 2. This sphere of reflection is constructed to surround the crystal which is located at the sphere's centre. It gives the condition of when and where a reflection from a single crystal will occur. The sphere of reflection may be derived in the following manner.

At point 0 in Fig. 2 let the line pp' depict the orientation of a set of crystal planes of spacing d . Let this set of planes be in the proper position for a reflection of the X-rays to result. Since

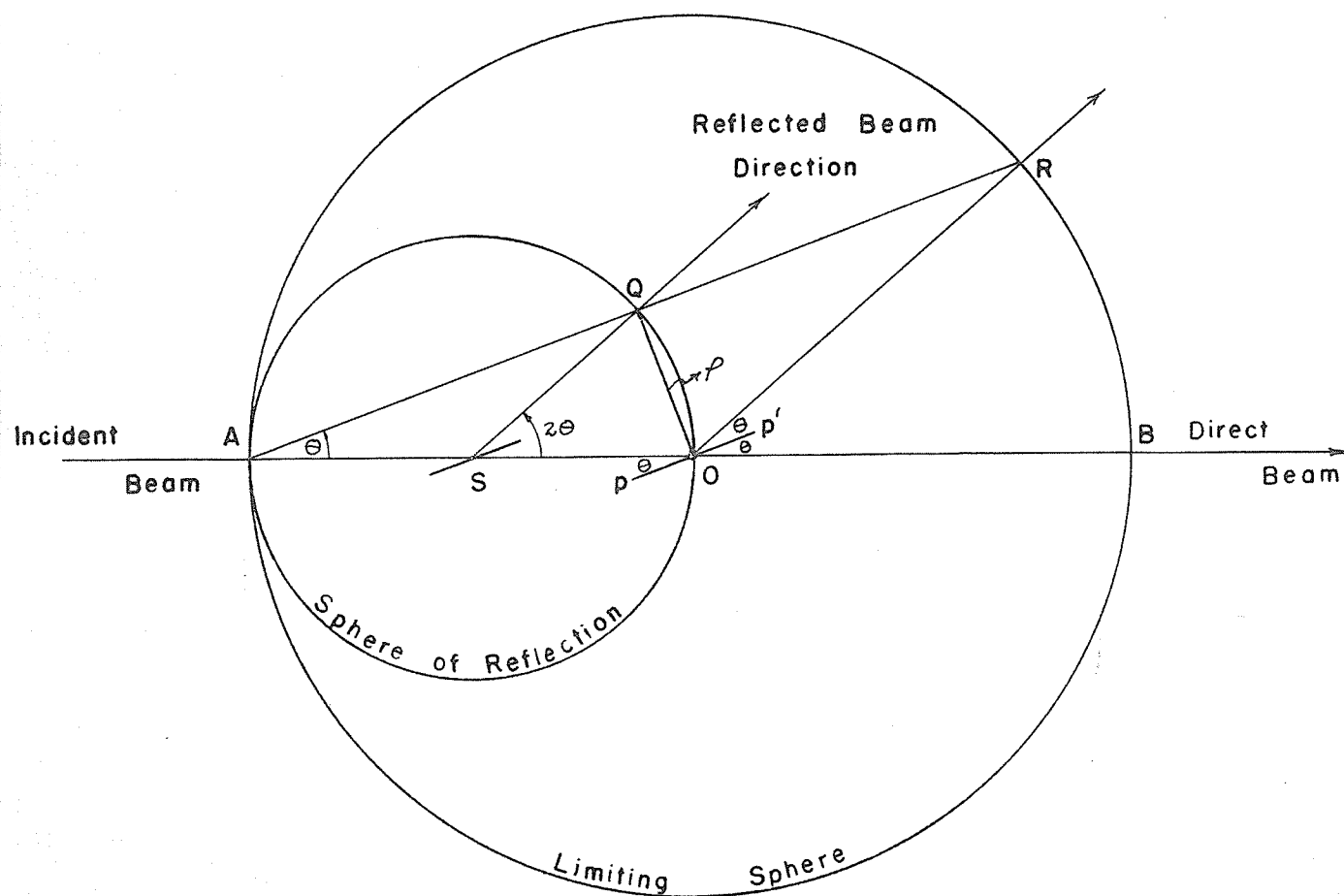


Fig. 2. The derivation of the sphere of reflection and the limiting sphere. The crystal is at S, the centre of the sphere of reflection and the origin of the reciprocal lattice is located at the point O.

this is a set of crystal planes one can construct a reciprocal lattice point to represent this set of planes by erecting a normal to the plane and choosing a unit length $OQ = \rho$ where $\rho = \lambda/d$ and d is the interplanar spacing of this set of planes. Let the line AB represent the path of the incident X-ray beam and the line OR represent the reflected beam from the plane pp' . The glancing angle AOp and the reflecting angle ROp' are both designated by θ . If pp' lies in the plane of AOR then $\angle AOp = \angle ROp' = \theta$. Angle $p'OB = \theta$ (vertically opposite $\angle AOp$) and so $\angle ROB = 2\theta$. From the reciprocal lattice point Q construct line QA perpendicular to OQ to meet the primary X-ray beam at A . Then QA will be parallel to pp' and $\angle QAO = \angle AOp = \theta$. From the diagram, $\sin \angle QAO = \sin \theta = \frac{\rho}{AO}$, but $\rho = \frac{\lambda}{d}$ so that $AO = \frac{\lambda}{d \sin \theta}$. For a first order reflection the Bragg equation must be $1 \lambda = 2d \sin \theta$ and thus AO must equal 2. It follows from this construction that all of the reciprocal lattice points of the type Q of all of the direct lattice planes will be corners of triangles of the type AQO in which $\angle s AQO$ are right angles. Thus the locus of all points Q in one plane will be a circle and in three dimensions a sphere whose diameter will be $AO = 2$ and whose radius will therefore be 1. Although in our construction the direction OR is the direction of the reflected beam, one can equally choose the parallel direction SQ to represent the reflected ray, thus allowing one to place the crystal at S , the centre of the sphere. Thus is derived the "sphere of reflection" which for reciprocal lattice distances of λ/d will have unit radius and will consist of a sphere with the crystal at the centre, the X-ray beam along one diameter and the origin of the reciprocal lattice at the point where the direct X-ray beam emerges from the sphere.

The final topic to be considered in this chapter is the concept of the "limiting sphere". The limiting sphere gives one the maximum number of possible reflections afforded by a certain crystal using a specific X-radiation. The crystal rotates about the point S in Fig. 2, while the reciprocal lattice is thought of as rotating about the point of emergence of the primary X-ray beam from the sphere of reflection (point 0). This permits only reciprocal lattice points with $\rho \leq 2$ units to possibly reflect. The volume containing such reciprocal lattice points is therefore contained approximately in a sphere known as the limiting sphere with radius 2.

CHAPTER IV

OSCILLATION AND ROTATION PHOTOGRAPHS:

CRYSTAL ALIGNMENT AND CELL DIMENSIONS

A Introductory Theory

It has been shown in the previous chapter that each time a reciprocal lattice point cuts the sphere of reflection a diffracted beam is produced along the direction SQ (Fig. 2). In the rotating crystal method a single crystal is placed in the X-ray beam with one principal axis of the direct lattice parallel to the axis of rotation. A fixed cylindrical film is placed around the crystal to record the diffraction pattern. The manner in which the reflections are recorded on the film can be deduced from Figs. 3 and 4 modified from Bunn (1961 Fig. 83). As shown in the last chapter, the reciprocal lattice rotates about the point at which the primary X-ray beam emerges from the sphere of reflection, point O on Figs. 3 and 4. A particular case is shown in Fig. 4 in which the diffracted beam is flashing out in the direction ST striking the film at W . The crystal is assumed to be rotating about the c axis with the incident beam perpendicular to the axis of rotation. It can be seen in Figs. 3 and 4 that the reflected beams corresponding to reciprocal lattice points in the same plane (same value of l) will all lie on one conical surface. The semi-vertical angle of this cone (ϕ) has the same value for all reflections of the same l index (the reciprocal lattice plane of constant l). The base of this cone is at the film, and in general all reflections of the same l index will lie on one straight line on the film.

It now becomes necessary to determine the relationship between the separation of these "layer lines" and the rotation period of the

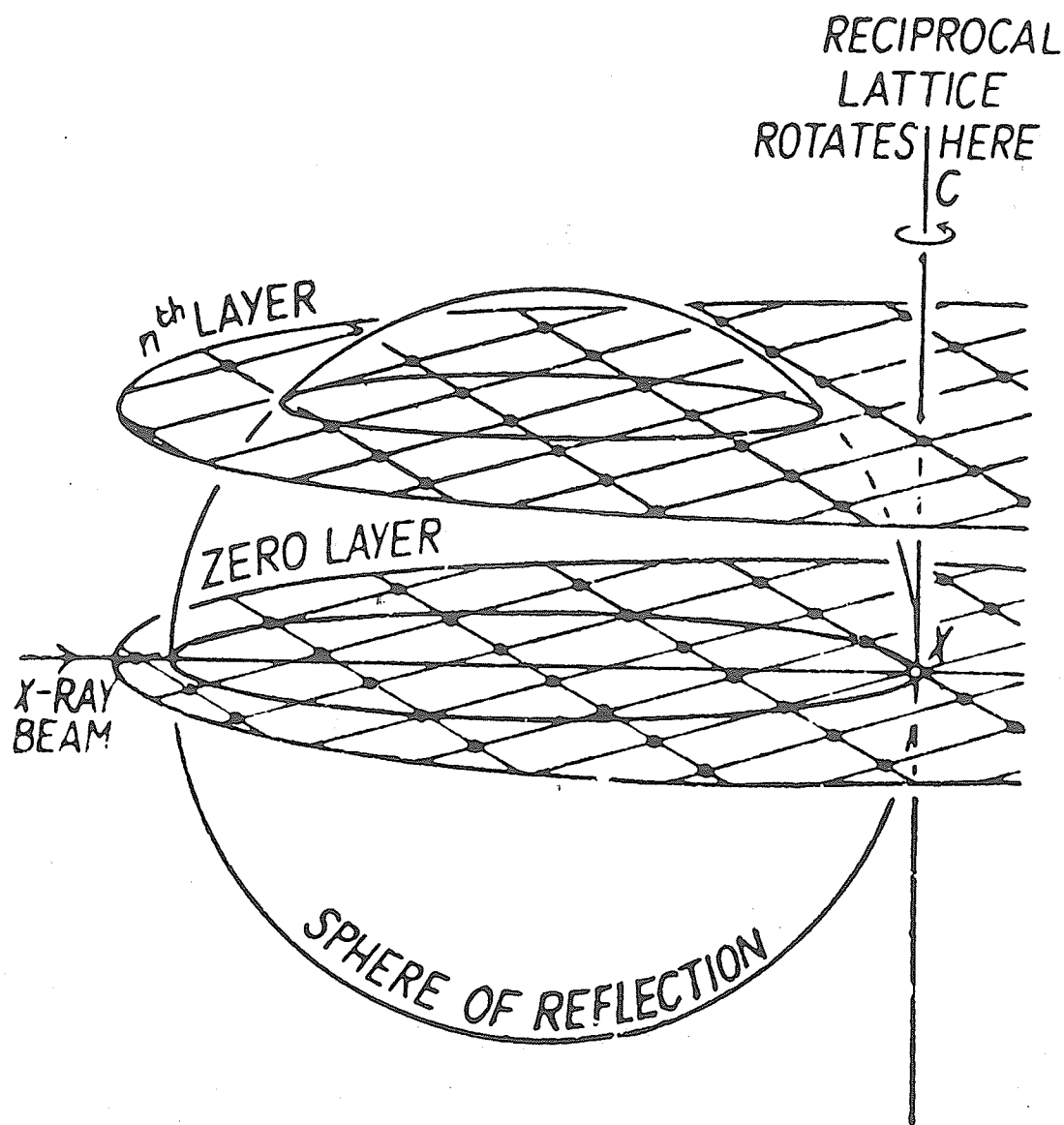


Fig. 3. Diagrammatic representation of the reciprocal lattice as it passes through the sphere of reflection. (Reproduced from Bunn (1961) Fig. 82.)

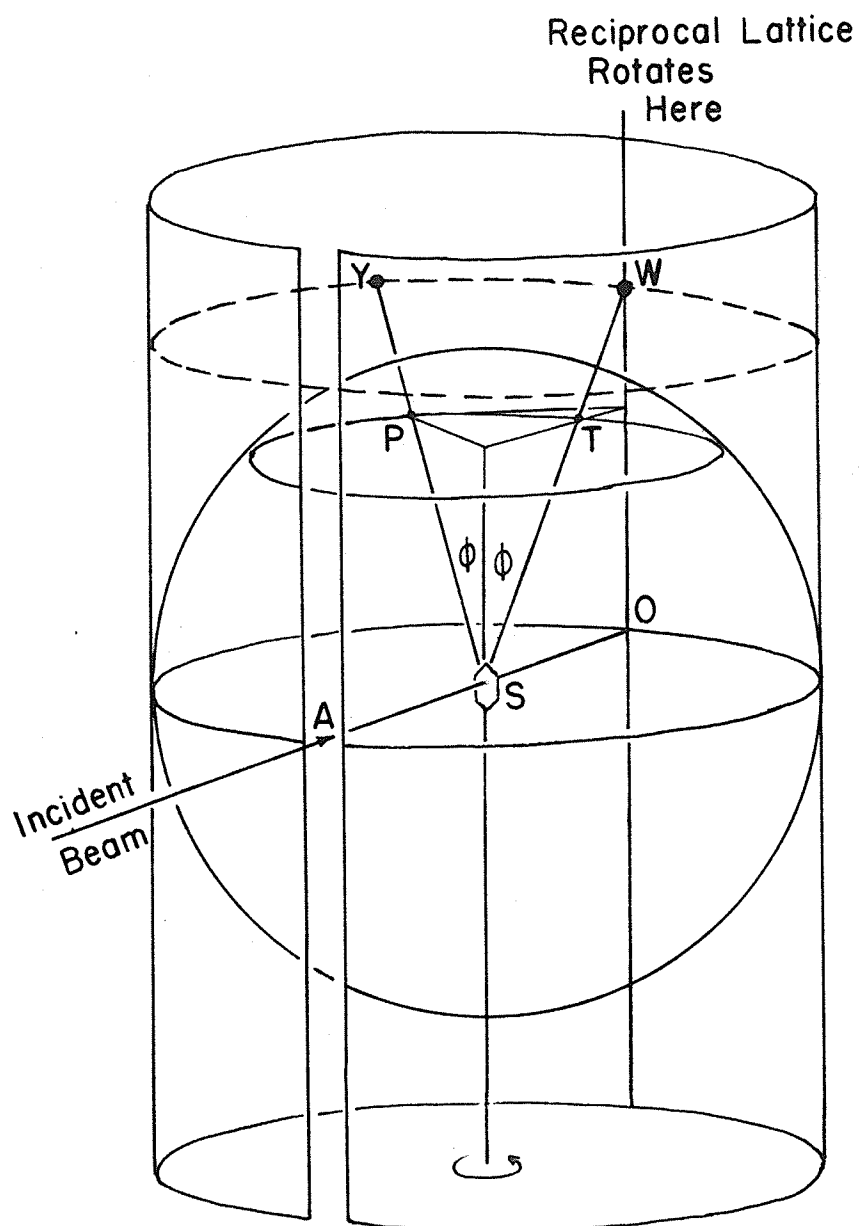


Fig. 4. The production of reflections on a cylindrical film surrounding the sphere of reflection. (Modified from Bunn (1961) Fig. 83.)

axis about which the crystal is rotating. When the difference between the path lengths of the rays scattered by neighbouring points (diffracting centres) along this rotation axis is either zero or a whole number of wave-lengths, reinforcement occurs and a diffracted beam is produced. By referring to a simplified diagram shown in Fig. 5, the condition necessary for diffraction to occur can be derived. Along the axis about which the crystal is rotating let there be diffracting centres at points separated by the repeat distance p , and let the incident X-ray beam (wave-length λ) strike this row at right angles. Let the angle which the diffracted beam makes with the diffracting row be ϕ , and the path difference between waves scattered from neighbouring diffracting centres be σ . Then $\sigma/p = \cos \phi$. The secondary scattered waves of wave-length λ in general interfere with each other destructively. For constructive interference (wavelets in phase) the path difference σ must be either zero or a whole number of wave-lengths,

$$\text{i.e., } p \cos \phi = n \lambda \text{ where } n=0, 1, 2, 3, \dots$$

For a particular value of n, λ and p in the above equation, it follows that the cosine of ϕ must be constant. The diffracted rays will thus lie on the surfaces of two cones symmetrically on either side of the zero layer with the lattice row as the axis (Fig. 6). If one then imagines the crystal surrounded with a cylindrical film that is coaxial with the axis of rotation, then these two cones will be recorded on the film as two straight lines, one on either side of the zero layer lines. There will be two such lines for each value of n . However, a crystal is not a single row of diffracting centres but rather many identical parallel rows extending in three dimensions. Therefore there is not a continuous diffracted beam making up the surfaces of these cones but rather only

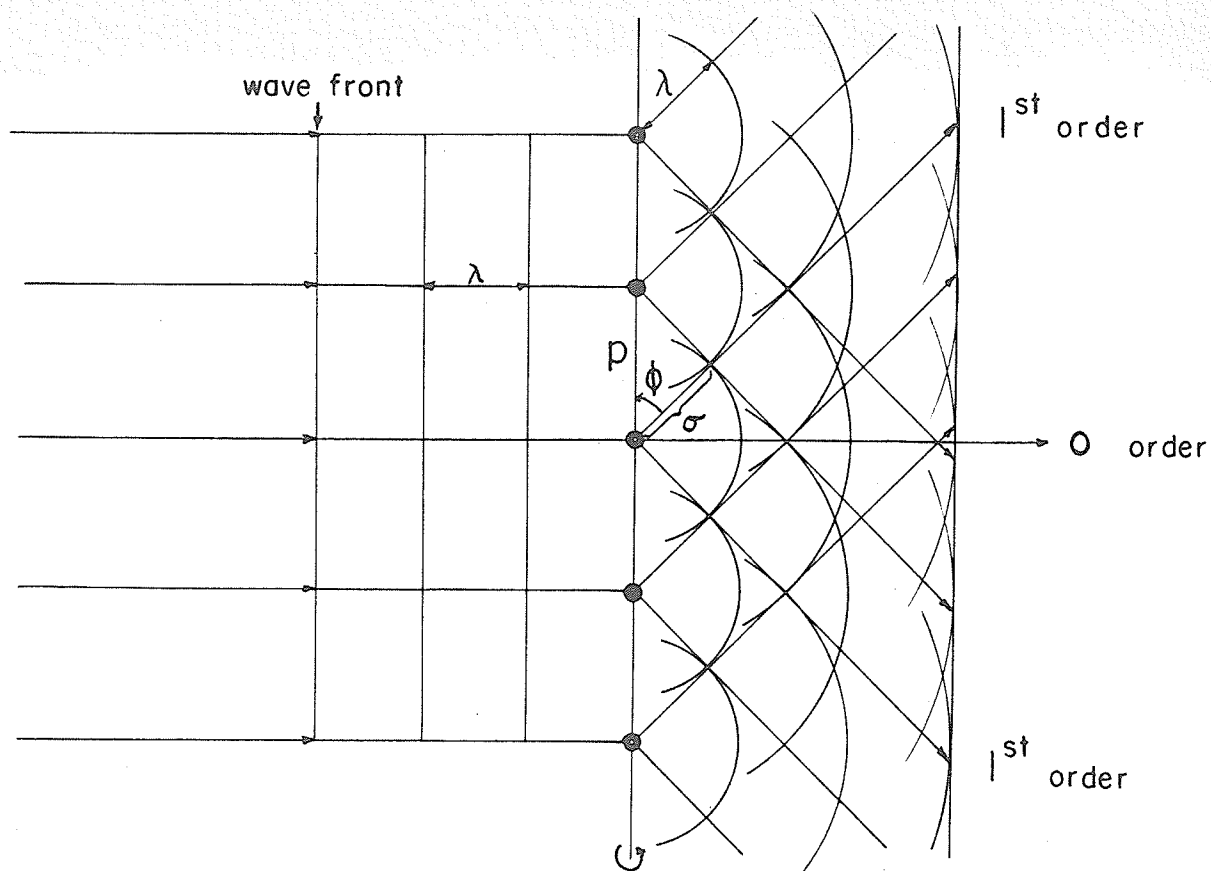


Fig. 5. Diagrammatic representation of the production of diffracted rays from a single row of diffracting points of repeat period p . The condition necessary for diffraction is $p \cos \phi = n \lambda$

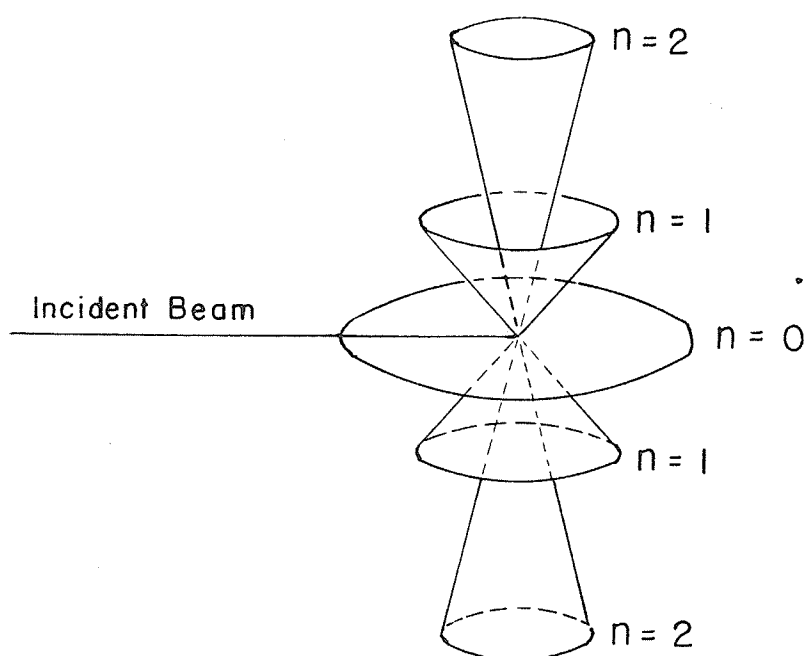


Fig. 6. Conical surfaces containing the diffracted beams of different orders of reflection (n) from a row of diffracting points with the incident X-ray beam perpendicular to the row.

individual beams on the surfaces of these cones. The directions of these beams are such that the Bragg equation is satisfied, and they will produce series of spots lying on the straight layer lines.

B Alignment of the Crystal on a Goniometer Head

The first step in any single-crystal study is to orient the crystal on the Weissenberg Goniometer head so that it will rotate about a chosen crystallographic direction, usually a principal axis. Since this investigation was a refinement and the approximate cell dimensions of the crystal were known beforehand, the problem of orienting the crystal about a principal axis were not as difficult as it would be were the structure unknown. In an unknown structure the unit cell dimensions must be chosen very carefully. If the crystal has well developed faces, then a knowledge of the morphology will permit the fairly accurate orientation of the crystal around a known axis on a reflecting goniometer.

In the present case, a suitable single crystal was chosen by crushing a small sample of the sillimanite specimen and selecting an appropriate fragment under the binocular microscope. The ideal size of the fragment depends upon its composition and the radiation used. The fragments chosen in this study were no larger than 0.025 cm. in any dimension and were as nearly equidimensional as possible. An examination of each fragment under a petrographic microscope revealed that twinning was absent. The selection and mounting procedures are discussed at length in Buerger (1960).

Since sillimanite has perfect cleavage on $\{010\}$, a preliminary alignment normal to this cleavage (about the b axis) was made using the reflecting goniometer. This alignment was approximate but rapid. The

goniometer head was then transferred to the Weissenberg unit without disturbing the alignment. Precise alignment of the crystallographic axis with the rotation axis was then achieved by a series of oscillation photographs using the methods of correction described in Bunn (1961). These oscillation photographs consist of double exposures each taken 180° on the Weissenberg drum reading from the other. When the camera was loaded and fixed in a central position relative to the X-ray collimator, the crystal was oscillated over seven and one-half degrees on either side of a setting on the goniometer drum at which one of the rockers of the goniometer head was parallel to the direction of the incident beam, so that it would be known to which rocker a given correction must be applied. The correct exposure time had to be determined by a preliminary photograph. After this exposure had been recorded, the crystal was rotated 180° so that it would oscillate with the same amplitude about a position 180° from the first. The exposure time for this orientation was one-third of the time used for the long exposure so that the direction of the correction may be determined. An example of the setting pictures is given in Figs. 7 (b), (c), and (d). Fig. 7 (a) is a single exposure to show the position of the equatorial line (zero layer). Notice that when the crystallographic axis is offset, the zero layer reflections are found to lie not on the equatorial line but on a curve; the shape of which determines the magnitude and direction of the correction. The nature of the offset of the curve from the equatorial line is provided by the double exposure.

The shapes of these curves can be explained as follows. Fig. 8 shows diagrammatically the two possible corrections that need to be applied to a crystal not aligned properly. The offsets are of two types: (a) the

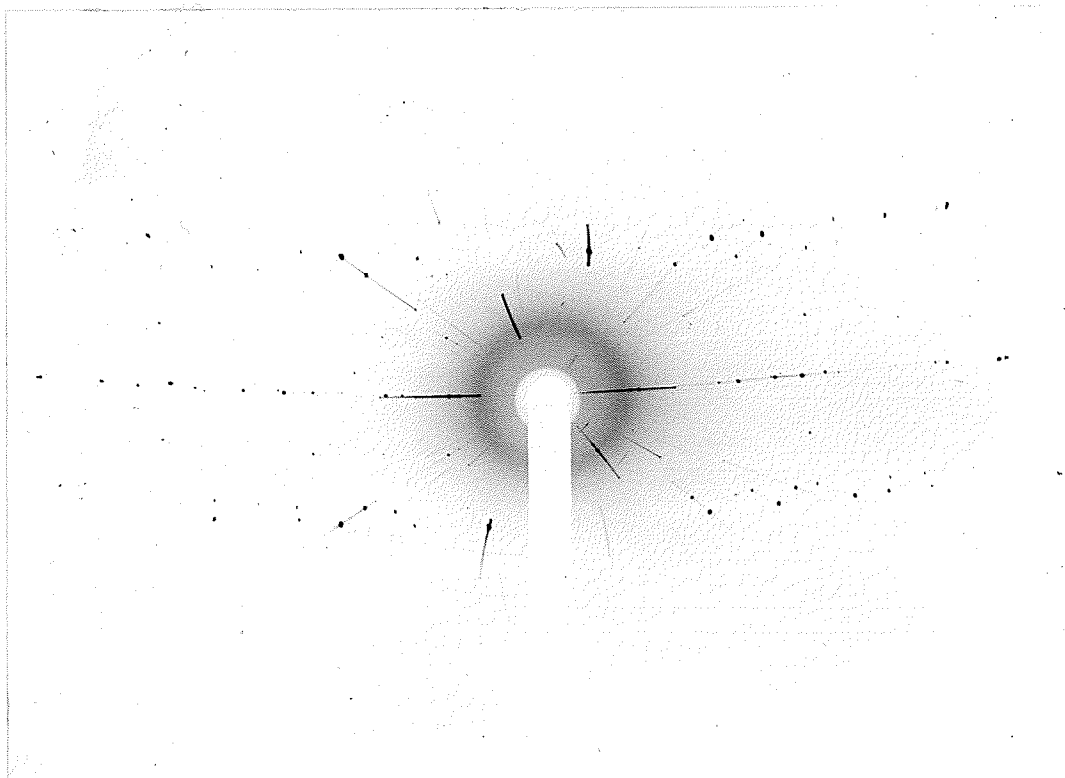


Fig. 7(a). Preliminary oscillation photograph
 Cu c [001] showing the position
 of the equatorial line. Single
 exposure $\text{Cu}/-.$

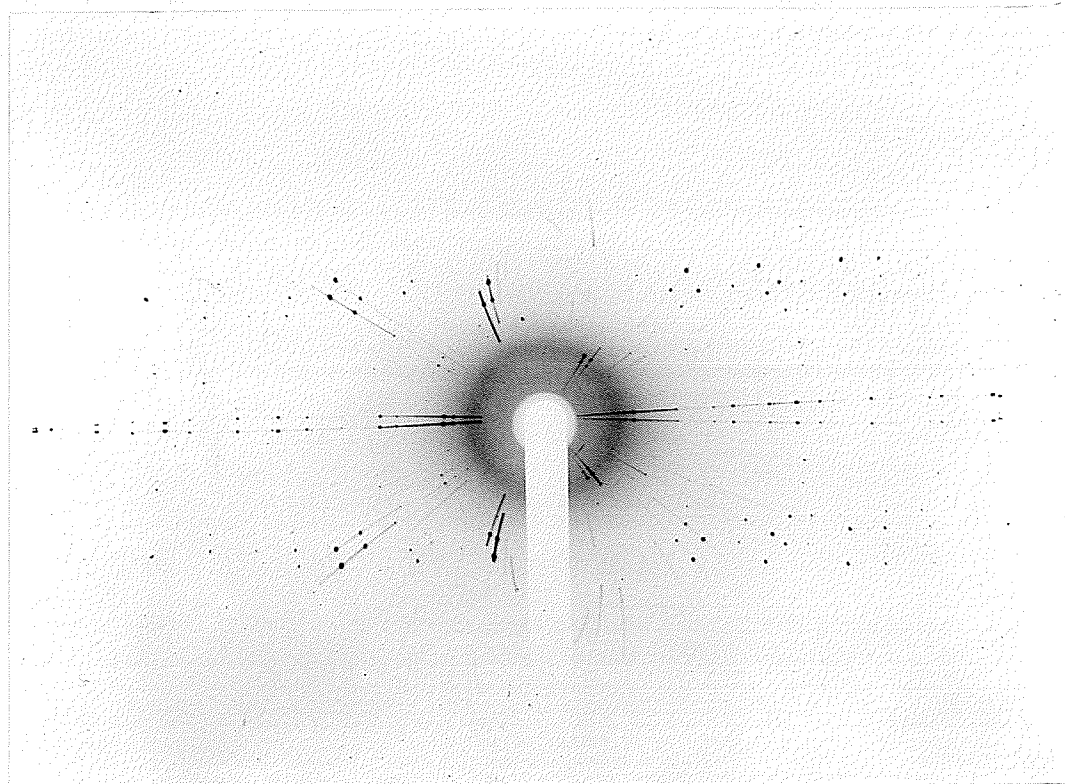


Fig. 7(b). Double exposure oscillation photograph
 Cu c [001] 1st stage in alignment.
 $\text{Cu}/-.$

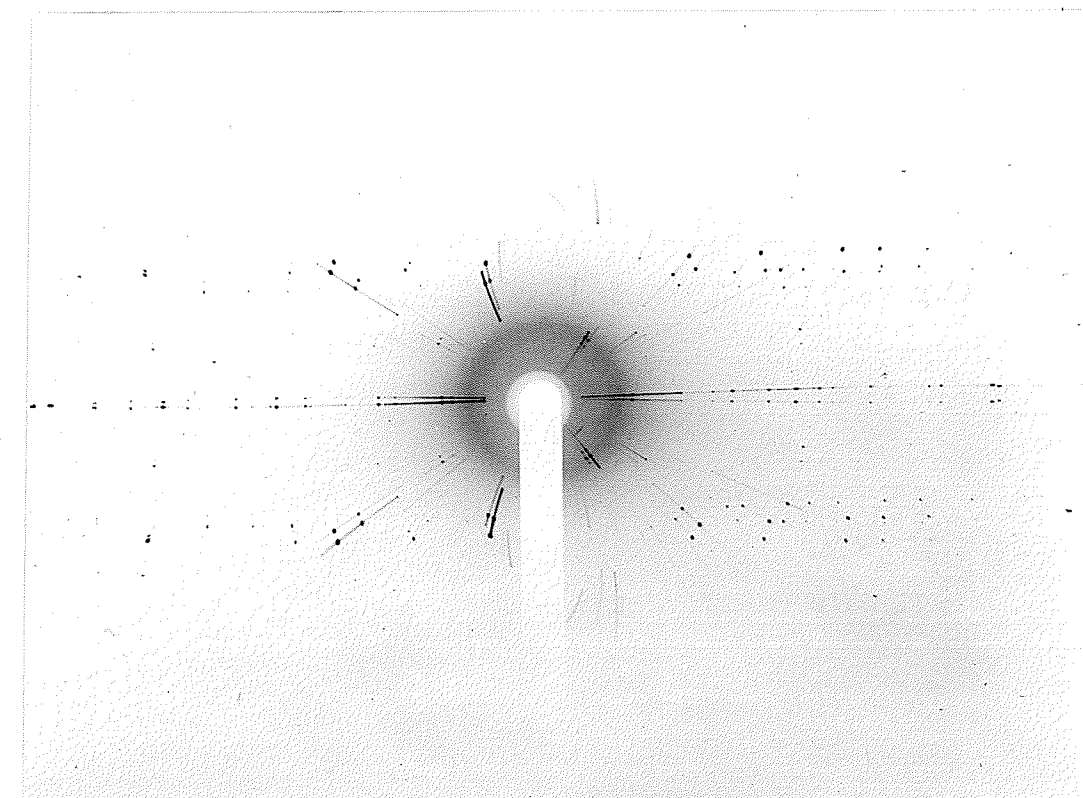


Fig. 7(c). Double exposure oscillation photograph
 Cu_2O 2nd stage in alignment.

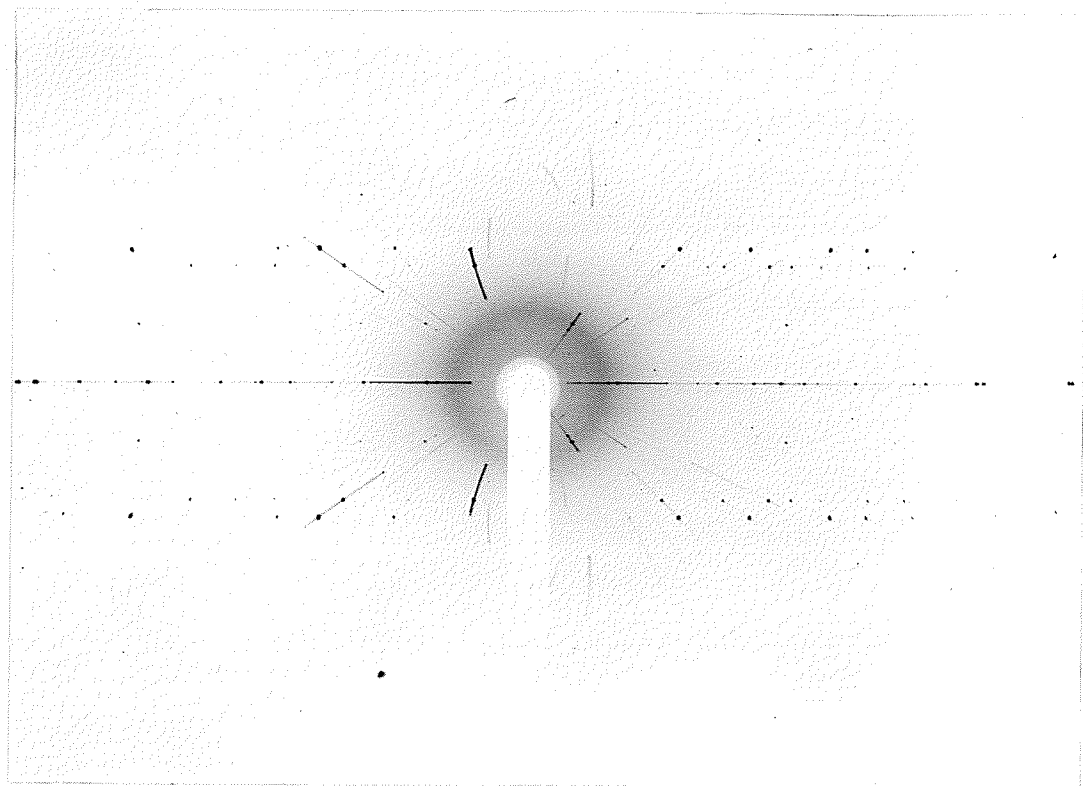


Fig. 7(d). Double exposure oscillation photograph
 Cu_2O crystal axis oriented
 exactly with rotation axis.

principal axis is offset in a plane normal to the incident beam and (b) the axis is offset in a plane containing the incident beam. The resulting curves on the flattened out film are shown in Figs. 8 (c) and (d) respectively, in relation to the equatorial line. In general the crystal is offset in both these directions and the resulting curve is a combination of these two special cases (Fig. 8 (e)). From such a curve it is possible to calculate both components of the correction.

Before discussing the practical method of determining these corrections a theoretical proof of the corrections is given. Fig. 9 (a) shows a diagrammatic sketch of the camera in cross section and the position of the sphere of reflection. An arbitrary reciprocal plane has been included also. Curve (c) of Fig. 8 results from a displacement of the crystallographic axis from the axis of rotation in a plane that is perpendicular to the X-ray beam (chained curve in Fig. 9 (a)). The distance of this curve from the equatorial line is a maximum when the Bragg angle $\Theta = 45^\circ$ and zero when $\Theta = 90^\circ$. Curve (d) of Fig. 8 is obtained when the crystallographic axis is displaced from the axis of rotation in a plane containing the incident beam (curve in crosses Fig. 9 (a)). The reflections in this case fall on a curve whose maximum distance from the equatorial line occurs at $\Theta = 90^\circ$.

A vertical section of the camera through the two 45° positions is shown in Fig. 9 (b). R is the radius of the camera and δ is the angle which the crystallographic axis makes with the axis of rotation. At $\Theta = 45^\circ$ the angle between the equatorial line plane and the zero-level reciprocal plane is also δ because the angle between their normals is δ .

The separation of the zero-layer line from the equatorial line

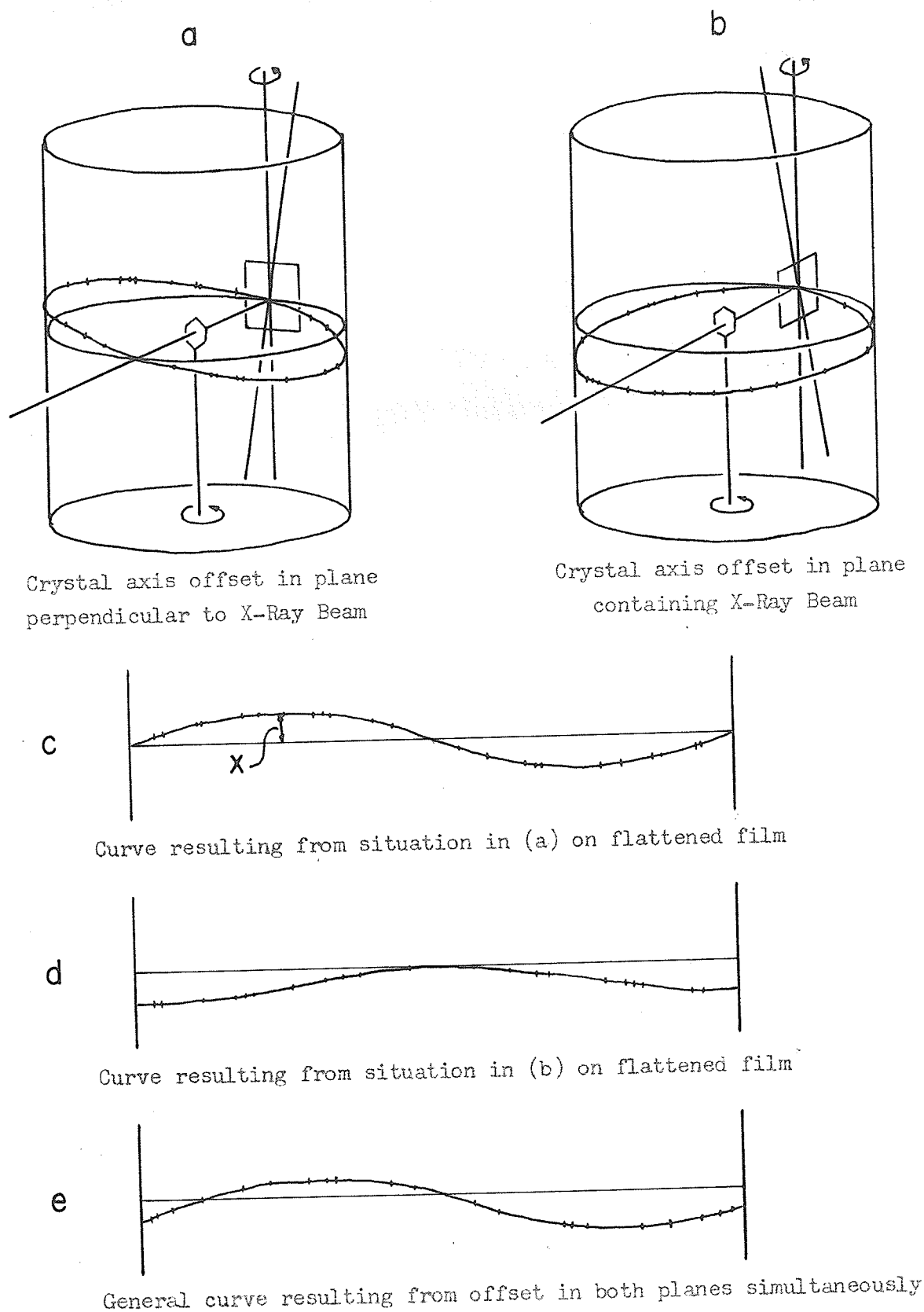


Fig. 8. Diagrammatic representation of the two conditions of offset in the alignment of a crystal axis with the rotation axis. (Reproduced from Bunn (1961) Fig. 108.)

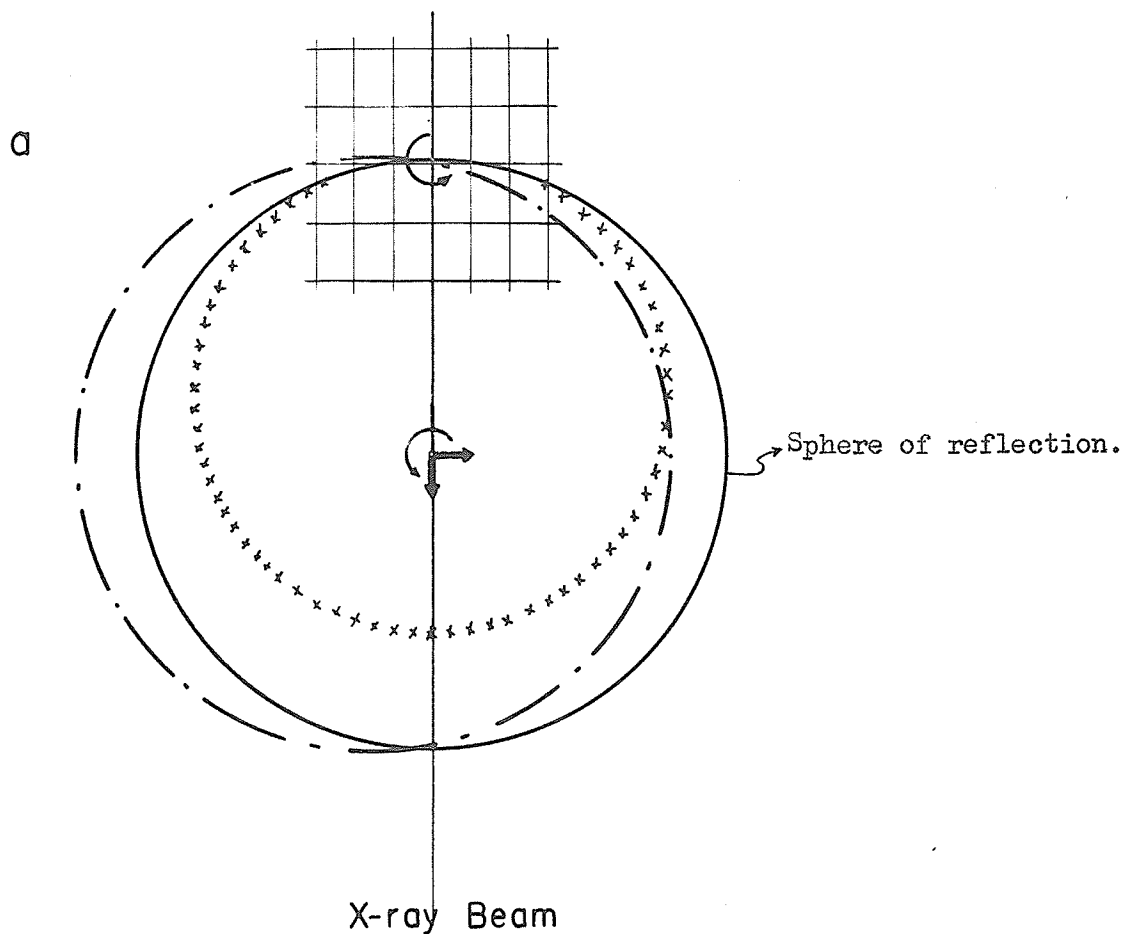


Fig. 9(a). Vertical cross section of camera showing sphere of reflection and the two curves resulting from the two special cases of offset of the crystallographic axis from the rotation axis.

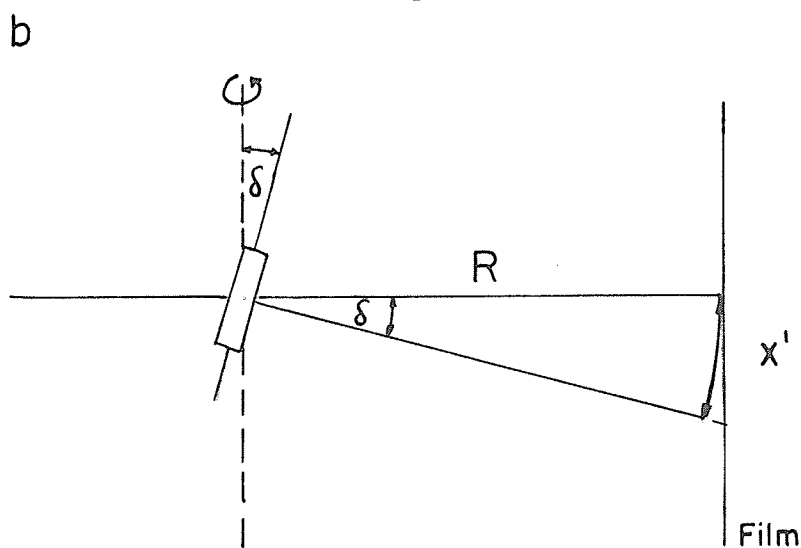


Fig. 9(b). Horizontal cross section of the camera showing the film at the 45° position. Radius of the camera is R and the angle of offset is δ .

is x (see Fig. 8 (c)). To a first approximation when the angle δ is small, x measured on the film is equal to x' the arc length on a circle of radius R , the radius of the camera (see Fig. 9 (b)). For this particular camera the radius is $R = 360/4\pi \text{ mm.} = 90/\pi \text{ mm.}$

x' is the arc length subtending the angle δ , thus

$$x' \text{ mm.} = \frac{\pi R \delta}{180} \text{ mm.}$$

$$\text{Then } \delta^\circ = \frac{180 x'}{\pi R} = \frac{180 x'}{\pi} \cdot \frac{\pi}{90} = 2x' \text{ mm.}$$

$$\therefore \delta^\circ = 2x' \text{ mm.}$$

$$= 2x \text{ mm. on the film.}$$

It is this distance $2x$ that is measured from the film. At a distance of 45 mm. from the direct beam the separation of the two curves obtained from a long and short double exposure is measured. This distance in millimeters, $2x$, will be the correction in degrees that must be applied to the rocker controlling the direction of the crystallographic axis in the plane perpendicular to the X-ray beam. A similar result is arrived at if one considers curve (d), Fig. 8, which is for an offset in a plane containing the incident beam.

Generally, these two kinds of error are combined i.e., the crystal is offset in both planes, and then it is necessary to make corrections to both rockers. The separation of the curves at $\Theta = 45^\circ$ is measured on the upper and the lower halves of the film. The larger correction to be made on one rocker is one-half the sum of these two distances and the smaller correction to be made on the other rocker is one-half the difference between these two distances. If the separation of the two curves is the same magnitude on the upper and lower half of the film, then the correction required is entirely in one plane and thus

TABLE II

EXAMPLE OF CORRECTIONS TO ALIGNMENT OF A CRYSTAL AXIS WITH
THE ROTATION AXIS USING OSCILLATION SETTING PHOTOGRAPHS

<u>Photograph in Fig. 7 (b)</u>	<u>Darker line Position</u>	<u>Separation</u>
Upper half of film	left	1.70 mm.
Lower half of film	right	3.30 mm.

Crystal axis in relation to rotation axis is:

(a) too far up by $\frac{1.70 + 3.30}{2} = 2.5^{\circ}$ in the plane $\perp$ to X-ray beam.

(b) too far back by $\frac{|1.70 - 3.30|}{2} = 0.8^{\circ}$ in the plane containing the
X-ray beam.

<u>Photograph in Fig. 7 (c)</u>	<u>Darker line Position</u>	<u>Separation</u>
Upper half of film	left	1.0 mm.
Lower half of film	right	2.2 mm.

Crystal axis in relation to rotation axis is:

(a) too far up by $\frac{1.0 + 2.2}{2} = 1.6^{\circ}$ in the plane $\perp$ to X-ray beam.

(b) too far back by $\frac{|2.2 - 1.0|}{2} = 0.6^{\circ}$ in the plane containing the
X-ray beam.

The photograph in Fig. 7 (d) is the result of making this final correction to the rockers of the goniometer head. The crystallographic axis is oriented exactly along the axis of the instrument.

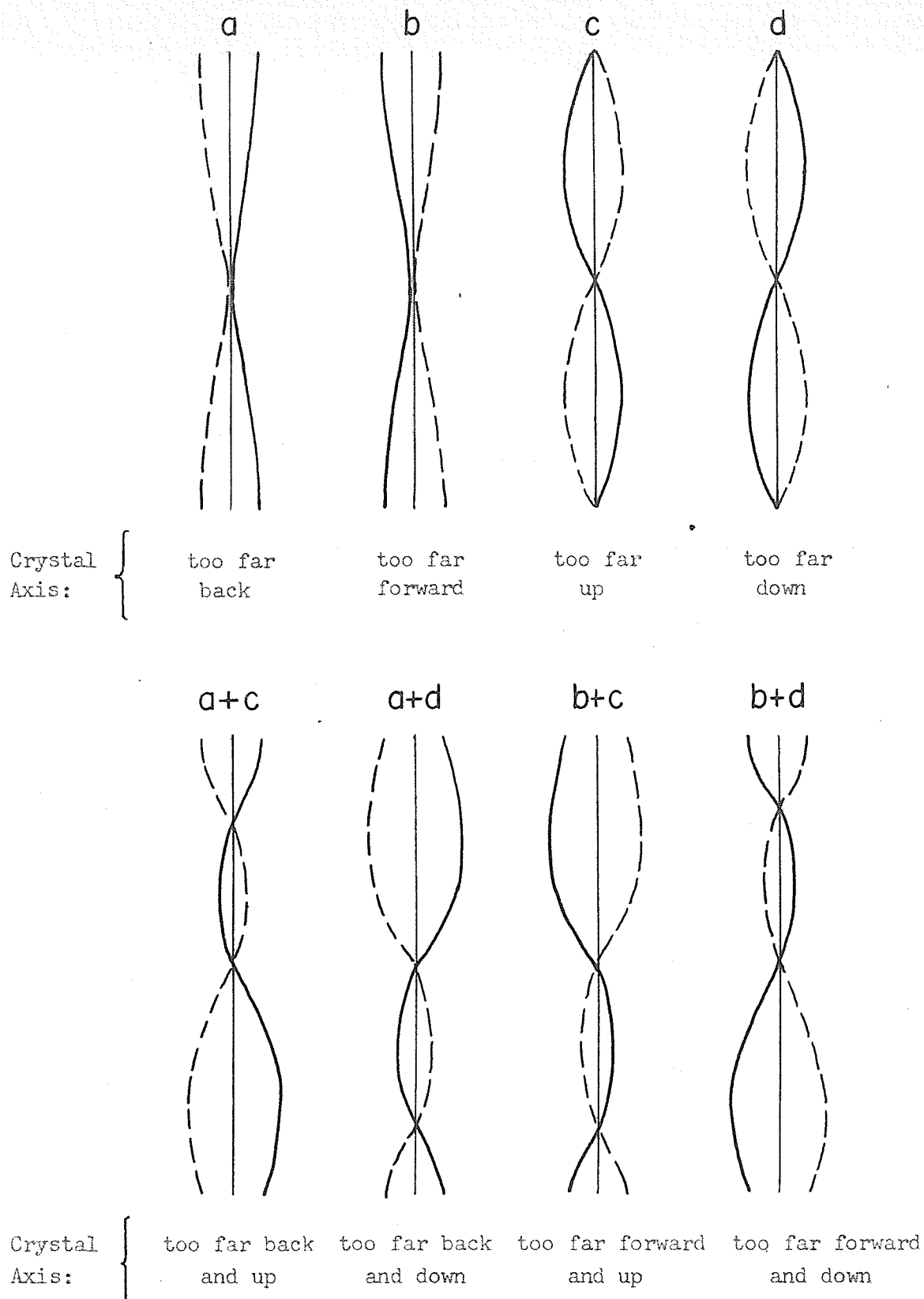


Fig. 10. Diagrammatic representation of all the possible curve shapes on oscillation photographs resulting from an offset of the crystallographic axis from the rotation axis.

on one rocker. If the separation of the curves is zero on either the upper or lower half of the film, then equal corrections must be applied to both rockers. In general, neither reading is zero and the two readings are different, in which case different corrections will be required on each rocker.

There are only eight possible types of curve that may be obtained from any one setting in which the crystallographic axis is a few degrees offset from the axis of rotation. These curves are tabulated in Fig. 10. The first four, (a), (b), (c) and (d), are errors in alignment in one plane only, while the other four are the possible combinations of these curves. To give meaning to the curves, they are oriented such that the camera axis is horizontal, with the observer viewing the photograph along the direction of the incident X-ray beam from the X-ray tube.

An example of these corrections is given in Table II which gives measurements that were made on the photograph in Figs. 7 (b) and (c). Fig. 7 (d) shows the result of making these corrections and the type of oscillation photograph that is obtained when the crystallographic axis corresponds exactly to the axis of rotation. The exposure times for all of these films were 45 minutes for the long exposure and 15 minutes for the short exposure.

C Determination of the Rotation Period

The rotation period can be determined by measuring the film in the manner shown in Fig. 11. Here the film is shown with the layer lines corresponding to $n=0, 1, 2$. By knowing the radius of the camera R and measuring the separation y of the n^{th} layer line from the zero

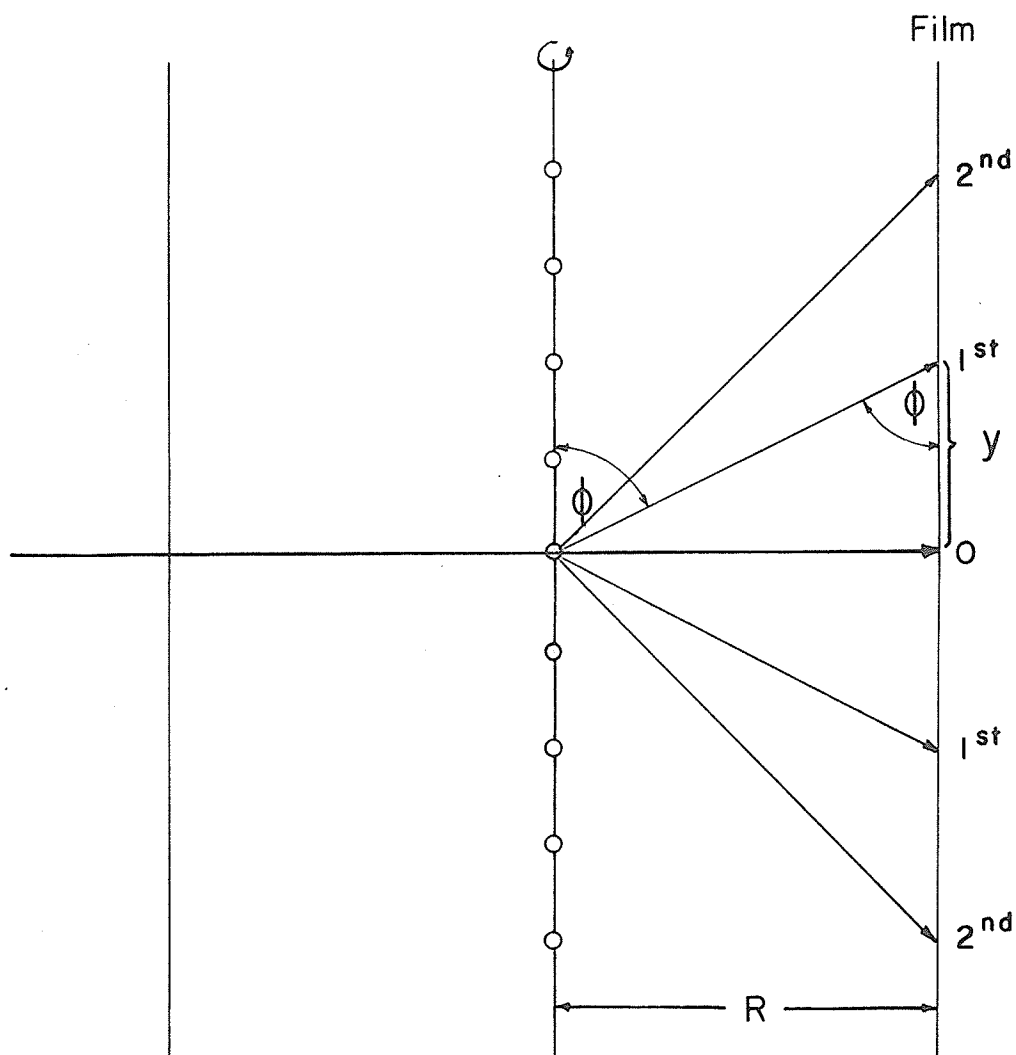


Fig. 11. Diagrammatic representation of the determination of the rotation period p from the measurement of the separation y of the n^{th} layer lines from the zero layer line.

layer line, one can determine the angle

$$\phi = \tan^{-1} R/y .$$

From the relationship given in Section A of this chapter, the rotation period then becomes

$$p = \frac{n \lambda}{\cos \tan^{-1} R/y .}$$

An example of such a determination is given in Table III.

This table contains data measured from the oscillation photograph of sillimanite shown as Fig. 12 (a) in which the axis of rotation is a [100] and the radiation molybdenum K_{α} . It can be seen from this table that each layer line gives one value of the rotation period of that particular axis. Fig. 12 shows prints of oscillation photographs obtained about each of the three principal axes in sillimanite. The values of the rotation periods obtained from these photographs are,

$$a_o = 7.58 \text{ \AA}$$

$$b_o = 7.78 \text{ \AA}$$

$$c_o = 5.83 \text{ \AA}$$

It was later found that all three values were too large by approximately 1.4%. The reason for this method producing inaccurate results is due to the inaccurate knowledge of the effective camera radius. It was necessary to include extra paper in the jacket to make it light tight. This would effectively reduce the radius of the camera thus increasing the calculated rotation period. The larger the n value of the layer line, the more accurate the value of the rotation period because of the reduction of error in measuring the separation of the two lines.

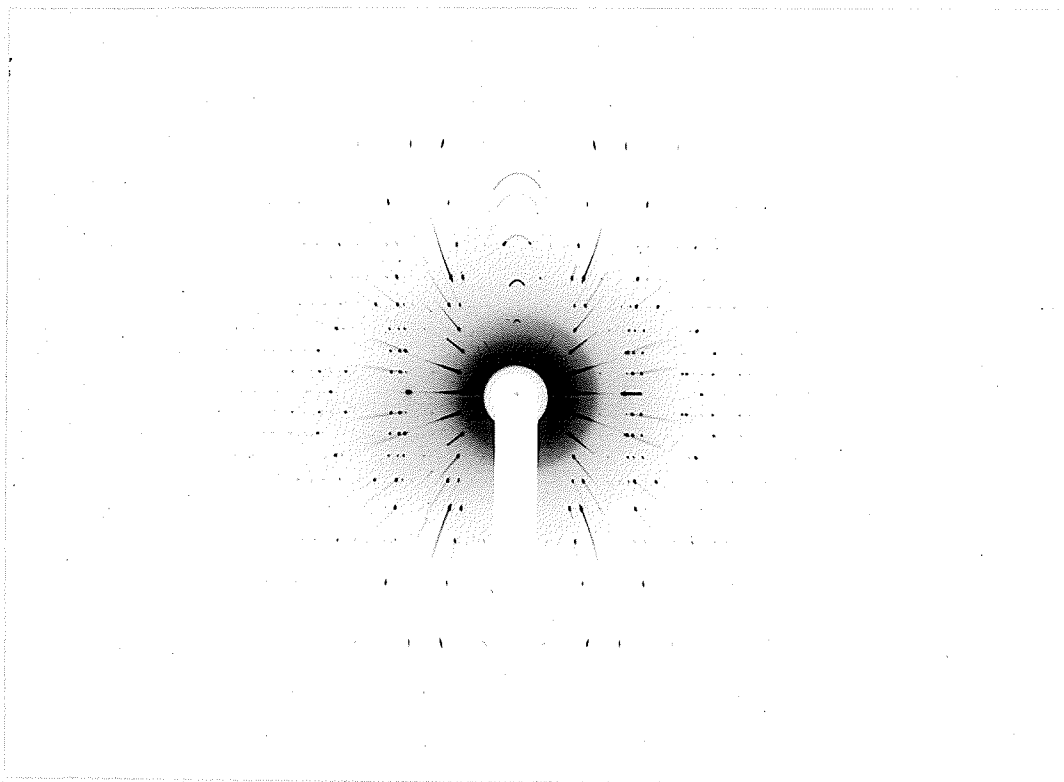


Fig. 12(a). Oscillation photograph taken about $a[100]$, Mo/Zr radiation. Rotation period = 7.58 Å.

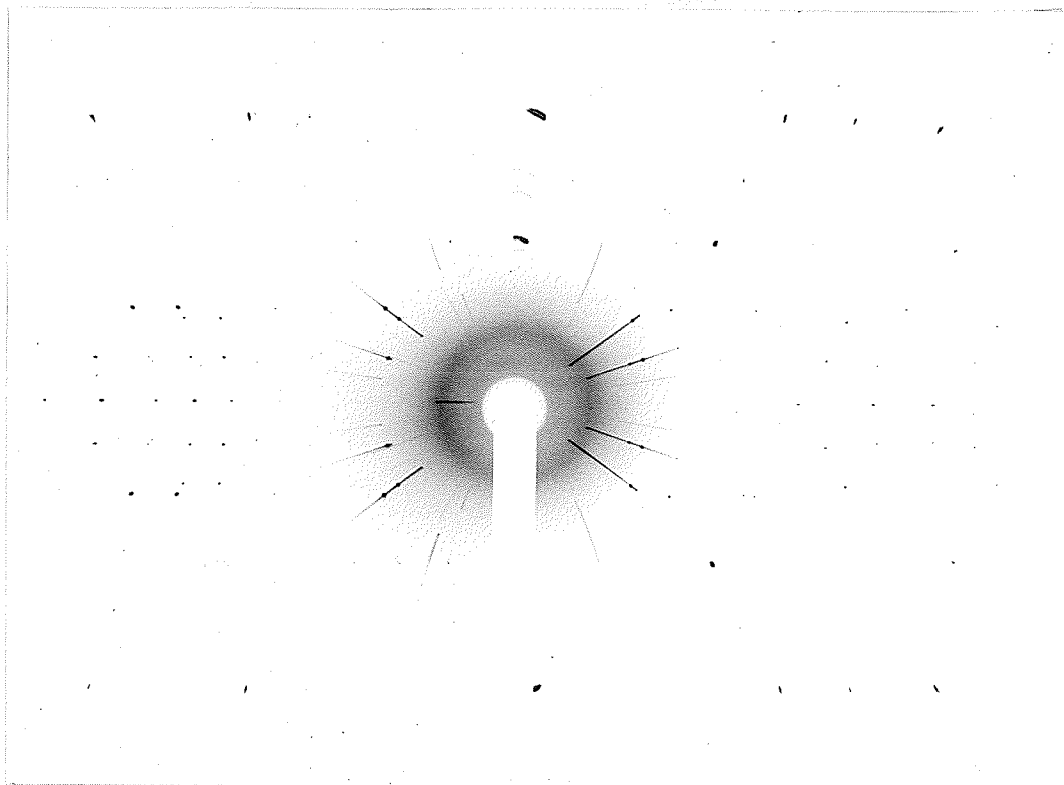


Fig. 12(b). Oscillation photograph taken about $b[010]$, Cu/-radiation. Rotation period = 7.78 Å.

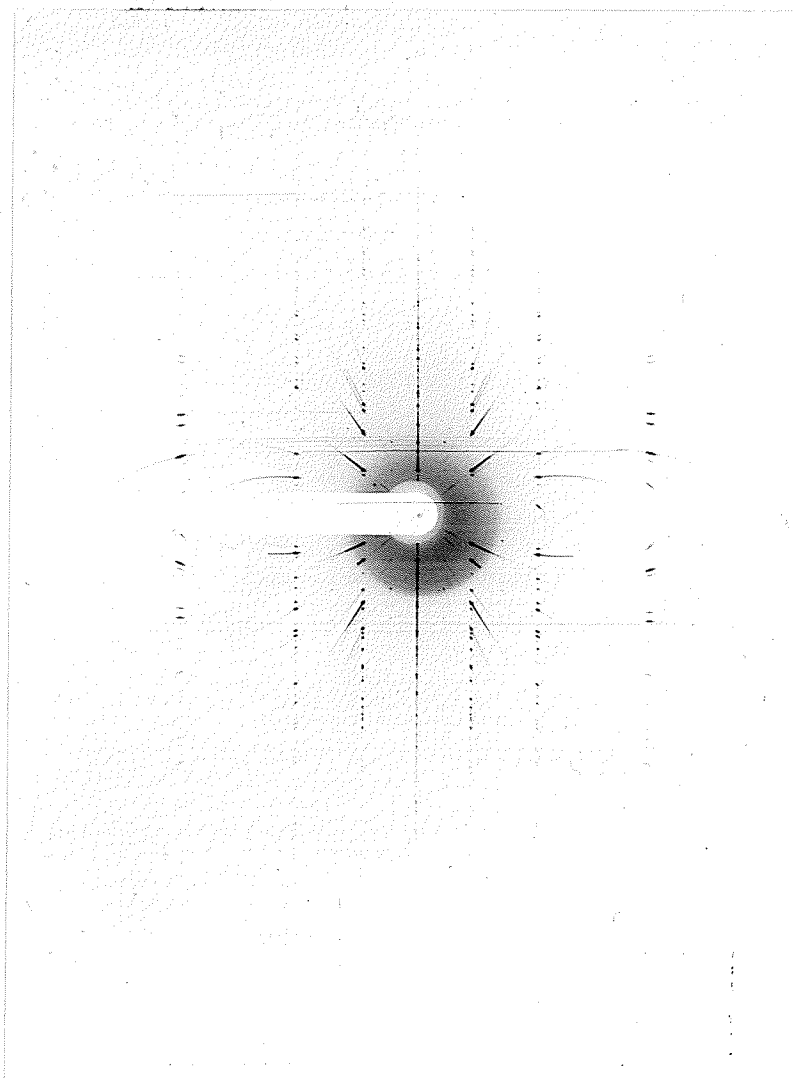


Fig. 12(c). Oscillation photograph taken
about c $[001]$ Mo/Zr radiation.
Rotation period = 5.83° .

TABLE III

DETERMINATION OF ROTATION PERIOD FROM
OSCILLATION PHOTOGRAPH ABOUT $a [100]$

Radiation: Molybdenum K_{α} , $\lambda = 0.7107 \text{ \AA}$.

Radius of the camera: $R = 28.65$ millimeters.

n	1 α	2 α	3 α	4 α	5 α	6 α	7 α	8 α
Right (mm.)	84.90	87.65	90.60	93.77	97.45	101.72	107.33	115.30
Left (mm.)	79.52	76.77	73.84	70.60	66.99	62.66	57.15	49.30
2 y (mm.)	5.38	10.88	16.76	23.17	30.46	39.06	50.18	66.00
y (mm.)	2.69	5.44	8.38	11.59	15.23	19.53	25.09	33.00
$\tan \phi = \frac{R \text{ (mm.)}}{y \text{ (mm.)}}$	10.650	5.266	3.4186	2.4729	1.8810	1.4669	1.1418	0.8681
$\cos \phi$	0.0935	0.1866	0.2810	0.3743	0.4695	0.5633	0.6585	0.7552
$n \lambda \text{ (\AA)}$	0.7107	1.4214	2.1321	2.8428	3.5535	4.2642	4.9749	5.6856
$p = \frac{n \lambda \text{ (\AA)}}{\cos \phi}$	7.60	7.62	7.59	7.59	7.57	7.57	7.55	7.53

Average value of $a [100] = 7.58 \text{ \AA}$.

Fig. 13 (a) shows a photograph obtained while attempting to orient the crystal about a $[100]$. This photograph lacks the symmetry characteristic of orthorhombic crystals rotated about a principal axis, and it yields a large value for the rotation period, $16.24 \overset{\circ}{\text{\AA}}$. (Notice that there are very weak reflections half way between the prominent layer lines.) From a knowledge of the known cell dimensions it is possible to identify the lattice row with a period of about $16.2 \overset{\circ}{\text{\AA}}$. The manner in which the approximate value of the rotation period was found is shown in Fig. 13 (b) where it can be seen that the rotation period in this case is likely $[201]$ which has a value of $16.15 \overset{\circ}{\text{\AA}}$. By measuring the angle between $[100]$ and $[201]$, (21°) , an angular correction was determined but the direction of the correction could only be determined by trial and error. Subsequent photographs finally produced the one shown in Fig. 12 (a) in which the crystal is accurately oriented around a $[100]$.

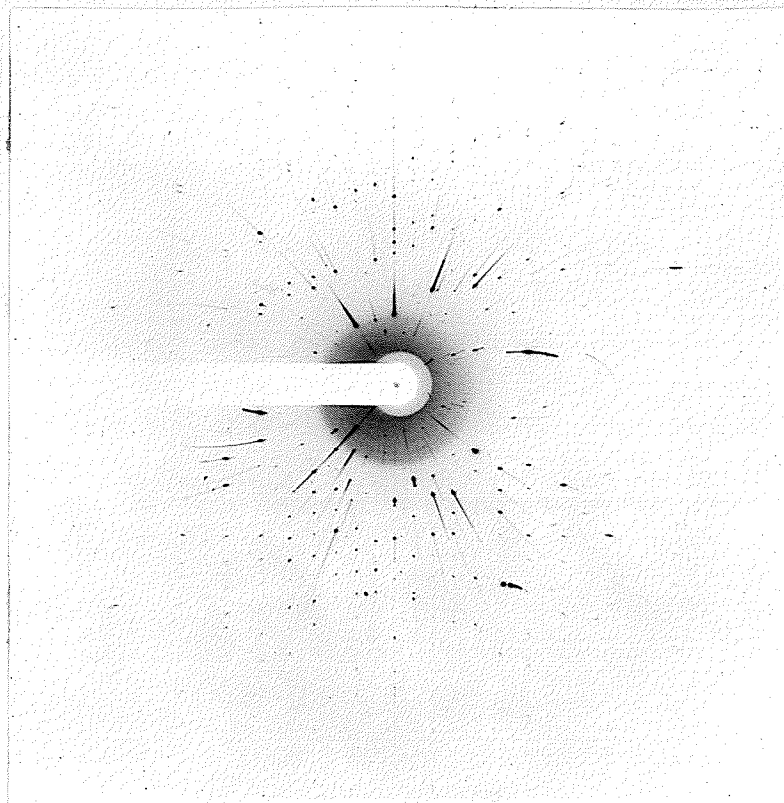


Fig. 13(a). Oscillation photograph obtained while attempting to orient the crystal about a $[100]$. Rotation axis $[201]$ rotation period $16.24^\circ \text{ Mo/Zr}$.

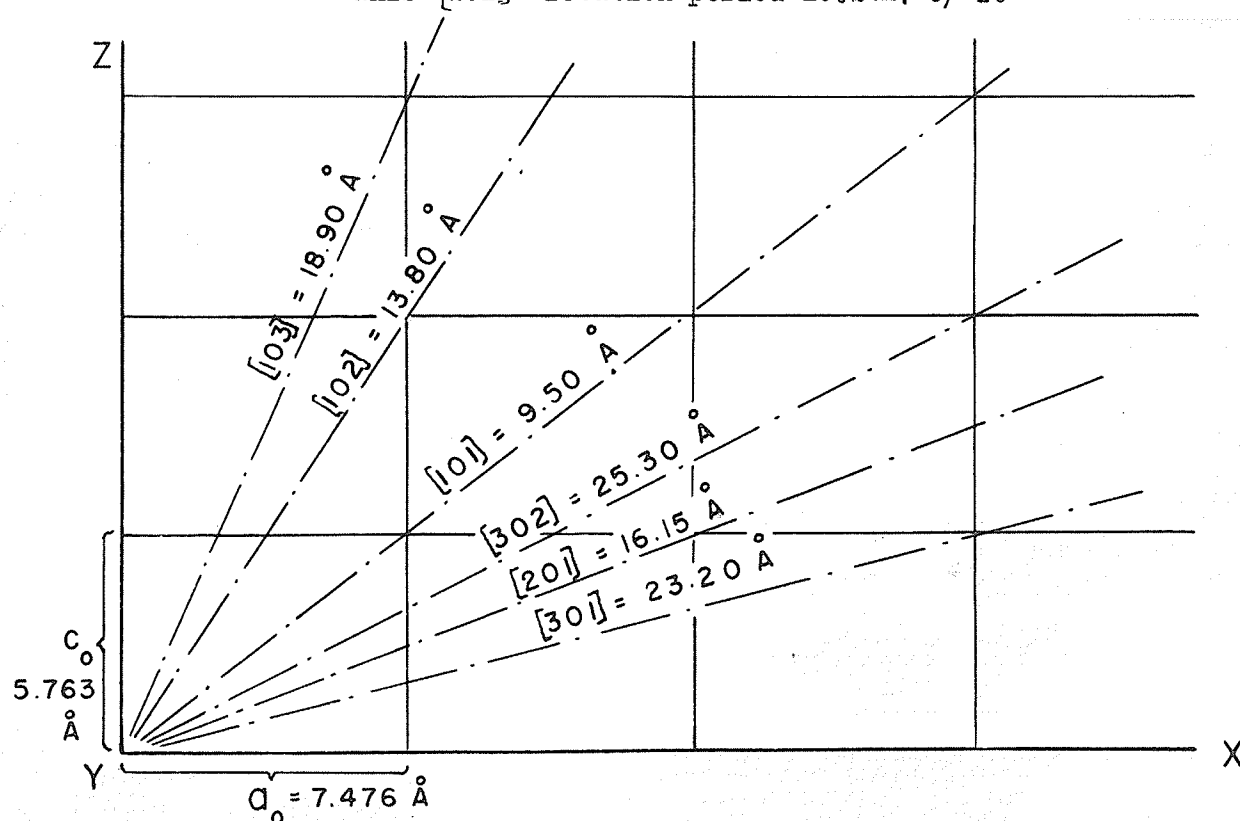


Fig. 13(b). Determination of the approximate value of the rotation period $[201]$ from a knowledge of the cell dimensions a_0 and c_0 .

CHAPTER V

THE WEISSENBERG METHOD: CELL DIMENSIONS, SPACE GROUP AND INTENSITIES

A Introduction

Until recently the Weissenberg method was the commonest of the moving-film methods but now the precession method often supplements or replaces the Weissenberg. Weissenberg photographs are distorted pictures of the reciprocal lattice whereas precession photographs are undistorted pictures of the reciprocal lattice. The disadvantage of the precession method is the use of a flat film to record the reflections, thus limiting the number that may be observed.

It is possible to index all the reflections observed on an oscillation photograph, and so such photographs may be used to gather intensity data. The details of the technique are described in Henry, Lipson and Wooster (1960), and in Bunn (1961). The disadvantage of this method lies in the number of oscillation photographs that are required to record all the reflections of one zone, say all the $hk0$ reflections. The interpretation of these photographs for the purpose of indexing is also tedious and there is the possibility of ambiguity in the indexing of some reflections.

It has been shown in the previous chapter that when a crystal is rotated about a crystallographic axis in a monochromatic X-ray beam, cones of reflections are sent out and they appear on the cylindrical film as straight rows called layer lines. If the axis of rotation is the c axis then the central or equatorial layer line is made up of $hk0$

reflections, the first layers on either side of the central row are the hkl and $h\bar{k}l$ rows, etc. In the Weissenberg method, one of these layer lines is chosen to the exclusion of all others and the reflections are spread out over the whole area of the film. By this method all of the $hk0$ reflections can be recorded on one photograph, and all the hkl on another, etc. When each film has been interpreted one obtains projections of the reciprocal lattice from which the correct axes, cell dimensions, and space group extinctions may be obtained.

The experimental set-up for a normal-beam Weissenberg photograph is shown diagrammatically in Fig. 14. The same general arrangement of the rotating crystal method is used except that a slotted screen is placed between the crystal and the film. The normal-beam method is characterized by having the axis of the crystal rotation normal to the incident X-ray beam. The camera containing the film translates coaxially with the crystallographic axis and the axis of rotation, and synchronously with the rotation of the crystal. The slotted screen is adjusted to permit the passage of only one of the cones of reflections.

In most Weissenberg cameras, the arrangement is such that, as the crystal rotates through 180° the camera translates 90 mm. Thus a translation of 1 mm. of the camera is equivalent to a 2° rotation of the crystal. By measuring the lateral distance between any two reflections on a film, the amount the crystal has turned between these two reflecting positions can be measured. In all systems but the hexagonal and triclinic, the lattice planes $(h00)$ and $(0k0)$ are at right angles to each other. Therefore when a Weissenberg photograph is taken about c $[001]$, the distance between the two rows on the film which contain

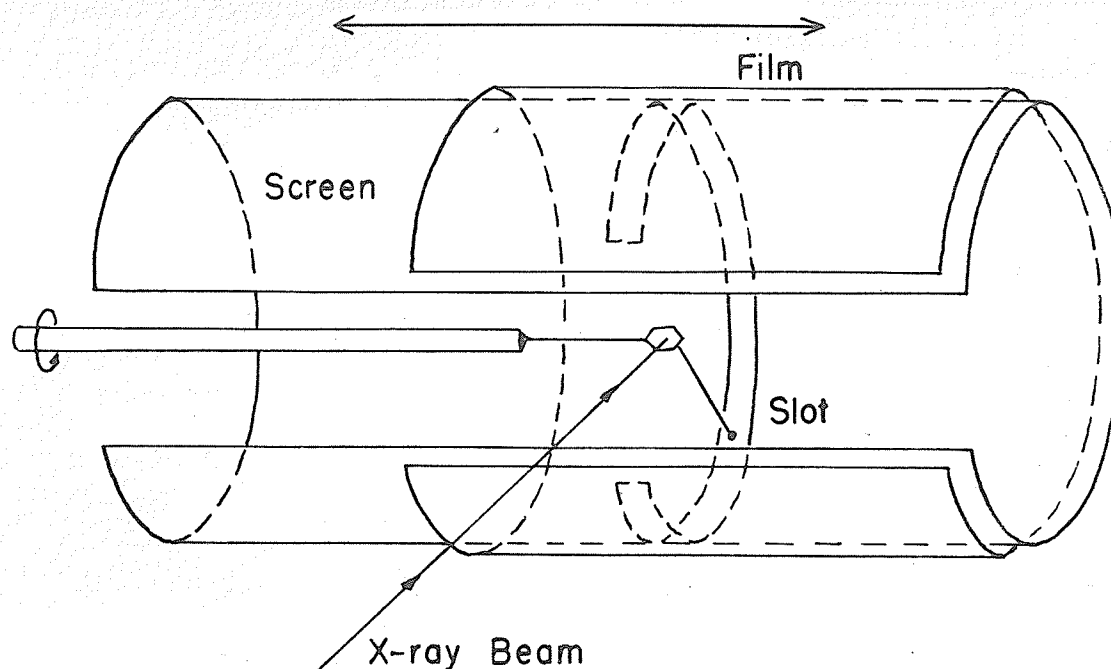


Fig. 14. Experimental arrangement of the Weissenberg moving film goniometer for the recording of the equatorial layer by the normal beam method (Reproduced from Bunn (1961) Fig. 103(a)).

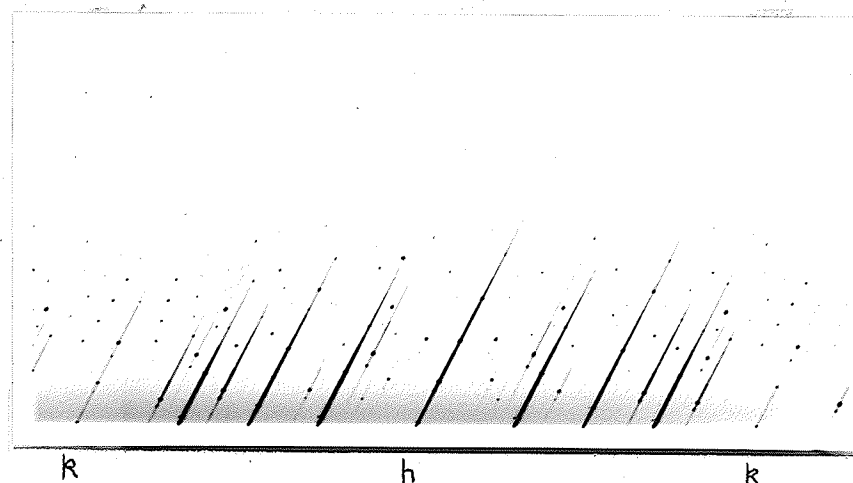


Fig. 15. Weissenberg photograph $0c [001]$ of the zero layer $hk0$ reflections taken by normal beam method using $\text{Mo}/\text{-radiation}$. Only the upper half of the film is included. Prominent primary lattice rows are shown by the white radiation streak. Principal axial rows are marked h and k and the festoons are also shown on this photograph.

the different orders of reflection from these two planes is 45 mm. (=90°). Similarly, in any crystal system the distance between the rows of reflections from (h00) and ($\bar{h}$ 00) is 90 mm. (=180°).

Due to the synchronous translation of the camera with the rotation of the crystal, successive reflections from one reciprocal lattice row passing through the origin fall along a straight line making an angle of $\tan^{-1} \frac{2}{1} = 63^\circ 26'$ with the horizontal. Reflections corresponding to reciprocal lattice rows that are parallel to rows that pass through the origin are arranged on a family of curves called festoons as may be seen in Fig. 15. A rotation-translation corresponding to at least 180° is required to photograph all of the points in a reciprocal lattice plane possible with a particular X-radiation.

B Plotting the Reciprocal Lattice from a Weissenberg Photograph

In order to plot the undistorted reciprocal lattice from a Weissenberg photograph it is necessary to locate each reflection by two coordinates that can be measured from the film. It is possible to read cartesian coordinates from the film referred to the edges of the film but these are not convenient as they must be corrected for the translation of the camera. A special template that is described in Buerger (1942, Chapter 14) is used to determine the necessary coordinates for plotting. This template is shown in Fig. 16 reproduced from Buerger (1942, Fig. 145). The horizontal coordinate of a spot is read from a millimeter scale placed along the bottom of the template. This reading (x) corresponds to the angle of turn or the angle of azimuth ω of the reciprocal lattice point. Since 1 mm. = 2°, x in mm. must be multiplied by 2 to give ω in degrees. The second coordinate (z)

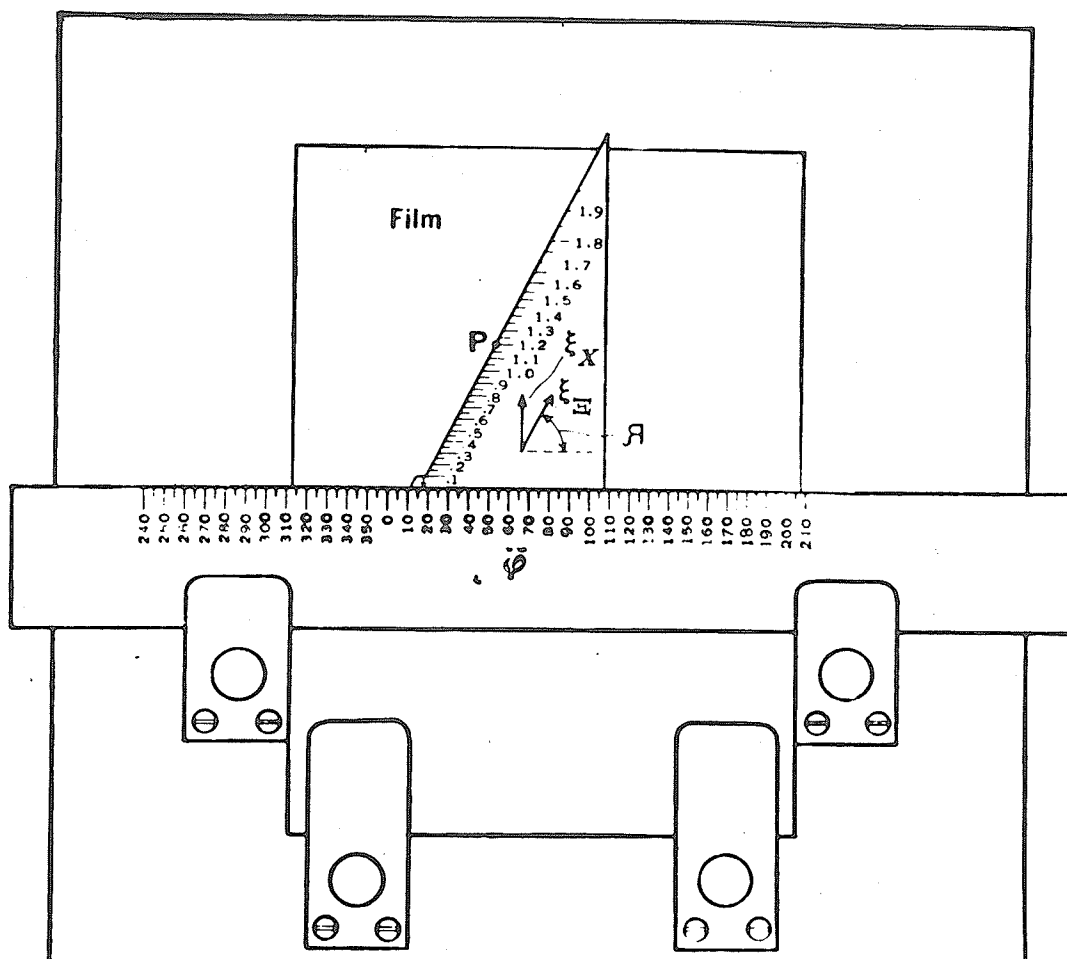


Fig. 16. Special template to measure x and z coordinates from a normal beam Weissenberg photograph in order to prepare a plot of the reciprocal lattice. x in mm., is measured on the horizontal scale and z in reciprocal lattice units is measured on the inclined scale. (Reproduced from Buerger (1942) Fig. 145).

giving the polar coordinate in reciprocal lattice units, is read from the inclined edge of the template. In order to produce a convenient size for the reciprocal lattice representation it is customary to multiply z by 10. These two coordinates and the estimated intensity (v.s., s., m., w., v.w.) are read for each $\propto$ reflection on the Weissenberg photograph. It is usual to start at the extreme left hand side and read the points successively from left to right. For the purpose of determining the correct reciprocal unit cell, only one half of the film need be read.

Once the readings have been recorded for the complete half of the film (see Table 4) it is a simple matter to plot them on polar coordinate paper. Fig. 17 shows the reciprocal lattice zero-layer ($h0l$) of sillimanite for Mo K_{α} radiation. From this figure it is usually apparent which are the axial rows so these may be traced back to the film. All the reflections appearing on one festoon will fall along the same straight line in the projection. All the reflections that are on one inclined straight line on the film (central lattice row) appear as a straight line that passes through the centre of the reciprocal lattice projection.

C Choice of the Reciprocal Unit Cell

Once the axial rows have been determined from the reciprocal lattice plot, a mesh may be drawn that passes through all the points. In the case of sillimanite which is orthorhombic an orthogonal net was drawn (See Figs. 17 and 18). However the reciprocal lattice cell defining this mesh will not necessarily be the true reciprocal cell because of systematically missing reflections. Therefore it is necessary

TABLE IV

DATA FOR PLOTTING A WEISSENBERG PHOTOGRAPH: $h0l$ REFLECTIONS OF SILLIMANITE

x is the azimuthal coordinate in mm., z the polar coordinate in
reciprocal lattice units (r.l.u.)

Refl. No.	1	2	3	4	5	6	7
I	$\overline{m}$	$\overline{w}$	$\overline{m}$	$\overline{w}$	$\overline{w}$	$\overline{s}$	$\overline{m}$
hkl	$16^{\circ}0.2$	$18^{\circ}0.2$	$14^{\circ}0.4$	$18^{\circ}0.6$	$16^{\circ}0.6$	$8\ 0\ 4$	$14^{\circ}0.8$
x , mm.	31.1	31.1	36.3	38.1	39.0	42.5	44.4
z , r.l.u.	1.52	1.71	1.40	1.84	1.67	0.89	1.63

Refl. No.	8	9	10	11	12	13	14
I	$\overline{s}$	$\overline{vs}$	$\overline{w}$	$\overline{vs}$	$\overline{vs}$	$\overline{m}$	$\overline{mw}$
hkl	$10^{\circ}0.6$	$6\ 0\ 4$	$10^{\circ}0.8$	$2\ 0\ 2$	$4\ 0\ 4$	$6\ 0\ 6$	$7\ 0\ 7$
x , mm.	45.0	46.2	49.0	52.2	52.2	52.2	52.2
z , r.l.u.	1.18	0.74	1.35	0.31	0.61	0.92	1.08

Refl. No.	15	16	17	18	19	20	21
I	$\overline{ms}$	$\overline{mw}$	$\overline{s}$	$\overline{vs}$	$\overline{vw}$	$\overline{s}$	$\overline{m}$
hkl	$8\ 0\ 8$	$10^{\circ}0.10$	$6\ 0\ 8$	$4\ 0\ 6$	$8^{\circ}0.12$	$2\ 0\ 4$	$4\ 0\ 8$
x , mm.	52.2	52.2	56.1	57.5	57.5	60.6	60.6
z , r.l.u.	1.22	1.54	1.12	0.82	1.64	0.52	1.04

Refl. No.	22	23	24	25	26	27	28
I	$\overline{m}$	$\overline{m}$	$\overline{s}$	$\overline{w}$	$\overline{vw}$	$\overline{vs}$	$\overline{vs}$
hkl	$6^{\circ}0.12$	$4^{\circ}0.10$	$2\ 0\ 6$	$4^{\circ}0.14$	$1\ 0\ 5$	$0\ 0\ 2$	$0\ 0\ 4$
x , mm.	60.6	62.8	64.1	65.3	67.0	71.5	71.5
z , r.l.u.	1.57	1.27	0.75	1.74	0.61	0.24	0.48

Refl. No.	29	30	31	32	33	34	35
I	$\overline{m}$	$\overline{vs}$	$\overline{m}$	$\overline{vw}$	$\overline{s}$	$\overline{w}$	$\overline{ms}$
hkl	$0\ 0\ 6$	$0\ 0\ 8$	$0^{\circ}0.12$	$2\ 0\ 6$	$4^{\circ}0.14$	$4^{\circ}0.10$	$2\ 0\ 4$
x , mm.	71.5	71.5	71.5	77.9	78.5	80.0	81.9
z , r.l.u.	0.72	0.97	1.46	1.75	0.75	1.27	0.52

Refl. No.	36	37	38	39	40	41	42
I	$\overline{w}$	$\overline{w}$	$\overline{s}$	$\overline{m}$	$\overline{vs}$	$\overline{s}$	$\overline{m}$
hkl	$4\ 0\ 8$	$6^{\circ}0.12$	$4\ 0\ 6$	$6\ 0\ 8$	$2\ 0\ 2$	$4\ 0\ 4$	$6\ 0\ 6$
x , mm.	81.9	81.9	85.0	86.5	90.1	90.1	90.1
z , r.l.u.	1.04	1.56	0.82	1.12	0.30	0.61	0.92

Refl. No.	43	44	45	46	47	48	49
I	$\overline{m}$	$\overline{w}$	$\overline{vs}$	$\overline{m}$	$\overline{vs}$	$\overline{s}$	$\overline{vw}$
hkl	$8\ 0\ 8$	$10^{\circ}0.10$	$6\ 0\ 4$	$10^{\circ}0.6$	$4\ 0\ 2$	$8\ 0\ 4$	$7\ 0\ 3$
x , mm.	90.1	90.1	96.0	97.5	99.9	99.9	101.9
z , r.l.u.	1.22	1.54	0.73	1.18	0.44	0.88	0.74

Refl. No.	50	51	52	53	54	55	56
I	vw	m	m	vw	vs	vs	vs
hkl	10·0·4	6 0 2	10·0·2	7 0 1	2 0 0	4 0 0	6 0 0
x, mm.	102.9	104.8	109.1	111.1	116.3	116.3	116.3
z, r.l.u.	1.05	0.60	0.96	0.65	0.17	0.36	0.55

Refl. No.	57	58	59	60	61	62	63
I	s	vw	m	vw	m	vw	vw
hkl	8 0 0	7 0 1	10·0·2	14·0·4	6 0 2	16·0·6	10·0·4
x, mm.	116.3	121.7	123.3	126.6	128.0	129.7	130.2
z, r.l.u.	0.73	0.65	0.95	1.38	0.60	1.66	1.04

Refl.No.	64	65	66	67	68	69	70
I	vvw	s	ms	w	m	vs	vvw
hkl	7 0 3	4 0 2	8 0 4	14·0·8	10·0·6	6 0 4	10·0·8
x, mm.	130.9	132.7	132.7	134.8	135.2	136.6	139.7
z, r.l.u.	0.73	0.43	0.87	1.62	1.17	0.72	1.33

Refl. No.	71	72	73	74	75	76	77
I	vs	s	m	w	w	s	s
hkl	2 0 2	4 0 4	6 0 6	8 0 8	10·0·10	6 0 8	4 0 6
x, mm.	142.4	142.4	142.4	142.4	142.4	146.7	146.7
z, r.l.u.	0.30	0.60	0.90	1.21	1.52	1.10	0.80

Refl. No.	78	79	80	81	82	83
I	m	w	s	w	vs	vs
hkl	2 0 4	4 0 8	2 0 6	1 0 5	0 0 2	0 0 4
x, mm.	150.2	150.2	154.0	157.0	161.2	161.2
z, r.l.u.	0.51	1.02	0.73	0.60	0.24	0.47

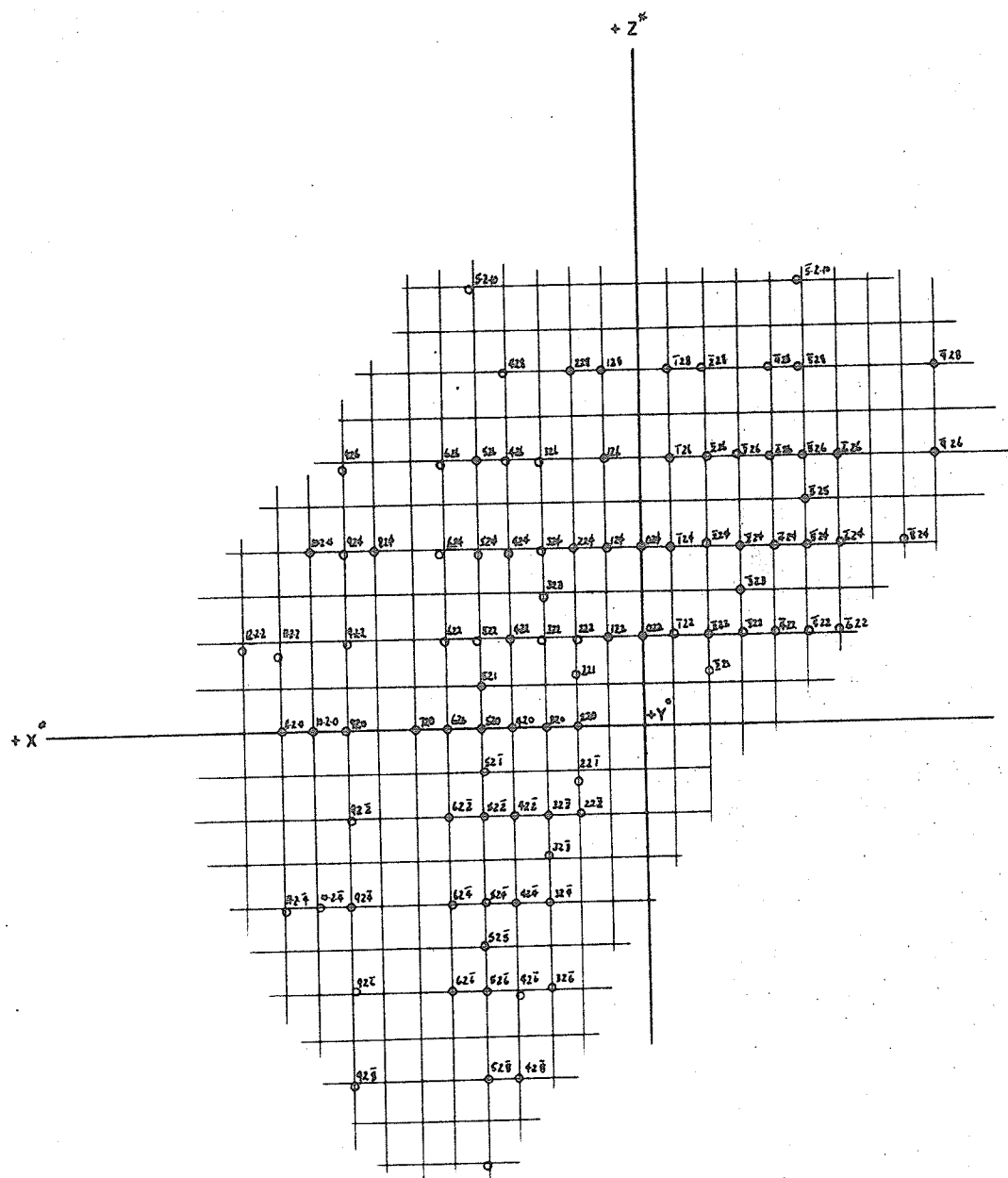


Fig. 18. Reciprocal lattice plot of the upper $h2l$ level of sillimanite. This was used in conjunction with the plot in Fig. 17 to choose the reciprocal unit cell.

to examine upper level Weissenberg plots, usually the 1st and 2nd, along with the 0 level plot to determine the true cell. The plots of the upper-level photographs are superimposed on the zero-level plot so that the true reciprocal lattice net which includes all the reflections of all layers may be correctly chosen.

This situation occurred in the case of sillimanite: on the $0k\ell$ projection all reflections with $k=2n+1$ are systematically absent but first and second-level Weissenbergs revealed the true reciprocal lattice net. The reciprocal unit cell of sillimanite was determined by the above methods. A right hand rule was used to define the positive ends of the three principal axes, x^* , y^* , and z^* . This cell was chosen to make $c^* > a^* > b^*$ which resulted in the direct cell having the conventional setting $c < a < b$.

D Indexing the Reflections on Weissenberg Photographs

Once the unit net has been chosen on a reciprocal lattice plot all points can be indexed directly. One need only use the reciprocal lattice plot in conjunction with the measured data (such as that in Table IV) to index all the reflections on a Weissenberg photograph. This is the way in which the indices hkl in Table IV were arrived at.

There is a second method that is described in Buerger (1942, p. 280) which makes use of a "Weissenberg chart" or template that can be superimposed on the film to read the indices of each reflection. This template has been reproduced from Buerger (1942, Fig. 148) and is shown as Fig. 19. A dot copy of the photograph, made on tracing paper, is placed on the template so that the two principal axial lines such as $h00$ and $\bar{h}00$ correspond with the sloping left and right margins

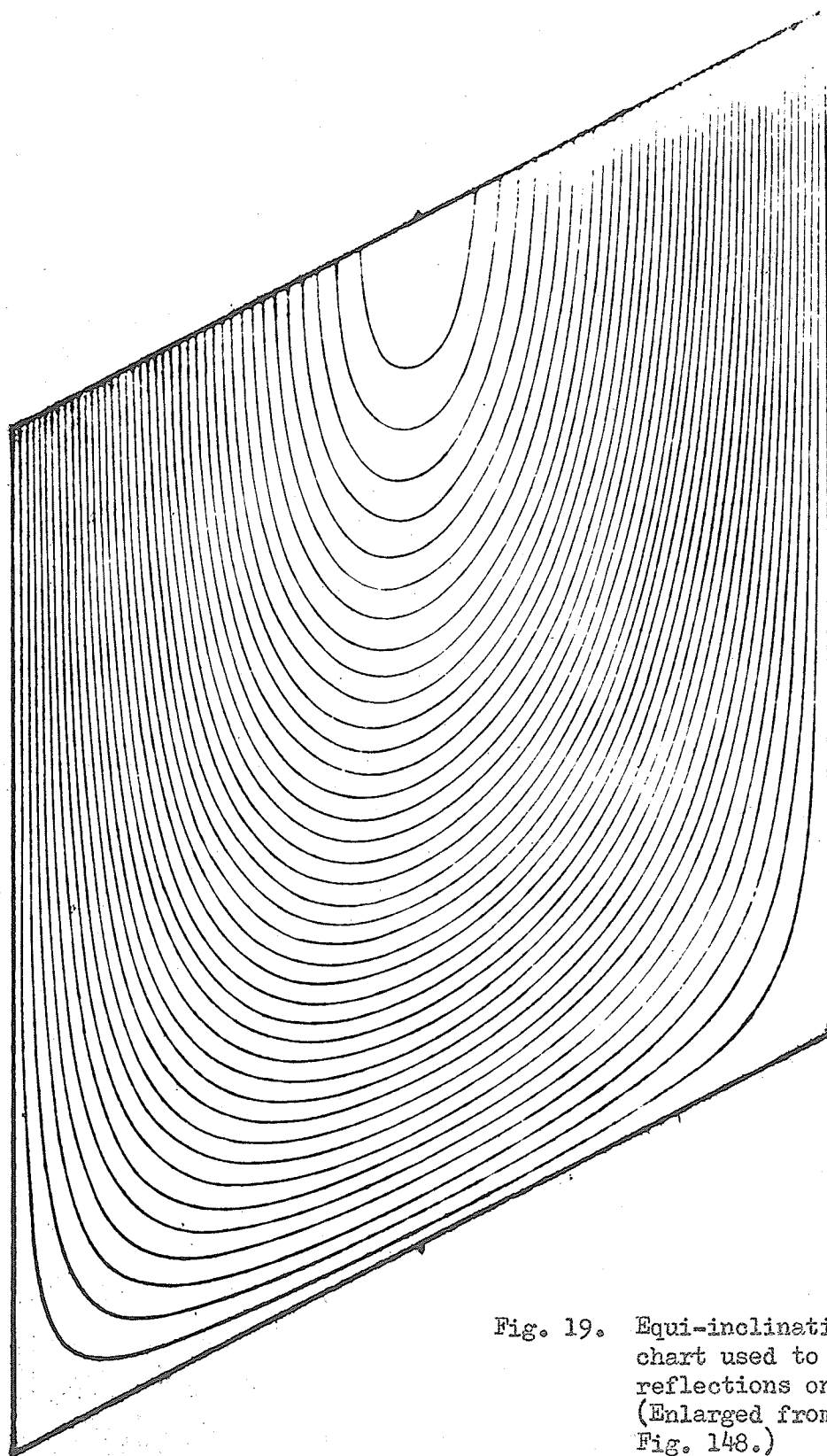


Fig. 19. Equi-inclination Weissenberg chart used to index the reflections on the photographs. (Enlarged from Buerger (1942) Fig. 148.)

of the template. The reflections on the film or dot copy are then found to line up on or between the lines (this depends upon the d spacing and camera constants). Thus lines parallel to ones on the template may be drawn through the spots, each line representing lattice points arranged in a lattice row. When all lattice rows of the one type have been traced on the template, it is then shifted so that it lines up with the second principal axial lines such as $00l$ and $00\bar{l}$ and the reciprocal lattice rows again drawn in as before.

One system of lines is labelled, $10l$, $20l$, $30l$, etc., while the other is labelled $h01$, $h02$, $h03$, etc. Each spot or reflection now lies at the intersection of two of the above lines and can be indexed accordingly. Care must be taken not to omit any of the accidentally missing lattice rows by observing the regularity of the d spacings.

E Determination of the Space Group

The term point group symmetry implies that all symmetry elements must pass through one point. However, in considering space groups there is the added degree of freedom of translation, in which the symmetry elements do not have to pass through a single point. These additional translations result in certain modifications in the diffraction of X-rays. Lattice centering and symmetry operations involving translation have the effect of extinguishing certain classes of reflections. Thus a list of the extinctions of a given crystal is characteristic of the translation operations which produced them.

The determination of a space group from a list of systematically absent reflections is given here using sillimanite as an example.

This mineral was reported by Taylor (1928) to be orthorhombic in symmetry. This has been confirmed in the present work by measuring the separation of the principal axial lines of the Weissenberg photographs. In all three cases the separations were 45mm. corresponding to interaxial angles of 90° . The non-equality of the three axial lengths ($c < a < b$) was demonstrated in rotation photographs and also from a preliminary examination of the Weissenberg patterns, which is discussed in a later section.

Examination of the reflections of type $hk\ell$ provides information on the type of lattice. In the orthorhombic system the presence of glide planes is determined from the zones of reflections $hk0$, $h0\ell$ and $0k\ell$ and screw axes are detected from an examination of the reflections of type $h00$, $0k0$ and 00ℓ . The theory behind this is discussed in Buerger (1942, Chapter IV). This work confirmed Taylor's (1928) observations that reflections with $\ell = 2n+1$ were scarce and the intensities were weak in comparison with reflections having $\ell = 2n$.

From the indexed Weissenberg photographs the following extinctions were determined.

- $(hk\ell)$: all present
- $(hk0)$: all present
- $(h0\ell)$: present only with $h+\ell = 2n$
- $(0k\ell)$: present only with $k = 2n$
- $(h00)$: present only with $h = 2n$
- $(0k0)$: present only with $k = 2n$
- (00ℓ) : present only with $\ell = 2n$

The fact that the $\{hk\ell\}$ reflections showed no extinction conditions confirmed the fact that the lattice is primitive (P). The

other extinction conditions lead to two possible space groups as listed in the International Tables (Vol. I, 1952) $Pna2_1$ and $Pnma$ (numbers 33 and 62 respectively).

The present author's choice of axes ($c < a < b$) requires that these symbols be cyclically permuted to correspond with the observed extinctions. The two possible space groups are thus written as $Pbn2_1$ and $Pbnm$. The final choice between these is discussed in the following section.

F X-ray Analysis for Centrosymmetry

The space group $Pbn2_1$ has no centre of symmetry whereas $Pbnm$ is centrosymmetric. Thus if it can be determined whether or not sillimanite is centrosymmetrical, a choice between these space groups can be made.

An analysis for centrosymmetry in sillimanite was made using the X-ray method devised by Howells, Phillips, and Rogers (1950). This is a statistical test that may be applied to intensities observed for reflections of the type hkl . The presence of a centre of symmetry tends to create large intensity differences from reflection to reflection whereas the absence of a centre of symmetry smoothes the intensity distribution so that it is more uniform. This test is not applied to special reflections of the type $hk0$, $h0l$, or $0kl$ because the zone which they represent may be centrosymmetric, even though the crystal has no centre of symmetry.

The $N(Z)$ test of Howells, Phillips and Rogers is described in Lipson and Cochran (1953). The reflections are divided into several groups according to their $\sin \Theta/\lambda$ values. The range of $\sin \Theta/\lambda$

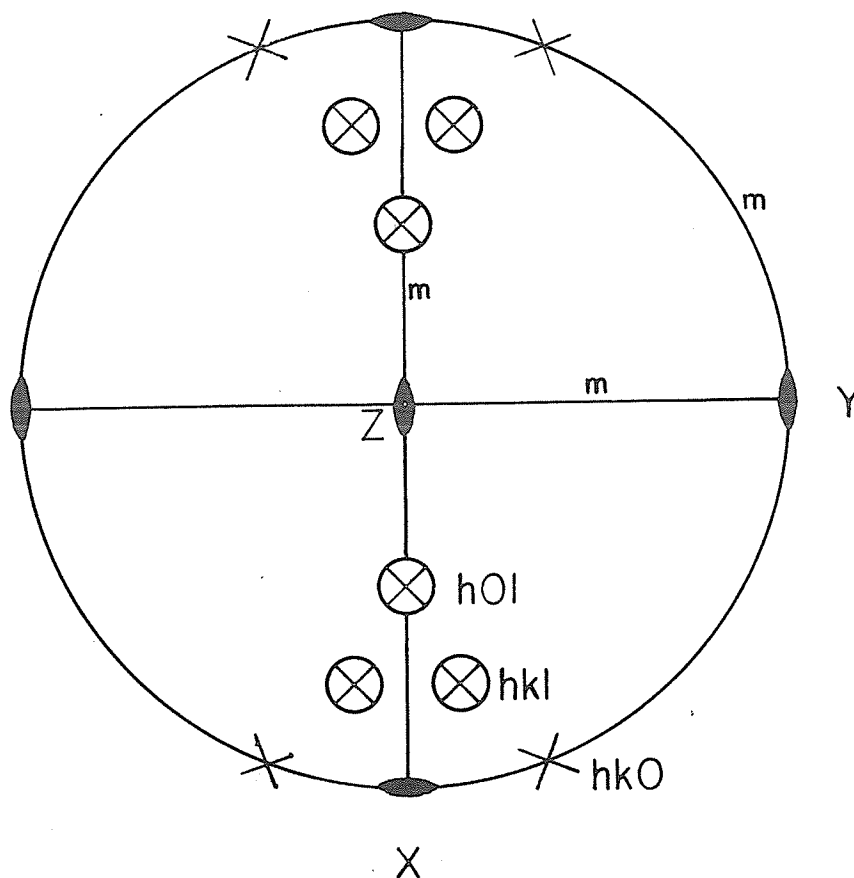


Fig. 20. Stereographic projection of the symmetry elements of point group $2/m\ 2/m\ 2/m$, showing the different multiplicities of the reflections $hk0$, $h0l$ and hkl .

for each group is chosen so that the number of reflections contained in each group is approximately the same, and the number of reflections in each group is large enough to have statistical meaning. Systematically absent reflections are not included but accidentally absent reflections must be included with zero intensity. The theory does not apply to very low values of $\sin \theta / \lambda$.

In practice one calculates the sum of the uncorrected intensities and then the average intensity $\langle I \rangle$ of that group. In the orthorhombic system for the calculation of $\langle I \rangle$ half weight is given to reflections such as $hk0$, $h0l$ and $0kl$. The reason for this may be seen from Fig. 20. This is a projection of the point group $2/m \ 2/m \ 2/m$. Examples of the different types of reflections are shown as $hk0$, $h0l$ and $hk l$. Notice that the intensity of the reflection from an $hk l$ plane is divided into eight positions while that from the $hk0$ and $h0l$ zones is divided only into four.

Progressive fractions, Z , of the average intensity are selected and the percentages $N(Z)$ of the total number of reflections whose intensities are less than or equal to the fraction Z are calculated. Howells et al. have shown that the fractions $N(Z)$ are given by $N(Z) = 1 - \exp(-Z)$ for non centrosymmetric crystals, and by $N(Z) = \text{erf}(\frac{1}{2}Z)^{\frac{1}{2}}$ for centrosymmetric crystals, where "erf" is a complicated error function for which values have been determined. Finally the calculated values of $N(Z)$ are compared graphically with the theoretical values for centrosymmetry and for non-centrosymmetry.

This test was applied to the hk^4 , $5kl$ and $h5l$ reflections of sillimanite. In order to include enough reflections in each $\sin \theta / \lambda$

TABLE V

EXPERIMENTAL DATA OF TEST FOR CENTROSYMMETRY IN SILLIMANITE

Group	Number of Reflections	Limits of $\sin \theta/\lambda$	$\langle I \rangle$	N(Z)%										
				N(0.1)	N(0.2)	N(0.3)	N(0.4)	N(0.5)	N(0.6)	N(0.7)	N(0.8)	N(0.9)	N(1.0)	
$5\ k\ \ell$	A	31	12.1	38.7	54.8	64.5	66.1	72.6	74.2	74.2	77.4	77.4	82.2	
	B	$39\frac{1}{2}$	2.45	55.7	60.7	60.7	69.6	69.6	69.6	69.6	72.1	72.1	72.1	
	Average	-	-	47.2	57.8	62.6	67.9	71.1	71.9	71.9	74.8	74.8	77.1	
$5\ k\ \ell$	A	15	23.5	26.7	36.7	53.3	53.3	63.3	63.3	70.0	70.0	70.0	70.0	
	B	19	5.0	28.9	36.8	36.8	42.1	42.1	47.4	57.9	57.9	57.9	57.9	
	Average	-	-	27.8	36.7	45.1	47.7	52.7	55.4	64.0	64.0	64.0	64.0	
$h\ 5\ \ell$	A	15	66.3	36.6	36.6	50.0	56.7	56.7	70.0	76.7	76.7	83.3	83.3	
	B	$18\frac{1}{2}$	8.8	24.3	29.7	40.5	43.2	48.6	59.4	64.9	64.9	64.9	64.9	
	Average	-	-	30.0	33.2	45.3	50.0	52.7	64.7	70.8	70.8	74.1	74.1	
$h\ k\ 4$	A	42	33.0	34.5	45.2	54.8	56.0	60.7	65.5	67.9	67.9	71.4	71.4	
	B	$50\frac{1}{2}$	6.73	21.8	25.7	40.6	43.6	49.5	53.5	55.4	59.4	65.3	65.3	
	Average	-	-	28.2	35.5	47.7	49.8	55.1	59.5	61.7	63.7	68.4	68.4	
Theoretical (centrosymmetric)				24.81	34.53	41.87	47.38	52.05	56.14	59.72	62.89	65.72	68.33	
(non-centrosymmetric)				9.52	18.13	25.92	32.97	39.35	45.12	50.34	55.07	59.34	63.21	

* Group calculated N(Z) omitting reflections with $\ell = 2n + 1$.

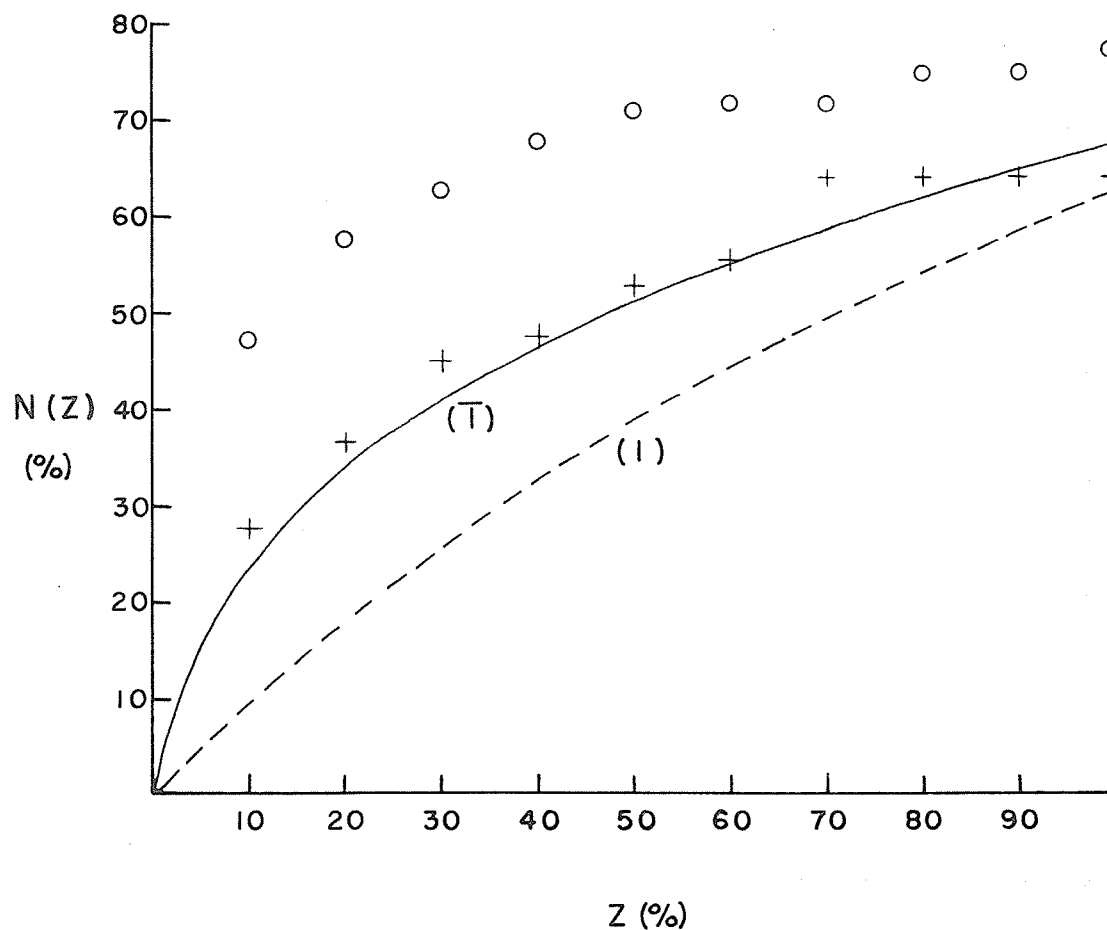


Fig. 21(a). Graphical representation of the results of the $N(Z)$ test for centrosymmetry on the $5k\ell$ reflections of sillimanite. The experimental points indicated by crosses refer to the groups in Table V in which reflections of $\ell=2n+1$ are omitted whereas the points denoted with circles refer to the groups of $5k\ell$ including all reflections. The theoretical curve for centrosymmetry is indicated as a solid line, that for non-centrosymmetry as a dashed line.

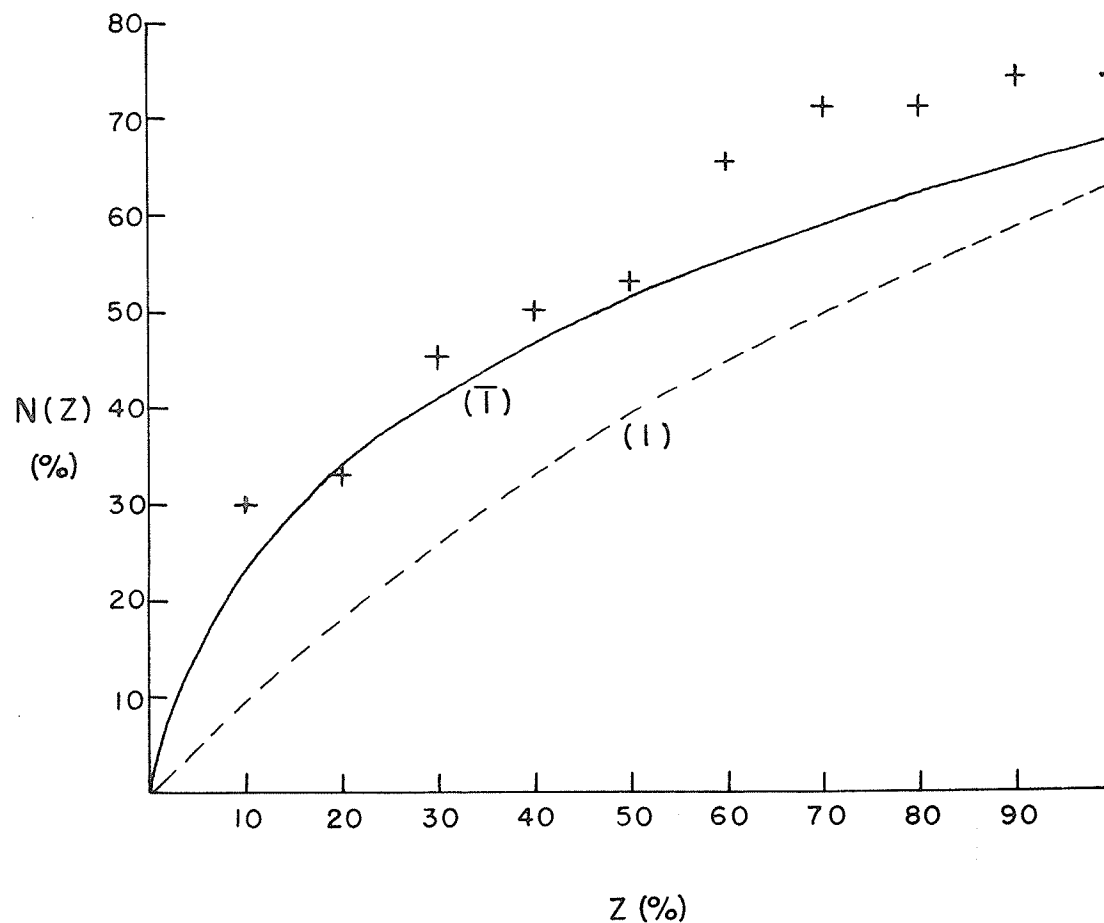


Fig. 21(b). Graphical representation of the results of the $N(Z)$ test for centrosymmetry on the $h5l$ reflections of sillimanite. The experimental points are indicated by crosses and refer to the groups omitting the reflections with $l=2n+1$. The theoretical curve for centrosymmetry is indicated as a solid line, that for non-centrosymmetry as a dashed line.

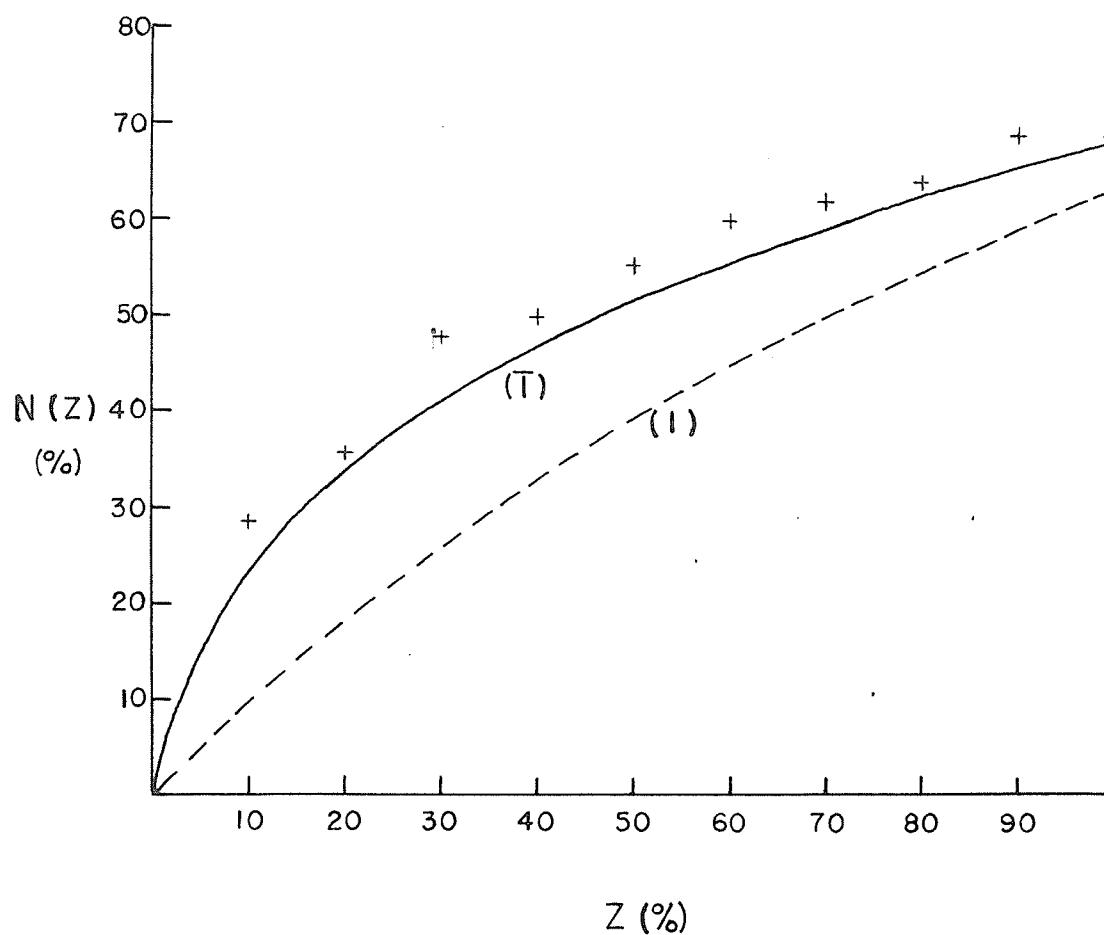


Fig. 21(c). Graphical representation of the results of the $N(Z)$ test for centrosymmetry on the $hk4$ reflections of sillimanite. The experimental points are indicated by crosses. The theoretical curve for centrosymmetry is indicated as a solid line, that for non-centrosymmetry as a dashed line.

group, only two groups were chosen for each of the three zones of reflections. In the course of applying this test it was found that the groups of reflections $5kl$ and $h5l$ gave values that were much too large for the low values of Z , even for the case of centrosymmetry. This was due to the fact that reflections with $l = 2n+1$ are very weak or unobserved thus tending to increase the number of reflections in the groups of low Z value. In order to correct for this, all reflections with l odd were omitted from the calculations in zones $h5l$ and $5kl$. Details of the calculations are given in Table V which includes the two cases for $5kl$ only for comparison. Graphical comparisons with the theoretical values are reproduced in Figs. 21 a,b,c. In all three cases the experimental curve is in reasonable agreement with the theoretical case for centrosymmetry. Thus the space group can be chosen most likely as $Pbnm$.

G Determination of Accurate Unit Cell Dimensions of Sillimanite

Approximate cell dimensions may be obtained from rotation photographs by the methods outlined in the previous chapter. However, since the interatomic distances and bond angles depend upon the values of these cell edge lengths, it is desirable to measure them to an accuracy of one part in one thousand. There are several methods listed in the literature of obtaining this precision in measurement. Buerger (1937) suggests the use of a Weissenberg "back-reflection" camera. Farquhar and Lipson (1946) employ this same technique using the oscillating crystal principle. Weisz, Cochran and Cole (1948) describe a method using a conventional Weissenberg camera in which one scans for the exact position of high order pinacoidal reflections and thus accurately measures θ values. This is called the "theta" method. C.L. Christ (1956)

describes a method for the precise determination of lattice constants of single crystals using a Weissenberg photograph using an internal standard. In essence the method involves the determination of a film correction factor, as a function of angle θ , by the superposition of the powder pattern of a standard calibration substance on a zero-level Weissenberg photograph of the single crystal in which one is interested. It was this last method that was used by the author for the determination of the cell dimensions of sillimanite.

Weissenberg photographs of the zero layers ($hk0$, $h0l$ and $0kl$) were prepared in the usual way, except that the translation of the camera was set so that there would be two centimeters of unexposed film on either side of the Weissenberg pattern. The goniometer head containing the crystal was then removed and replaced by a head containing a thin wire of 59 grade Aluminum (99.999%) which was used as the standard. The Weissenberg layer screen was replaced by a specially prepared screen with a slot of 1 cm. width, and powder patterns of the Aluminum were recorded on either side of the Weissenberg pattern. The regular Weissenberg layer screen was used to record the narrow pattern seen on the right hand side of Fig. 22. This is a photograph that was obtained around $[001]$ of sillimanite using $\text{Cu } K_{\alpha,\beta}$ radiation whereas the powder patterns were recorded using Ni filtered Cu radiation.

The films were measured as follows. First, the Al powder patterns were measured by means of a travelling microscope to the nearest .005 cm. Both patterns on either side of the film were read to give average values of $\theta_{\text{meas.}}$. The Weissenberg patterns were read in a manner which differed slightly from the normal method. The

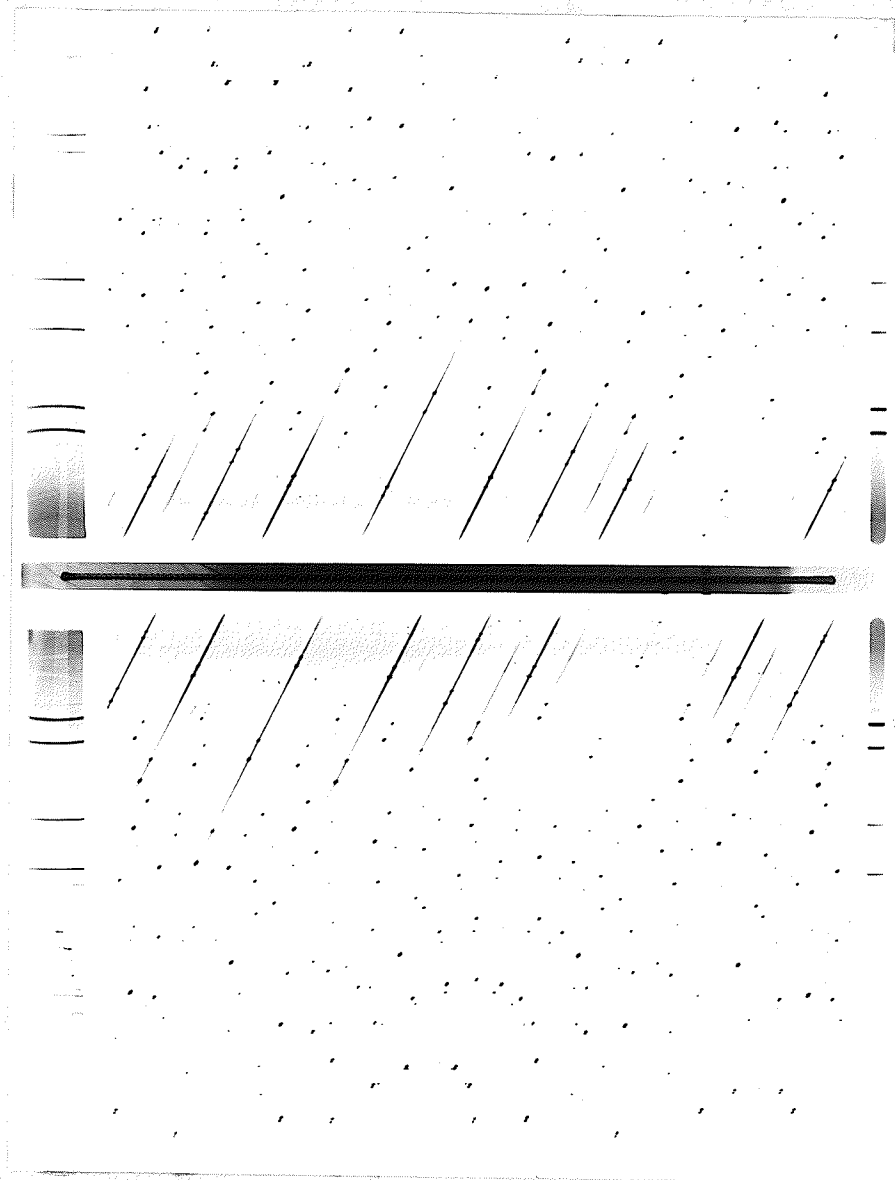


Fig. 22. Zero layer Weissenberg taken about c $[001]$ with $\text{Cu}/-$ and superimposed Al powder pattern used as an internal standard for the determination of accurate cell dimensions by the method of C. L. Christ (1956). The Al pattern was recorded with Cu/Ni radiation. The cell dimensions from this film are given in Table VI.

travelling microscope was used to measure the separations of the indexed reflections along a principal lattice row, i.e. along the white radiation streak ($2s'$ in Table VI). In order to determine the true separations normal to the direct beam streak ($2s$ mm.) the separations of the spots were measured in this manner and then corrected for the traverse of the camera by multiplying each separation by $\sin 63^\circ 26'$ (ie $\sin \tan^{-1} \frac{2}{I}$). Table VI contains the details of the calculations made for the photograph shown in Fig. 22.

The determination of the correction factor for the films, which is designated $k(\Theta) = \Theta_{\text{theor.}} / \Theta_{\text{meas.}}$, for the calibrating substance Aluminum, was made by first of all calculating the values of Al from the cell edge $a_0 = 4.0494\text{\AA}$ as determined by Swanson and Tatge (1953). Then the ratio $k(\Theta)$ for each reflection of the Al powder pattern was plotted against $\Theta_{\text{meas.}}$. Corrected Θ values from which d spacings were calculated for sillimanite were obtained by multiplying the value of $k(\Theta)$ as read from the graph (See Fig. 23) for the corresponding value of Θ measured from Weissenberg photographs of the sillimanite crystal.

The final values of the cell dimensions were calculated from the area of the film which was felt to be most free of errors. This area of the film was $30^\circ < \Theta < 60^\circ$. For each of a_0 and b_0 a total of ten separate determinations were made, eight were made for c_0 . The results of these determinations are listed in Table VII. The accuracies in Table VII are the root mean square deviations of the total number of determinations for each cell dimension.

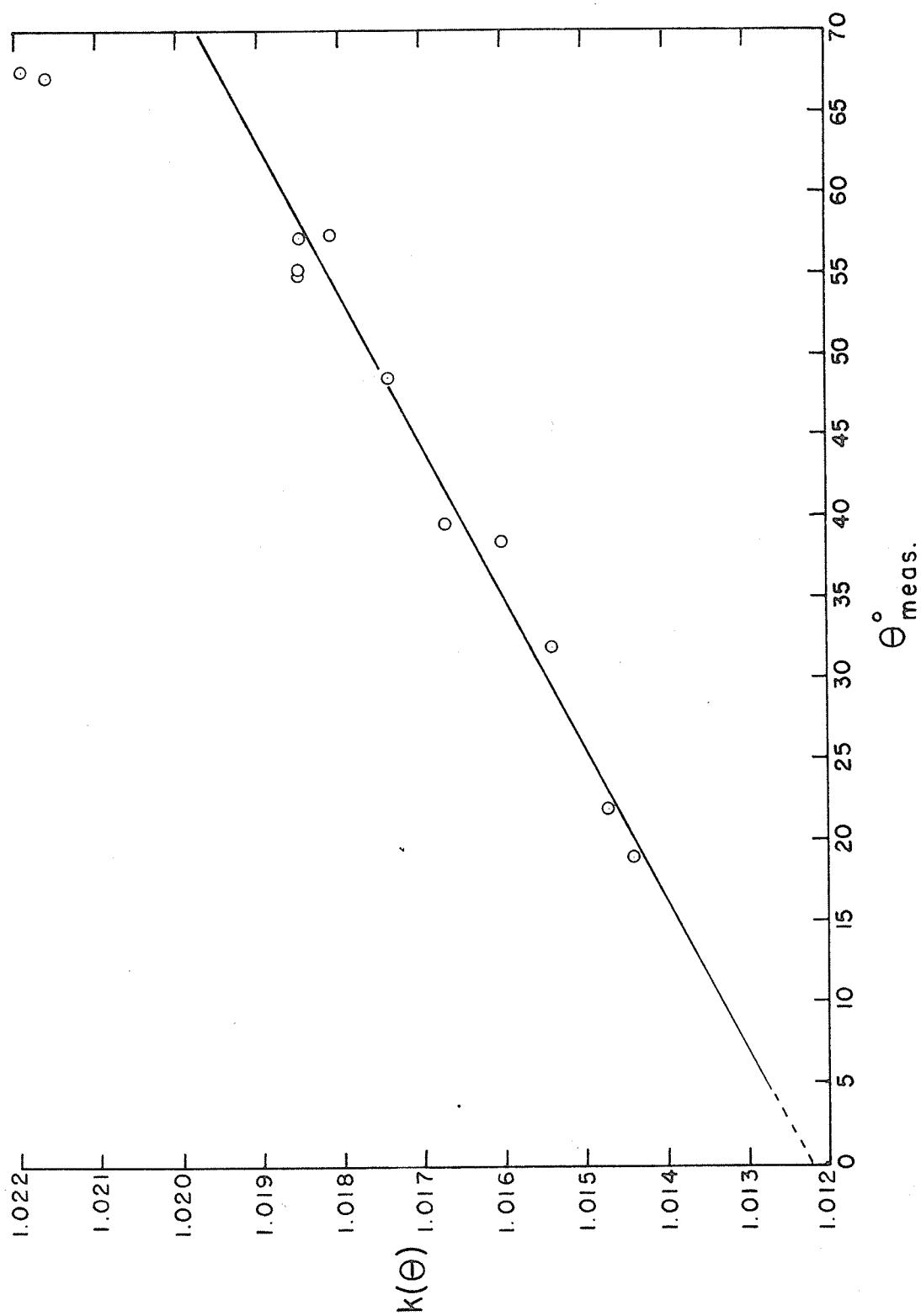


Fig. 23. Graph of $k(\theta)$ vs. θ_{meas} for the calibrating substance, Al. The data used to plot this graph were measured from the powder patterns on the photograph in Fig. 22.

ACCURATE DETERMINATION OF a_0 and b_0 FROM hko WEISSENBERG

The data here refer to Fig. 22

$2s'$ is the separation measured along the white radiation streak, $2s$ is the separation normal to the direct beam streak.

a_0

Index	Refl.	Right(mm.)	Left(mm.)	$2s'$ (mm.)	$2s$ (mm.)	$\theta^\circ(\text{Cu})$	$\theta^\circ_{\text{corr}}(\text{Cu})$	$d_{\text{meas.}}^\circ \text{\AA}$	$d(100)^\circ \text{\AA}$
2 0 0	β	105.60	81.92	23.68	21.146	10.57	10.710	3.745	7.490
	α	106.88	80.62	26.26	23.45	11.725	11.882	3.741	7.482
4 0 0	β	117.84	69.66	48.18	43.02	21.51	21.822	1.8725	7.490
	α	120.60	66.94	53.66	47.92	23.96	24.315	1.8725	7.490
6 0 0	β	131.16	56.34	74.82	66.82	33.41	33.940	1.2467	7.479
	α	135.86	51.68	84.18	75.18	37.59	38.203	1.2465	7.479
8 0 0	β	146.80	40.76	106.04	94.69	47.345	48.164	0.9343	7.474
	α_1	164.39	42.24	122.15	109.08	54.54	55.527	0.9342	7.474
	α_2	164.60	42.00	122.60	109.48	54.74	55.731	0.9343	7.474
10.0.0	β	178.40	103.31	75.09		67.06	68.361	0.7489	7.489

From this photograph, best $d(100) = 7.476^\circ \text{\AA}$

b_0

Index	Refl.	Right(mm.)	Left(mm.)	$2s'$ (mm.)	$2s$ (mm.)	$\theta^\circ(\text{Cu})$	$\theta^\circ_{\text{corr}}(\text{Cu})$	$d_{\text{meas.}}^\circ \text{\AA}$	$d(010)^\circ \text{\AA}$
0 2 0	β	122.86	99.66	23.20	20.72	10.36	10.50	3.820	7.640
	α	124.10	98.42	25.68	22.93	11.46	11.61	3.828	7.656
0 4 0	β	134.80	87.74	47.06	42.02	21.01	21.31	1.9154	7.662
	α	137.46	85.06	52.40	46.79	23.40	23.75	1.9150	7.660
0 6 0	β	147.70	74.85	72.85	65.06	32.53	33.04	1.2767	7.660
	α	152.20	70.32	81.88	73.12	36.56	37.15	1.2768	7.661
0 8 0	β	111.26	59.94	51.32		45.83	46.61	0.9579	7.663
	α_1	111.26	52.38	58.88		52.58	53.52	0.9579	7.663
	α_2	111.26	52.16	59.10		52.78	53.72	0.9579	7.663

From this photograph, best $d(010) = 7.662^\circ \text{\AA}$

TABLE VII

ACCURATE UNIT CELL DIMENSIONS OF SILLIMANITE

Best values from the three zero-level Weissenberg photographs

$$a_o = 7.476 \pm .003 \text{ \AA}^*$$

$$b_o = 7.666 \pm .005 \text{ \AA}$$

$$c_o = 5.763 \pm .003 \text{ \AA}$$

$$V = 330.28 \text{ \AA}^3$$

* The $\pm$ values listed here are the estimated standard deviations, not the probable errors.

H Measurement of the Intensities

Photographs for intensity measurement were taken with unfiltered Molybdenum radiation by the Weissenberg camera using the normal beam method as described in Sections A and B of this Chapter. Great care was taken in aligning the crystal for these measurements. The intensities of the reflections were recorded using a multiple film pack technique to provide as wide a range of intensities as possible in order to facilitate the reading of these intensities by visual estimation. The multiple film pack consisted of three sheets of film interleaved with brass foil 0.001 inches thick. Also, to further increase the range of measurable intensities, a long and short exposure of each zero-layer was recorded. The time ratio of the long to short exposure was approximately 4.8; the ratio I_L/I_S calculated from the films after the intensities were read was 4.48.

Since at the outset of this project only a 2-dimensional refinement was planned, only 2-dimensional intensity data were recorded and measured. Two sets of photographs, a long and a short exposure, were recorded for each of the three zero layers, $hk0$, $h0l$ and $0kl$. Indexing of the Weissenberg photographs was accomplished by means of Weissenberg charts as described in section D of this Chapter and one chart was drawn for each zero layer.

The intensities were measured by visual comparison of the spots on the Weissenberg pattern with a standard intensity scale. This intensity scale was prepared in the following manner. First of all a suitably strong reflection had to be isolated. Such a reflection would be one sufficiently strong to give a barely perceptible spot on the film with one oscillation. Starting at the extreme left

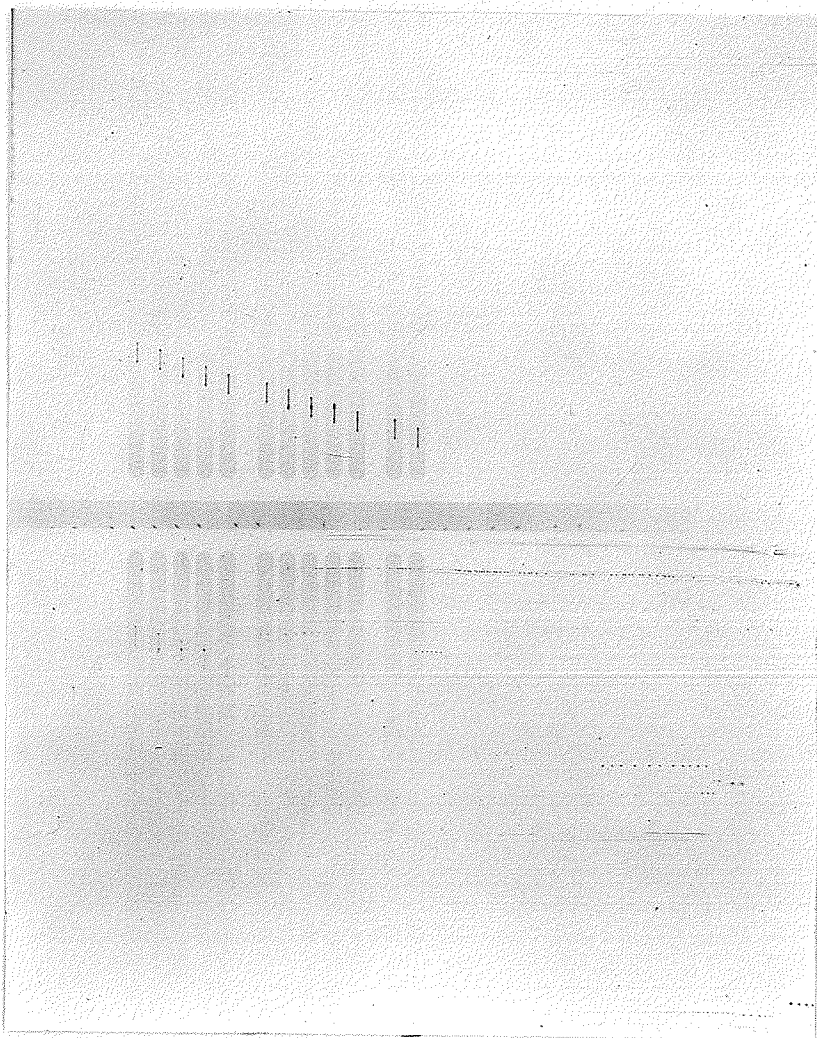


Fig. 24. The isolation of a suitable reflection used to prepare the intensity scale. The reflection is in the eighth range recorded. The exposure time for each range was 3 minutes and the camera was moved laterally through 3 mm. between each exposure.

end of the camera traverse the corresponding reading on the goniometer drum was recorded. Successive three-minute exposures with an oscillation angle of twelve degrees including a two degree overlap on either side of the range were recorded. After each exposure the camera was moved a distance of three millimeters on the camera scale so that the patterns are all recorded on one film (see film in Fig. 24). A total of sixteen overlapping ranges were recorded and a suitable reflection was found in the eighth range. The above procedure was again employed in order to isolate the chosen reflection using an oscillation amplitude of two degrees on the goniometer drum with a one degree overlap between each exposure. The camera was moved laterally through three mm. between each exposure as before. The reflection was found in only the eighth range of the twelve ranges photographed, and the 2° oscillation of this eighth range was used to prepare the intensity scale. Using a triple film pack like that used to collect the intensity data, the intensity resulting from one oscillation of the crystal was recorded. The camera was then displaced several millimeters and the intensity resulting from two oscillations was recorded. This procedure was continued so that the final intensity scale consisted of 32 spots ranging in intensity from one to 354. The recording of the scale on a triple film pack meant that each film of the Weissenberg pack had its own intensity scale. The scale and a Weissenberg pattern are shown in Fig. 25.

The intensities were measured successively along each lattice row and the results recorded on large squared sheets. Both the upper and lower halves of the films were examined and all possible visual intensities were estimated. Due to the orthorhombic symmetry of sillimanite reflections with indices of the type $hk0$, $\bar{h}k0$, $h\bar{k}0$ and

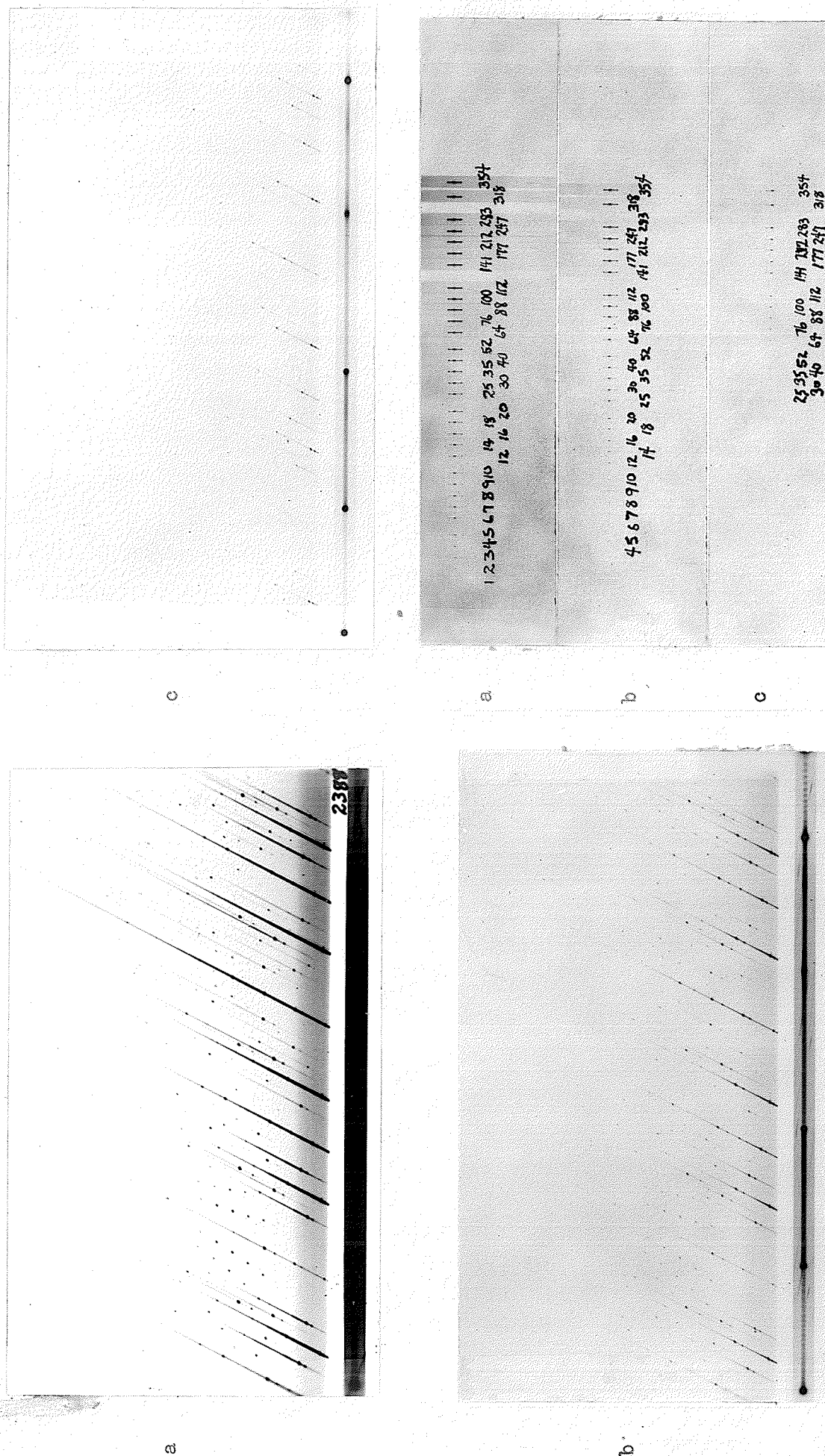


Fig. 25. Triple film pack for the measurement of the intensities of the hko reflections from a Weissenberg photograph. The innermost film (a) of the pack is shown at the top left of the page. Also included is the intensity scale (triple film pack) that was used to estimate each intensity. Only the upper halves of the Weissenberg patterns are included.

$\bar{h} \bar{k} 0$ are all equivalent, and thus only the positive indices had to be recorded ($hk0$, $0kl$, and $h0l$). This multiplicity however, allowed in some cases a maximum of eight readings to be made for one intensity on one film using both upper and lower halves of the film. In the case of the axial reflections $h00$, $0k0$ and $00l$, at least three readings of each were recorded. The best value of the intensity was chosen as the average of all the estimated values for that particular reflection. The short exposure Weissenberg photographs were used to measure the intensities of only the very strong reflections which were too strong to be read even from the outermost film of the three film pack used to record the long exposure. The moderately strong reflections were used to put the long and short exposures on the same relative scale.

By measuring the intensities in the above manner one obtains values for the intensities which are on a relative scale. No attempt was made to put the three zones on the same relative scale, since in the computations each zone ($hk0$, $0kl$, $h0l$) was to be treated as a separate job, and because after the first calculation of structure factors using Taylor's (1928) parameters scale factors were determined for placing the F_0 's on an absolute scale. These factors were found to be very close to 10.

I. Derivation of Structure Factors from the Intensities

Having obtained a set of experimentally observed intensities it is desirable to convert them to a set of structure amplitudes. The structure amplitude is the magnitude of the "structure factor" which is directly related to the kinds and positions of the atoms in the unit cell, and so may be calculated when the structure is known. These structure factors are discussed more fully in Chapter VI.

The amount of energy determining the intensity I of reflections on a Weissenberg photograph is related to the structure factor F by the expression

$$I = KL_p F^2$$

where K is a proportionality constant, L the Lorentz factor and p the polarization factor.

The Lorentz factor takes account of the variation in observed intensities due to certain reflection planes remaining in a reflecting position longer than others. This factor is dependent on the geometry of the method used to record the reflections. Buerger (1960, Chapter VII) deals quantitatively with the Lorentz corrections that must be applied for each single-crystal method. For the Weissenberg method this factor is expressed as $L = \frac{1}{\xi \cos \theta}$ where ξ is a reciprocal lattice coordinate and thus a function of h , k and l .

The polarization factor p depends only on the glancing angle θ and not on the X-ray method employed to record the intensities. The intensities vary with θ due to the polarization of the X-ray beam after reflection from crystallographic planes. This factor is expressed by the relation $p = (1 + \cos^2 2\theta)/2$.

It may be seen that both these factors are simple trigonometric functions of θ , and they are usually applied together in a single L_p correction factor expressed as

$$2L_p = \frac{1 + \cos^2 2\theta}{\xi \cos \theta}.$$

In solving the equation for I expressed above for F^2 each intensity may be corrected for these two geometrical factors by multiplying by $\frac{1}{2L_p}$.

These $\frac{1}{2L_p}$ values were determined graphically by means of the reciprocal

lattice projections, and scales prepared from curves of constant $\frac{1}{2Lp}$ as a function of reciprocal lattice coordinates ζ and ξ published by Cochran (1948). Relative values of F were obtained by taking the square root of the values of F^2 so obtained for each reflection. These relative values of F were placed on an absolute scale by the methods described in the previous section.

Another factor which is usually corrected for in full scale structure determinations is absorption of the X-ray beam by the crystal. This absorption depends upon the chemical composition and the size of the crystal and on the radiation used. It can be shown by calculations that for a crystal of sillimanite 0.25 mm. across, the absorption using molybdenum X-radiation is negligible.

In order to distinguish between the observed structure factors and those calculated from atomic positions, the conventional symbols F_o and F_c respectively are used throughout the remaining chapters in this dissertation.

CHAPTER VI

THE STRUCTURE FACTOR

A Derivation of the Equations

A structure determination involves the elucidation of the arrangement of the atoms in a crystal and this is done by analyzing the effect of the arrangement on the intensities of the diffracted X-ray beams. The wave scattered from each hkl plane is characterized by a complex quantity, F_{hkl} , called the structure factor. This structure factor can be written as a function of the coordinates of the J atoms in the unit cell of a crystal. Thus for a particular arrangement of atoms in a unit cell, there is a set of specific diffraction waves F_{hkl} .

In a structure analysis a structure model is proposed, the validity of which is determined by the comparison of the structure factors, F_c , calculated for this model and the observed structure factor F_o . For the proposed model to be the correct one the computed set of F_{hkl} 's must match the observed set of F_{hkl} 's.

As mentioned in Chapter III, the electrons of the atoms in a crystal are the scattering units. However, it is more convenient to think of the scattering units in a crystal as the chemical atoms. If the amplitude of the wave scattered by the j^{th} atom in a unit cell is f_j then the scattered wave is described in amplitude and phase by $f_j e^{i\phi_j}$, where ϕ_j is the phase angle of the wave referred to the origin of the coordinate system. A rigorous derivation of this is given in Buerger (1960). At the maximum of the reflection from the plane hkl the resultant wave from all the J atoms in the unit cell is given by

$$F_{hkl} = \sum_{j=1}^J f_j \exp(i \phi_j)$$

The phase angle ϕ_j may be expressed as a function of the fractional coordinates x_j , y_j and z_j of the atoms in the unit cell:

$$\phi_j = 2\pi(hx_j + ky_j + lz_j)$$

so that the structure factor can be written

$$F_{hkl} = \sum_{j=1}^J f_j \exp(i 2\pi(hx_j + ky_j + lz_j))$$

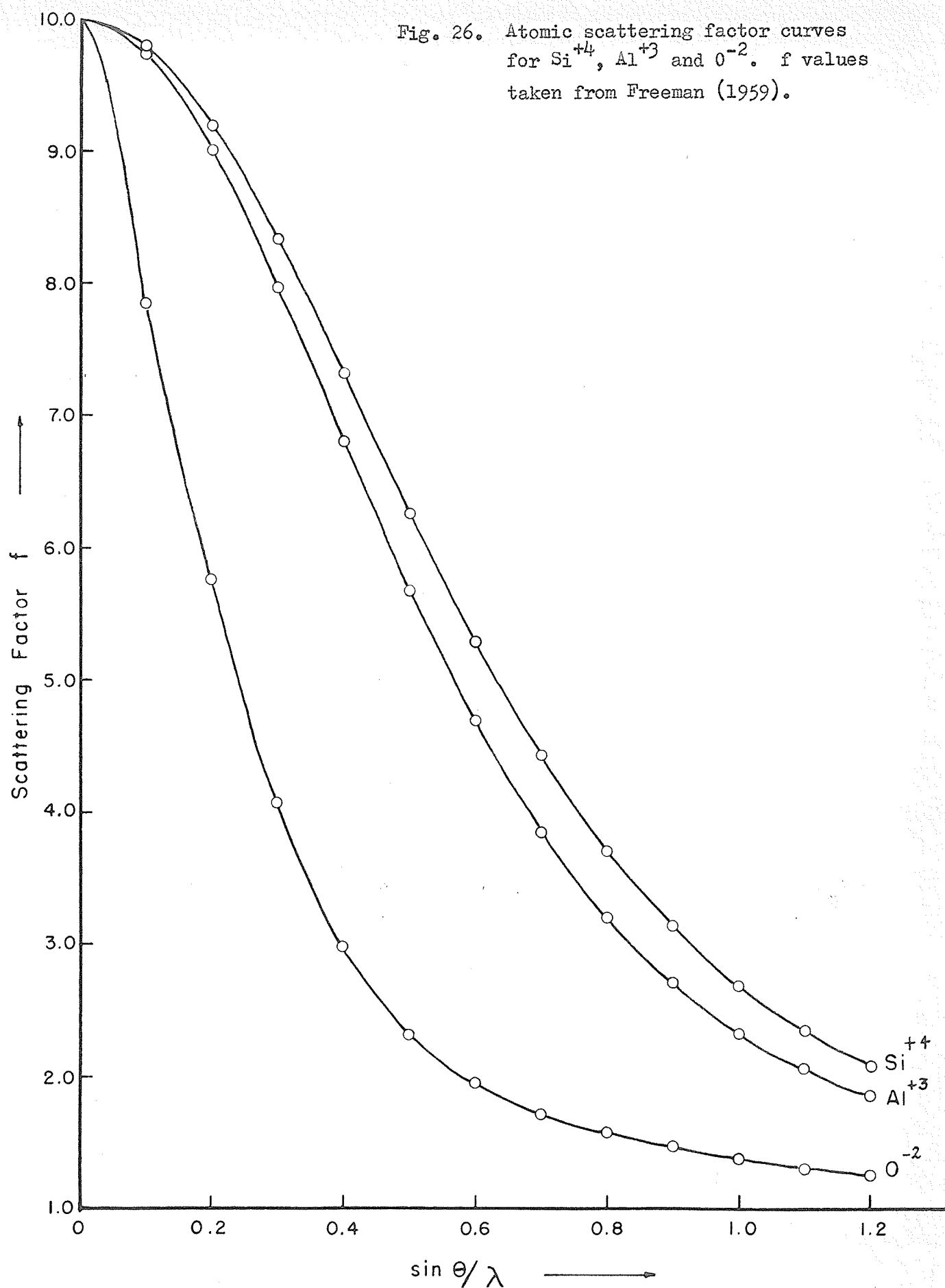
Notice that from these expressions the structure factor is a complex quantity and is in general characterized by a magnitude $|F_{hkl}|$ and a phase ϕ_{hkl} . The magnitude is observable by experimental methods but the phase cannot generally be observed by present day methods.

If the scattering power of one electron is taken as unity and all the electrons in an atom are assumed to be concentrated at a single point then the scattering power of an atom f_j will be its atomic number Z . However, in an atom the electrons are found in a volume and thus the waves scattered from the electrons in one atom will interfere with each other. This destructive interference effect increases with increasing θ and this is shown diagrammatically in Fig. 26 where f_j can be seen to fall off with increasing $\sin \theta / \lambda$. Notice that at $\sin \theta / \lambda = 0$ the diffracting power of an atom is equal to its atomic number Z .

The expression for the structure factor can be written in component form as

$$F_{hkl}^2 = A^2 + B^2$$

Fig. 26. Atomic scattering factor curves for Si^{+4} , Al^{+3} and O^{-2} . f values taken from Freeman (1959).



$$\text{where } A = \sum_{j=1}^J f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

$$\text{and } B = \sum_{j=1}^J f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

In these expressions all the terms have the meanings described above. From symmetry considerations, considerable simplification of these equations can usually be made.

For crystals having a centre of symmetry which is chosen as the origin of the coordinate system, there is no need to calculate the sine terms because, for every atom, x, y, z having a phase contribution of ϕ_{xyz} there is an identical atom $\bar{x}, \bar{y}, \bar{z}$ with phase contribution $-\phi_{xyz}$. Thus in summation their contributions are equal in magnitude but opposite in sign and so $B = 0$ for the origin at a centre of symmetry.

A further simplification is applicable due to any further symmetry of the space group. In any space group there are in general m equivalent positions. Thus by taking account of these m positions one need only calculate the summation over the structurally different atoms at one of these equivalent positions and the multiplicity of that position will take account of the other similar atoms at the other equivalent positions. This process may be demonstrated by the following example of the derivation of the structure factor formulae for the $hk0$ planes of the space group $Pbnm$. The extension to the 3-dimensional formulae is by no means difficult and the same procedures used in this example are applicable to it.

To begin this derivation consider the projection on to the plane (001) of the space group $Pbnm$ shown in Fig. 27. There is a problem encountered using this plane group $pgg2$, for the derivation of the

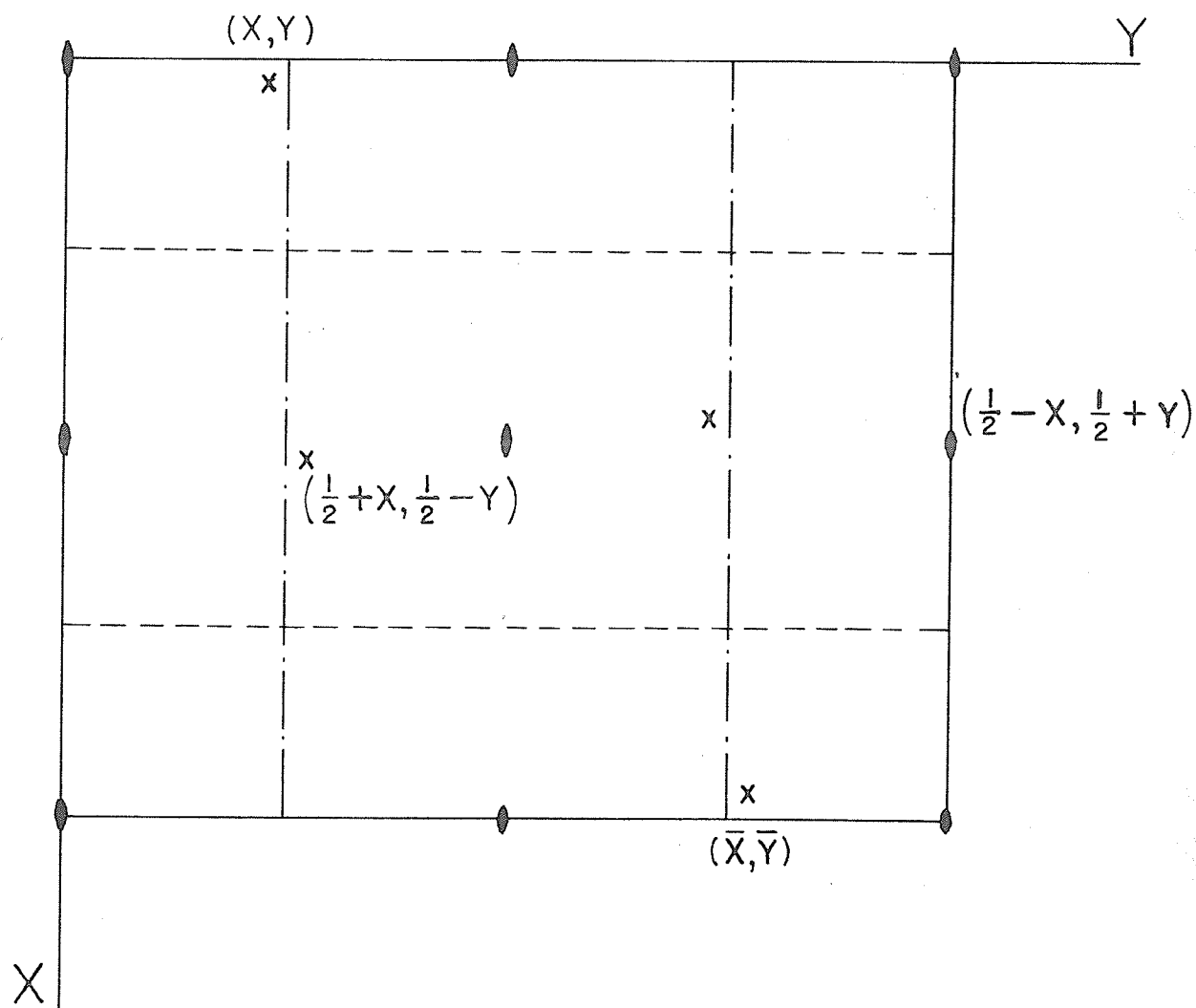


Fig. 27. Projection of the symmetry elements of the space group $Pbnm$ onto the (001) plane. The plane group so formed is pgg in the notation of the International Tables for X-ray Crystallography Vol. I (1952). The equivalent positions have been indicated by crosses and accordingly labeled.

structure factor equations. It appears from this figure that there are only four equivalent positions in the plane group, which is in fact so, whereas there are eight equivalent positions in the space group Pbnm. This is explained by the fact that the space group Pbnm contains a mirror plane perpendicular to c which introduces four more equivalent positions of the same values of x and y but different z . Account can be taken of the doubling of the multiplicities by considering that there are two identical atoms at each of the equivalent positions shown in the plane group of Fig. 27. Atoms that are in special positions such as the origin and on the symmetry planes will have a multiplicity of four in Pbnm. The z coordinates in the $hk0$ projection make no contribution to the structure factor since all the l indices are zero.

The "symmetry factor", the structure factor without the atomic scattering factor f_j , is defined as:

$$S = \sum_{j=1}^m \exp (i 2\pi(hx_j + ky_j))$$

for the $hk0$ projection, where all terms have the same meaning as before, and m is the multiplicity of the equivalent positions. In plane group $pgg2$ the equivalent positions are: x, y ; $\bar{x}, \bar{y}$; $\frac{1}{2} + x, \frac{1}{2} - y$; and $\frac{1}{2} - x, \frac{1}{2} + y$. Substituting these in the expression for the symmetry factor and taking account that in the projection of space group Pbnm there are two atoms at each equivalent position in $pgg2$ one obtains:

$$\begin{aligned} S &= 2 \left\{ e^{i 2\pi(hx+ky)} + e^{-i 2\pi(hx+ky)} + e^{i 2\pi(h(\frac{1}{2}+x)+k(\frac{1}{2}-y))} + e^{i 2\pi(h(\frac{1}{2}-x)+k(\frac{1}{2}+y))} \right\} \\ &= 2 \left\{ e^{i 2\pi(hx+ky)} + e^{-i 2\pi(hx+ky)} + e^{i 2\pi(hx-ky)} e^{i\pi(h+k)} + e^{-i 2\pi(hx-ky)} e^{i\pi(h+k)} \right\} \end{aligned}$$

Taking out the common factor, $e^{i\pi(h+k)}$ for the last two terms, and making

use of Euler's relation $e^{i\phi} + e^{-i\phi} = 2 \cos \phi$,

$$S = 4 \left\{ \cos 2\pi(hx+ky) + e^{i\pi(h+k)} \cdot \cos 2\pi(hx-ky) \right\}.$$

There are now two cases which one must consider, $h+k=2n$ and $h+k=2n+1$.

These two cases will account for all possible values of the term $e^{i\pi(h+k)}$.

Case 1. $h + k = 2n$ and $\therefore e^{i\pi(h+k)} = +1$.

$$\text{Then } S = 4 \left\{ \cos 2\pi(hx+ky) + \cos 2\pi(hx-ky) \right\}.$$

A further reduction can now be made by applying the trigonometric identity

$$\cos(\alpha+\beta) + \cos(\alpha-\beta) = 2 \cos \alpha \cos \beta$$

which immediately reduces the expression to

$$S = 8 \cos 2\pi hx \cdot \cos 2\pi ky.$$

Case 2. $h + k = 2n + 1$ and $\therefore e^{i\pi(h+k)} = -1$.

$$\text{Then } S = 4 \left\{ \cos 2\pi(hx+ky) - \cos 2\pi(hx-ky) \right\}.$$

Using the identity $\cos(\alpha+\beta) - \cos(\alpha-\beta) = -2 \sin \alpha \sin \beta$,

this case may be expressed as:

$$S = -8 \sin 2\pi hx \sin 2\pi ky.$$

For the atoms in the special positions these same equations are applicable except that the factor m in front of each one is 4 instead of 8. Table VIII gives a list of all the equations that were used in the calculation of the structure factors for the three zero levels in the space group $Pbnm$. In order to facilitate computing, all the reflections were divided into the two groups for each zero level as shown in this table.

TABLE VIII

TWO-DIMENSIONAL STRUCTURE FACTOR EQUATIONS FOR SPACE GROUP Pbnm

Projection	Group of Reflection type	Structure Factor Equations
hk0	$h + k = 2n$	$A = \sum_{j=1}^J f_j 8 \cos 2\pi h x_j \cos 2\pi k y_j, B=0$
	$h + k = 2n+1$	$A = - \sum_{j=1}^J f_j 8 \sin 2\pi h x_j \sin 2\pi k y_j, B=0$
	$h = 2n, \ell = 2n$	$A = \sum_{j=1}^J f_j 8 \cos 2\pi h x_j \cos 2\pi \ell z_j, B=0$
h0 ℓ	$h + \ell = 2n$	$A = - \sum_{j=1}^J f_j 8 \sin 2\pi h x_j \sin 2\pi \ell z_j, B=0$
	$k = 2n, \ell = 2n$	$A = \sum_{j=1}^J f_j 8 \cos 2\pi k y_j \cos 2\pi \ell z_j, B=0$
	$k = 2n, \ell = 2n+1$	$A = - \sum_{j=1}^J f_j 8 \sin 2\pi k y_j \sin 2\pi \ell z_j, B=0$

* These summations are taken over the structurally different atoms only, not over all the atoms of the unit cell.

B The Temperature Factor

The problem of thermal vibration in crystal structure analysis is quite complex. In the derivation of the structure factor equations it was assumed that the atoms were stationary. This condition only exists at absolute zero. Any temperature above this causes the atoms to vibrate in such a way that in general, the electron density is smeared over a triaxial ellipsoid. Thus the effect of thermal motion is to make the electrons occupy a larger volume than if the atoms were at rest. Since the scattering factor curves are derived with the atoms at rest, undergoing no thermal vibration, then this thermal motion will cause the f values to fall off more rapidly with $\sin \theta / \lambda$.

An accurate allowance for the thermal motion of the atoms is very difficult to make. However, Waller (1927) showed that a fair approximation may be made by correcting the scattering factors derived for atoms at rest with a factor

$f = f_0 \exp (- B \sin^2 \theta / \lambda^2)$, where B is a "temperature factor". In the case of an unknown structure the magnitude of B may be derived from a statistical examination of the intensities. In the present case values of B were chosen from a structure refinement of andalusite (Burnham and Buerger 1961) which is a polymorph of sillimanite Al_2SiO_5 . Values of the temperature factor B are obtained from a Fourier refinement. Final values determined in the present refinement proved that the temperature factors initially chosen in this manner were of the right magnitude.

C The Computation of Structure Factors

In the course of a crystal structure analysis, structure factors must be computed many times. Up to the introduction of electronic

digital computers these calculations as well as the Fourier summations had to be done by hand on desk calculators. The tedium of these computations lead to ingenious methods of cutting down the work involved. Tables of values of $\cos 2\pi hx$ and $\sin 2\pi hx$ for various values of h and x were used, and methods of Fourier summations were facilitated by such devices as Beevers-Lipson strips and Patterson-Tunell strips. However even with the use of these labor-saving devices many hours of calculations are still involved.

With this in mind the author decided to programme the University of Manitoba's IBM "1620" electronic digital computer to perform these calculations. The language used in programming the "1620" was the "FORTRAN" developed by IBM so that programming is greatly facilitated. The programme was fed into the machine on punched paper tape which stores it in the "memory". It is this programme that provides the machine with the necessary information to operate on the numerical data which are fed in on another paper tape. The programme prepared by the author for the IBM "1620" computer is described in Appendix II. The computation time was approximately seven seconds per structure factor. As a check, a few of the answers obtained from the computer were calculated with the use of a desk calculator and tables of $\sin 2\pi hx$ and $\cos 2\pi hx$. As described in the next Chapter most of the structure factors were calculated on an IBM "650" in conjunction with the Fourier calculations using programmes written and provided by Dr. F. R. Ahmed.

The diffracting powers of the atoms were taken from Freeman (1959) and the atoms were assumed to be in completely ionized states, i.e., Si^{+4} , Al^{+3} and O^{-2} . A graph of the diffracting powers f against

$\sin \theta / \lambda$ for these three atoms is shown in Fig. 26. To provide all possible values of f in the I.B.M. "1620" programme, polynomial equations were derived for each of the three curves from coordinates listed in Freeman (1959) using a "1620" programme developed by W. R. Graves (I.B.M. file No. 7.0.001). The polynomial is of the form

$$y = A_0 + A_1 x + A_2 x^2 + \dots + A_6 x^6$$

where y is the scattering factor f and x is $\sin \theta / \lambda$. The temperature correction was then applied to the scattering factors thus obtained for a particular plane by multiplying f_j by $\exp(-B_j \sin^2 \theta / \lambda^2)$.

CHAPTER VII

REFINEMENT BY FOURIER METHODS

A Introduction

There are several standard procedures of refinement listed in textbooks on crystal structure analysis. Some of these include the method of least squares initiated by Hughes (1941); Booth's (1947) method of steepest descents, and the Fourier series method of producing an image of the electron density in the unit cell, first suggested by W. H. Bragg (1915). This last method of refinement was used in the present work.

Any periodic function can be represented by an appropriate sum of sine and cosine terms known as a Fourier series. Since a crystal is periodic, that is it contains an infinitely repeating array of unit cells, its electron density can be represented by such a sum. The scattering units in a crystal are the electron clouds surrounding the nuclei of the atoms. Thus a representation of the electron density at any point in the unit cell may be described in terms of the amplitudes and phases of the waves scattered from the crystal. It has been shown that the expression for the electron density ρ at point (XYZ) is given by the 3-dimensional Fourier equation

$$\rho(X,Y,Z) = \frac{1}{V} \sum_h \sum_k^{\infty} \sum_l F_{hkl} e^{-i 2\pi(hX+kY+lZ)}$$

where $\rho(X,Y,Z)$ is the electron density at the point in the unit cell with coordinates X,Y,Z,

V is the volume of the unit cell, and

F_{hkl} is the structure factor of the wave from plane hkl in the crystal.

This expression may be rewritten in terms of a phase angle α referred to the origin.

$$\rho(X,Y,Z) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l \left| F_{hkl} \right| \cos \left\{ 2\pi(hX+kY+lZ) - \alpha_{hkl} \right\}$$

where α_{hkl} is the phase angle of the diffracted beam. If the structure is centrosymmetric and a centre of symmetry is chosen as origin, then the phase angle α_{hkl} will be 0° or 180° with respect to the centre of symmetry. The expression will thus reduce to:

$$\rho(X,Y,Z) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l F_{hkl} \cos 2\pi(hX+kY+lZ).$$

This expression for the electron density is not as explicit as it appears. In Chapter VI it was shown that the structure factor is described by a magnitude and a phase (either + or - for centrosymmetric crystals). The magnitude is experimentally observable but since the intensity is proportional to the square of the structure factor there is in general no means of observing the sign. The signs or phases of the structure factors must therefore be calculated from a knowledge of an approximate structure prior to the production of an electron density map.

The above expressions all deal with 3-dimensional electron density maps in which the electron density is computed at specific intervals throughout the volume of the unit cell. The intervals that are usually chosen are $\frac{1}{60}$ th or $\frac{1}{120}$ th's of the cell edge. If the interval chosen is $\frac{1}{60}$ th, the total number of sample points in the

unit cell is 60^3 or 216,000. This number in general may be reduced due to the symmetry of the particular crystal, however the number of computations involved is still large enough to limit 3-dimensional refinements to sections or planes through atomic positions in the cell where more detail is required.

Complete refinements of simpler structures utilize the much simpler projections of the electron density. In these so-called 2-dimensional electron density maps the 3-dimensional distribution of the electron density is projected parallel to a crystallographic translation direction. An image of the crystal structure is obtained by a synthesis of all reflections from planes parallel to the zone axis. Thus to produce a map of the electron density projected parallel to the c axis the Fourier summation is taken over all the reflections of the type $hk0$. The general expression for the electron density projected onto the plane parallel to c can be obtained from the 3-dimensional expression and is written as

$$\rho(X,Y) = \frac{1}{A_c} \sum_h \sum_{k=-\infty}^{\infty} F_{hk0} \cos 2\pi(hX+kY),$$

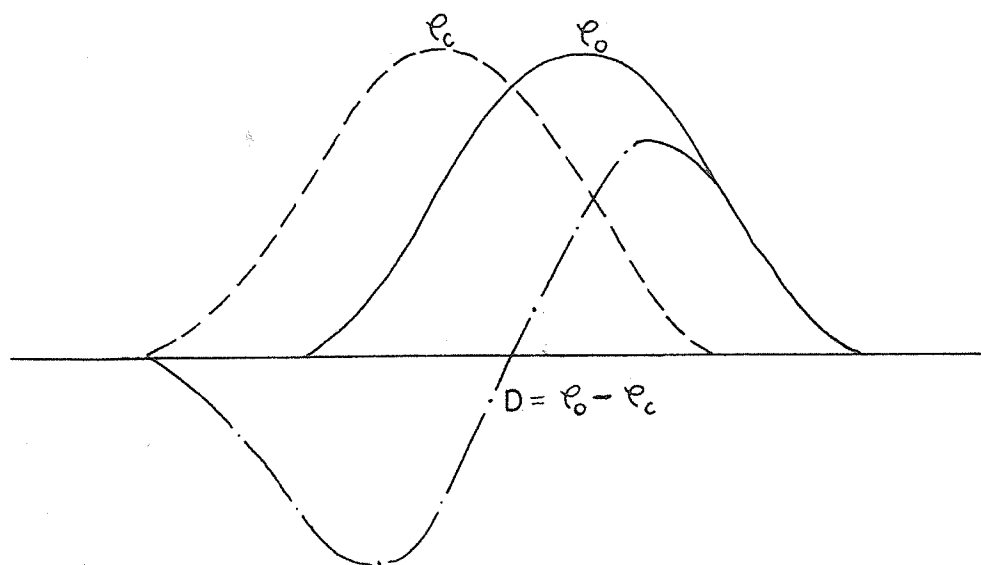
where the origin is chosen at a centre of symmetry and A_c is the area of the projected plane. A Fourier synthesis of this kind is commonly called an electron density or ρ_o synthesis. In it one uses the observed amplitudes and the signs calculated from a postulated crystal structure model. In the first instance generally only the signs of the strong reflections are known with any certainty so only these are used to calculate the first synthesis. New atomic coordinates may then be deduced from this map and the structure factors recalculated. Those

reflections for which the signs did not change are used in the next Fourier synthesis. This process is carried out until the signs for all the reflections have been determined or do not change on further small changes in the atomic parameters.

A modification of this method was introduced by Cochran (1951). This method is called the Difference Fourier synthesis since the structure factors of the Fourier waves (F_o) are replaced by the differences ($F_o - F_c$) as the Fourier coefficients. The advantage of the $F_o - F_c$ synthesis over the F_o synthesis results from the fact that the electron density given by a Fourier series of the observed structure factors, F_o , differs from the true electron density because of the use of a finite series; i.e., finite limits of h and k . Also when atoms overlap, the peaks of the F_o synthesis may not correspond to the true atomic positions. The difference synthesis affords a much more sensitive method of determining temperature factors than does a F_o synthesis.

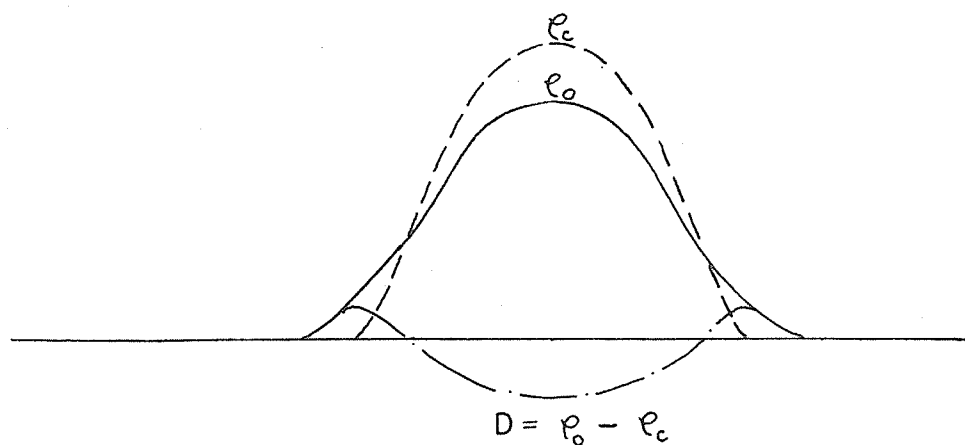
The interpretation of a $F_o - F_c$ map is quite simple. Reference to Fig. 28 (a) will show an ideal situation in which the assumed atomic coordinate does not correspond to the true coordinate. Atomic positions which are correctly chosen have no accompanying density gradient while incorrectly chosen positions fall on density gradients. The magnitude of the correction is directly proportional to the gradient $\frac{\partial D}{\partial r}$ and inversely proportional to the electron density at the centre of the n^{th} atom $(F_o)_n$. The magnitude of the correction as deduced by Cochran (Lipson and Cochran, 1953) is given by

$$\Delta r_n = \frac{(\partial D / \partial r)_n}{2p (F_o)_n}.$$



(a)

Fig. 28(a). Vertical section of the projected electron density showing the shape of $D = \rho_o - \rho_c$ when the assumed atomic position does not agree with the actual position.



(b)

Fig. 28(b). Vertical section of the projected electron density showing the result on the shape of $D = \rho_o - \rho_c$ when the temperature factor has been underestimated.

The direction of this correction is upslope from the assumed position. To use this expression, one determines $\partial D / \partial r$ from the difference map by taking ∂D , the difference in density between the peak maximum and the value at the assumed position and then divides it by the corresponding distance, ∂r in Angstroms, from the assumed position to the peak. $(\rho_0)_n$ is determined from a ρ_0 synthesis and is the electron density at the centre of the n^{th} atom. The constant p is determined from the ρ_0 map by the equation

$$\rho_r = \rho_0 \exp(-pr^2).$$

where ρ_r is the electron density at a point r from the electron density peak.

Information concerning the temperature factor for a particular atom can also be obtained from a difference synthesis. The effect of underestimating the temperature factor B , of an atom is to make the assumed peak more compact. This situation is shown in Fig. 28 (b) where the assumed and actual atomic positions are the same. There is a negative region at the atomic position and to remedy this one must increase the temperature factor. An overestimated temperature factor is characterized by ρ_c in the neighbourhood of the atomic position being more diffuse than ρ_0 , and so a positive region is produced on the $\rho_0 - \rho_c$ map.

Refinement of the crystal structure of sillimanite was accomplished by 2-dimensional Fourier methods using both ρ_0 and $\rho_0 - \rho_c$ maps of the electron density projections. The process may be described as follows.

(1) Structure factors were calculated from the atomic parameters of sillimanite derived by Taylor (1928). The F_o values were used to place the F_o values on an absolute scale and assign phase angles (+ or - sign) to them for use as coefficients in the Fourier series. Three ρ_o projections were prepared along the three principle axes.

(2) Using the atomic positions derived from a Fourier ρ_o projection ($hk0$, $0kl$, $h0l$) structure factors were calculated for all the observed reflections in the particular zone.

(3) $\rho_o - \rho_c$ maps of the three projections were prepared using the signs of the calculated structure factors with the observed F_o values.

(4) From these maps new atomic parameters and thermal parameters were derived and a second set of structure factors computed.

(5) The above two procedures, 2 and 3, were carried out successively until no further change occurred in the signs of the F 's. Then a final ρ_o map was prepared along each of the three axes and used in conjunction with the $\rho_o - \rho_c$ maps to estimate the accuracy of the final atomic parameters.

B Computational Aspects

An attempt was made to programme the University of Manitoba's IBM "1620" digital computer to perform the Fourier synthesis. The programme was prepared in the "FORTRAN" language and was run first of all to calculate an $hk0$ ρ_o synthesis. Spot checks on the computed values of ρ_o using this 1620 programme showed that the answers were erroneous; also the computing time was excessive. Since too much time was being spent in attempting to correct this programme, it was

abandoned, and an efficient and sophisticated Fourier series programme was obtained through the kindness of Dr. F. R. Ahmed at the National Research Council in Ottawa. With the aid of the staff at I.B.M. (Winnipeg) this programme (card input-output) was run with success on the I.B.M. "650" at the Great West Life Assurance Company (Winnipeg). The computing time for each synthesis was approximately one hour, using 240 observed structure factors and a mesh of 31 x 31 grid units.

A structure factor programme for the I.B.M. "650" was also obtained from Dr. Ahmed at the same time as the Fourier programme. Although the author's structure factor programme for the 1620 worked efficiently a great deal of time would have to have been taken to transfer the results of these computations to cards for input to the 650 Fourier programme. The author's 1620 programme which is described in Appendix II, calculated only the structure factors whereas the "650" structure factor programme supplied, along with the structure factors, a value of the scale factor necessary to place the observed data on the absolute scale as well as a value of the "reliability" factor R (which is discussed in the next section). Thus it was decided to do all the subsequent computations on the I.B.M. "650" through the generosity of the Great West Life Assurance Company.

The formula applicable for the projection of the electron density that is shown in Section A of this Chapter was not used in this form. The symmetry conditions that are contained in the plane groups of each of the projections were applied to this formula. It was these resulting formulae similar to those listed in the International Tables (Vol I. 1952) for the plane groups pgg , pmg and cmm , that were used to calculate the electron density projections for the three zones.

As an example, the formula for the determination of the electron density in the plane group pgg, which is the hk0 projection in sillimanite is given as

$$\rho(X,Y) = \frac{4}{A_c} \left[\frac{F(00)}{4} + \frac{1}{2} \left\{ \sum_{h=2}^H \sum_{k=2}^K F_{hk} \cos 2\pi hX \cos 2\pi kY + \sum_{h=1}^H \sum_{k=1}^K F_{hk} \cos 2\pi hX \cos 2\pi kY \right. \right. \\ \left. \left. - \sum_{h=1}^H \sum_{k=1}^K F_{hk} \sin 2\pi hX \sin 2\pi kY \right\} \right]$$

where H and K represent the maximum limits of the values of h and k. Similar expressions were used for the h0l and 0kl projections. The zero term of the Fourier series $F_{(00)}$ is the total amount of scattering matter in the unit cell, i.e., the total number of electrons in the unit cell, which in sillimanite is 320.

C The R Factor

The criterion used to measure the correctness of the structure at each stage of the refinement is the "reliability factor" or "residual factor" defined as

$$R = \frac{\sum | |F_o| - |F_c| |}{\sum |F_o|} \times 100 \%$$

The value of R is a relatively small percentage (<15%) when the structure is the correct one for the observed data, and a large percentage (~> 40%) when the structure is incorrect. The R factors were calculated for each projection following the derivation of each

new set of atomic parameters. Only the observed reflections were included in this calculation.

D The Refinement

(a) Initial Syntheses Starting with Taylor's (1928) Parameters

This refinement was started by using W. H. Taylor's (1928) parameters for the calculation of structure factors. Using the calculated phases of these structure factors with the observed structure amplitudes three ℓ_0 Fourier summations were prepared and the resulting electron densities were plotted on projections along the a, b and c axes. Each summation was computed over an asymmetric part of the unit cell so as to include at least one of each structurally different atom in the unit cell. The electron densities were computed at intervals of 1/60th of the cell edge in all three projections and the scale used to plot the projection was $1\text{\AA}^0 = 10\text{ cm}$. Contours of equal electron density were drawn at $2.0\text{ e/\AA}^0$ on each of the maps.

Upon examination of the ℓ_0 maps produced from Taylor's parameters it was evident from the shapes of the peaks and from the relief observed in areas that should have been flat, that Taylor's original structure was badly in error. New parameters were taken from these maps and the structure factors were recalculated. There was little improvement in the R factors at this stage. Two further cycles of refinement using F_0 and $F_0 - F_c$ syntheses were attempted in trying to improve Taylor's structure but little was accomplished. The ℓ_0 and $\ell_0 - \ell_c$ maps that were produced in this Stage I of the refinement are not included in this dissertation.

The ρ_0 maps were of value in calculating the constant p for the correction of the atomic parameters in the ρ_0 - ρ_c maps. As shown previously, the electron density near the centre of an atom is given by

$$\rho(r) = \rho(0) e^{-pr^2}$$

where $\rho(0)$ is the electron density at the peak maximum and $\rho(r)$ is the electron density at a point r from the atomic centre. The values of p for each type of atom (Si, Al and O) were calculated from this relationship by taking the width at one-half the peak height as r and solving for $p = \frac{-\ln \rho(r) / \rho(0)}{r^2} = \frac{0.693}{r^2}$. The values so calculated showed rather a wide range; the averages of these values were,

$$\begin{aligned} \text{Si} &= 19.8 \text{ \AA}^{0-2} \\ \text{Al} &= 18.1 \text{ \AA}^{0-2} \\ \text{O} &= 16.5 \text{ \AA}^{0-2} \end{aligned}$$

It should be noted here that these values are substantially larger than the expected values ($p=5.0$, Lipson and Cochran, 1953) and a probable explanation is given at the end of this Chapter. The use of these values, however, gave fairly good results for the corrections in the atomic position on subsequent ρ_0 - ρ_c maps.

Near the end of Stage I (including the three cycles) an oversight on the part of the author was discovered. It was not until this stage that the modification of the sillimanite structure by Hey and Taylor (1931) was found. This point started Stage II of the refinement as it is referred to in later sections of the thesis. Using Hey and Taylor's parameters new structure factors were calculated and a very large drop in R was noted for the $hk0$ projection, but the

R factor for the $0kl$ projection increased slightly over that derived from the final attempt in Stage I. Thus it was felt that something could be gained by using both of these parameters together as described in the next section of this Chapter.

The thermal parameters of the atoms used in computing the structure factors were those found by Burnham and Buerger (1961) in their refinement of andalusite. It was felt that these parameters were likely to be close to the thermal parameters in sillimanite, due to the close relationship of these polymorphs. An isotropic temperature factor for all the atoms in the cell of 0.40 was used to calculate the structure factors using Hey and Taylor's parameters. A list of the variation of the temperature factors throughout the refinement is given in Table X.

(b) Syntheses Starting with Parameters of Hey and Taylor (1931) and of Stage I.

Following the first attempt at refinement from the initial F_o maps that were prepared from Taylor's (1928) parameters, $F_o - F_c$ syntheses were performed both on the model proposed by Hey and Taylor (1931) and on the new set of coordinates derived in Stage I. Those reflections which observed an appreciable amplitude but calculated very low were omitted from these syntheses since their signs would be meaningless. On the other hand, those reflections which observed zero but calculated an appreciable amplitude were used in these $F_o - F_c$ syntheses. This was felt to be justified because the high value to which they calculated would contribute appreciably to the difference maps. All computations for these stages and those following were performed on the I.B.M. "650" using the programmes provided by Dr. F. R. Ahmed.

TABLE IX
ATOMIC COORDINATES AND R FACTORS AT VARIOUS STAGES OF REFINEMENT

The coordinates refer to the original setting of Taylor (1928) but with the prototype atoms changed to those with the coordinates all positive. (In Table XIV the parameters of these prototype atoms are doubly underlined.)

Stage I Taylor (1928)			Stage II Refined III			Stage II Hey & Taylor (1931)			Stage III			Stage IV			Stage V			Stage VI			
x	y	z	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z	
Al _I	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Al _{II}	0.36	0.17	3/4	0.339 ₆	0.170 ₀	3/4	0.36	0.15	3/4	0.360 ₀	0.150 ₀	3/4	0.357 ₀	0.150 ₀	3/4	0.355 ₁	0.151 ₆	3/4	0.355 ₁	0.153 ₄	3/4
Si	0.32	0.15	1/4	0.330 ₀	0.163 ₀	1/4	0.36	0.15	1/4	0.361 ₁	0.177 ₄	1/4	0.351 ₀	0.167 ₀	1/4	0.349 ₈	0.162 ₇	1/4	0.349 ₀	0.161 ₀	1/4
O _a	0.11	0.12	1/4	0.138 ₂	0.074 ₄	1/4	0.15	0.07	1/4	0.172 ₅	0.074 ₄	1/4	0.152 ₂	0.083 ₅	1/4	0.150 ₂	0.081 ₅	1/4	0.145 ₅	0.087 ₅	1/4
O _b	0.10	0.16	3/4	0.126 ₈	0.153 ₄	3/4	0.15	0.07	3/4	0.138 ₂	0.074 ₄	3/4	0.138 ₂	0.074 ₄	3/4	0.138 ₀	0.074 ₅	3/4	0.140 ₄	0.069 ₅	3/4
O _c	0.08	0.46	1/4	0.113 ₄	0.432 ₅	1/4	0.03	0.47	1/4	0.033 ₄	0.493 ₁	1/4	0.020 ₀	0.495 ₇	1/4	0.024 ₀	0.500 ₀	1/4	0.024 ₀	0.500 ₀	1/4
O _d	0.35	0.32	0	0.368 ₆	0.285 ₀	0	0.39	0.28	0	0.368 ₆	0.285 ₀	0	0.377 ₀	0.269 ₅	0	0.372 ₅	0.273 ₅	0.0052	0.372 ₅	0.276 ₅	0.0060
R (hko)	54.8			50.8		34.1				36.3		23.0		20.7		18.9					
R (h0l)	47.3			40.7						26.8		16.5		15.0		12.8					
R (0kl)	43.3			26.0		31.9				29.1		23.0		15.7		12.9					

TABLE X
VARIATION OF TEMPERATURE FACTORS(B)
DURING THE REFINEMENT

Projection	Atom	Stage I		Stage II	Stage III	Stage IV	Stage V	Stage VI
		Burnham and Buerger (1961)	Hey and Taylor (1931)					
hk0	Si	0.264	0.40	1.00	1.20	1.30	1.40	1.25
	Al _I	0.280	0.40	1.00	1.10	1.15	1.10	1.07
	Al _{II}	0.250	0.40	0.60	1.00	1.05	1.20	1.07
	O _a	0.394	0.40	0.40	0.40	0.45	0.65	0.83
	O _b	0.394	0.40	0.60	0.60	0.55	0.62	0.73
	O _c	0.394	0.40	0.70	0.70	0.80	0.85	0.87
	O _d	0.394	0.40	0.60	0.70	0.75	0.85	0.92
h0l	Si	0.264	0.40	1.00	1.20	1.00	0.97	0.90
	Al _I	0.280	0.40	1.00	1.10	0.90	0.75	0.60
	Al _{II}	0.250	0.40	0.60	0.70	0.70	0.68	0.60
	O _a	0.394	0.40	0.40	0.40	0.45	0.45	0.40
	O _b	0.394	0.40	0.60	0.60	0.60	0.65	0.63
	O _c	0.394	0.40	0.70	0.70	0.70	0.80	0.95
	O _d	0.394	0.40	0.40	0.50	0.55	0.52	0.62
0kl	Si	0.264	0.40	0.50	0.70	0.65	0.60	0.52
	Al _I	0.280	0.40	0.50	0.50	0.48	0.45	0.38
	Al _{II}	0.250	0.40	0.60	0.70	0.60	0.45	0.40
	O _a	0.394	0.40	0.40	0.40	0.45	0.50	0.58
	O _b	0.394	0.40	0.60	0.60	0.55	0.55	0.53
	O _c	0.394	0.40	0.70	0.70	0.75	0.80	0.65
	O _d	0.394	0.40	0.50	0.50	0.55	0.55	0.65

Four $F_0 - F_c$ syntheses were calculated at this Stage II. Three syntheses were performed on the model of Stage I along the a, b and c axes, whereas only the projection along the c axis was computed from Hey and Taylor's model. In all four syntheses $\rho_0 - \rho_c$ values were computed at $1/60^{\text{th}}$ of the cell edges over an asymmetric unit in the cell. The $\rho_0 - \rho_c$ maps assuming the model in Stage I are shown in Figs. 29 (a,b,c) and the c-axis projection of $\rho_0 - \rho_c$ using Hey and Taylor's structure is shown in Fig. 30. In these and subsequent maps the assumed positions of the atoms that were used to produce the maps are indicated by filled circles and the newly derived positions are shown as open circles with smaller accompanying lettering.

All the $\rho_0 - \rho_c$ maps at this stage were found to have considerable relief, especially those assuming the model derived from Stage I. All the atoms except the Al_I at the origin were found to lie on strong density gradients. In the c-axis projection based on the model of Stage I (Fig. 29 (c)) two atoms, O_b and O_c , were found to lie in strongly negative regions with no neighbouring high regions to indicate possible shifts. The coordinates of these two atoms proved to be badly in error resulting in the very large values of the R factors for the three zones of reflection.

Using mainly the $\rho_0 - \rho_c$ maps of Hey and Taylor in conjunction with the other three projections of Stage II and the expected values of bond distances in the silicon and aluminum tetrahedra, shifts were made to all atoms except the aluminum I at the origin and O_d . Five of the atoms were shifted in the x/a direction and four in the y/b direction as shown by the open circles on these maps (Fig. 29).

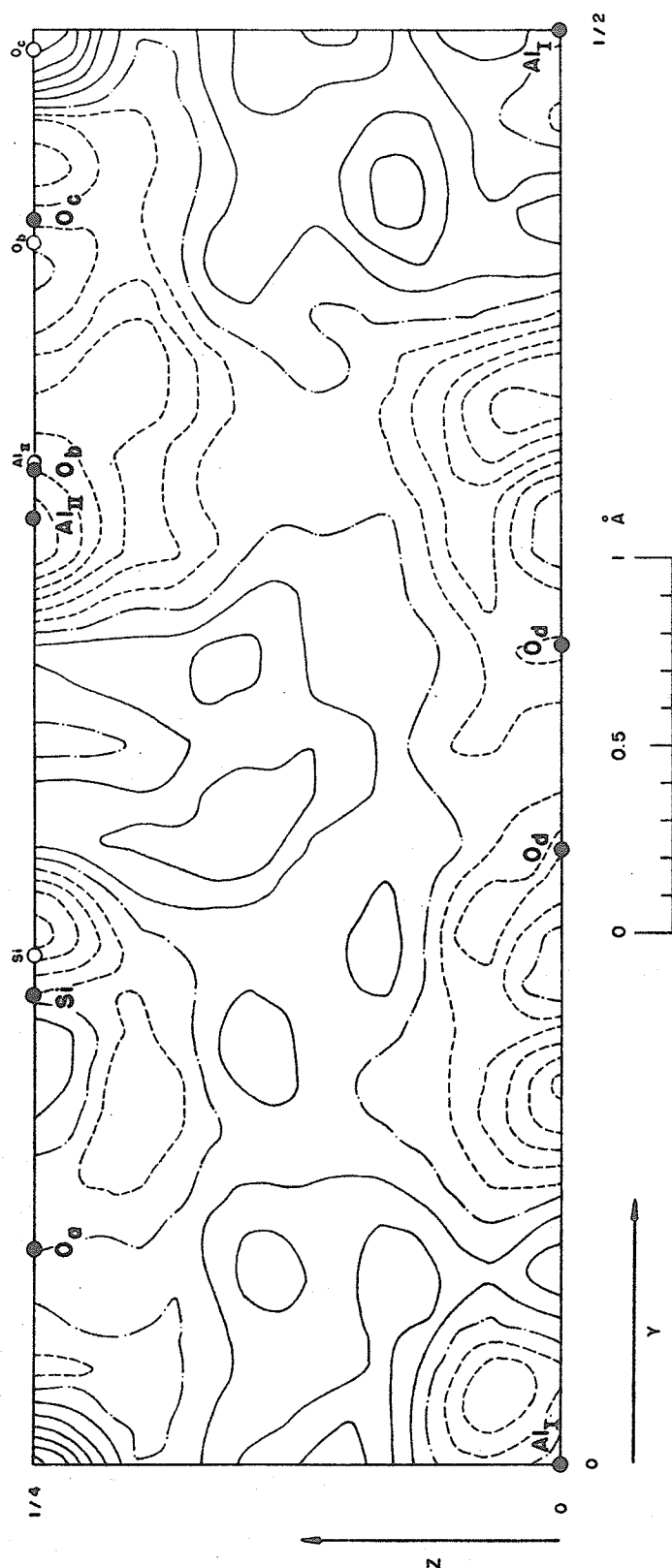


Fig. 29(a). $\rho_0 - \bar{\rho}$ projected along the a axis at Stage II of the refinement. The contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}$. Zero contours are indicated by chained lines; negative contours are shown as dashed lines. Filled circles represent the atomic positions used to produce the map, open circles are the newly derived atomic positions.

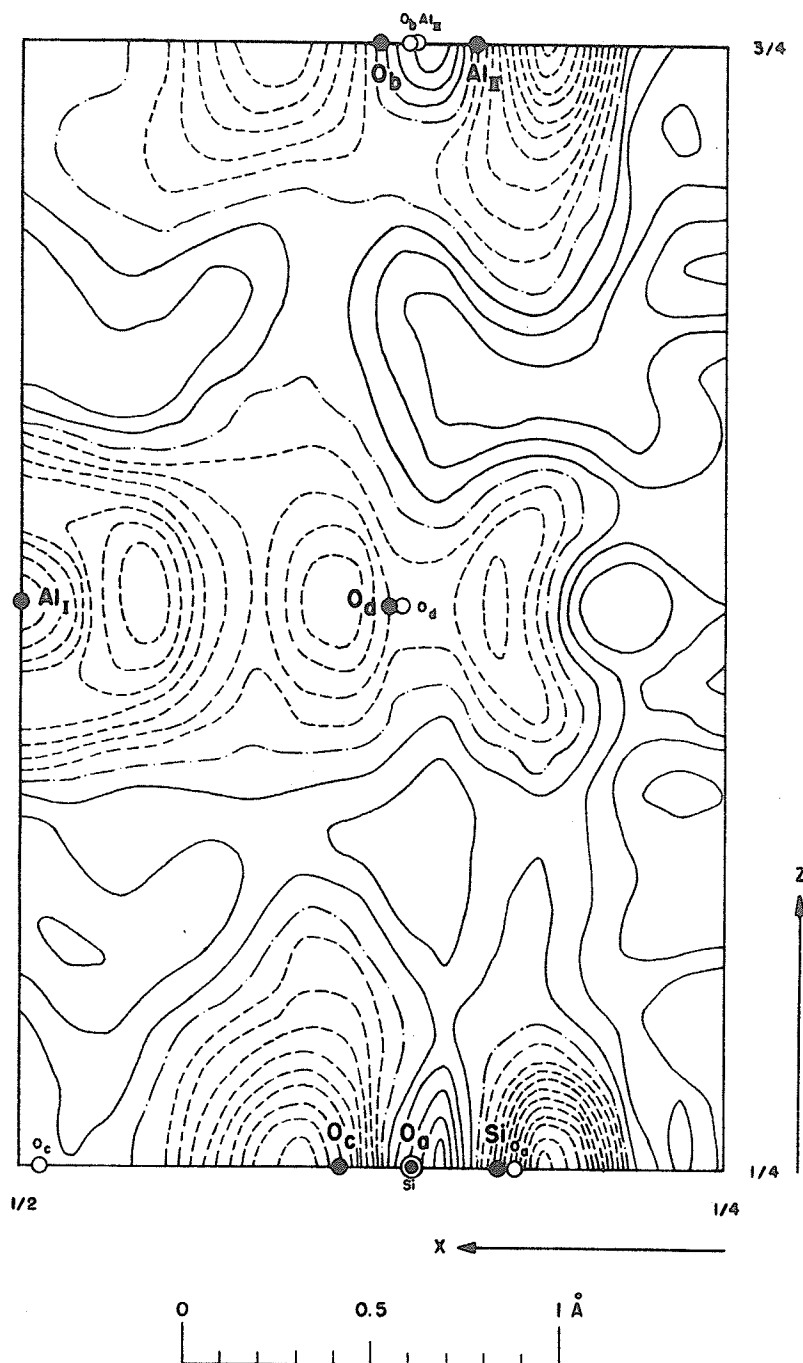


Fig. 29(b). $\rho_o - \rho_c$ projected along the b axis at Stage II of the refinement. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are chained lines; negative contours are shown as dashed lines. Filled circles represent the atomic positions used to produce the map, open circles are the newly derived atomic positions.

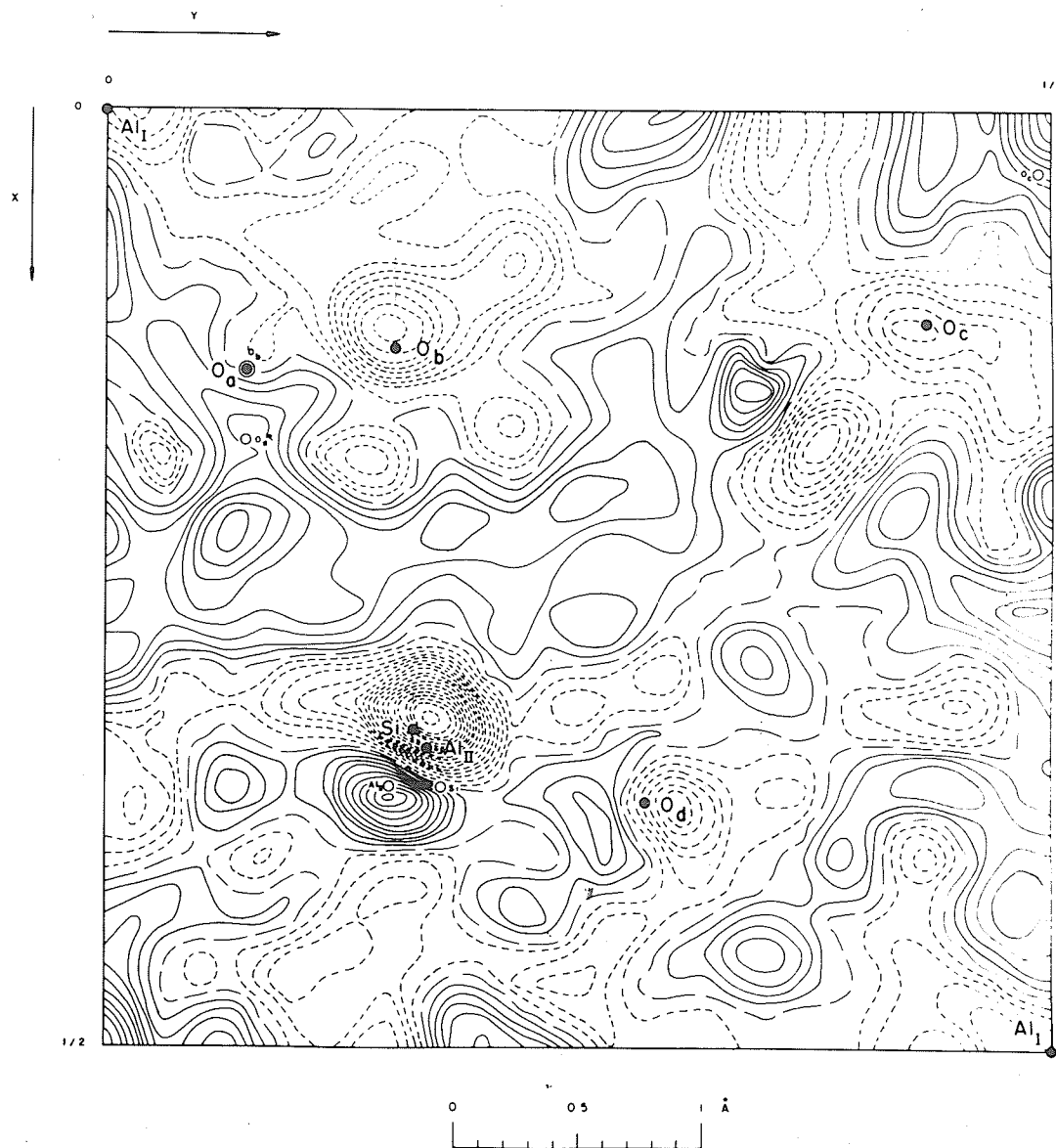


Fig. 29(c). $\rho_o - \rho_c$ projected along the c axis at Stage II of the refinement.² Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are shown as chained lines; negative contours as dashed lines. Filled circles represent the atomic positions used to produce the map, open circles are the newly derived atomic positions.

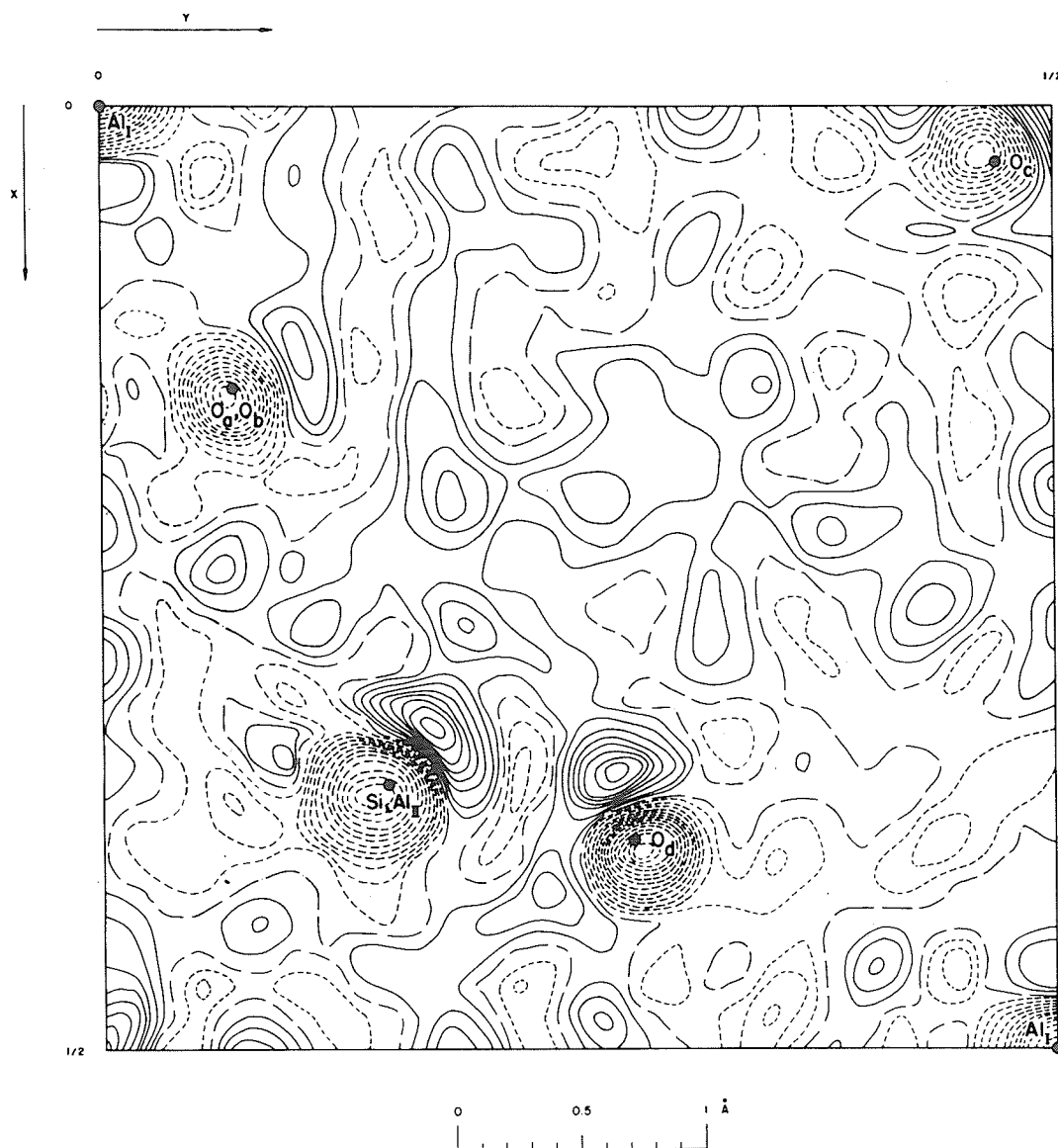


Fig. 30. $\rho_0 - \rho_c$ projected along the c axis at Stage II of the refinement. The atomic positions that are shown as closed circles are those of Hey and Taylor (1931). Contours are drawn at equal intervals of 2.0 e/Å with the zero contour as , chained lines and negative contours as dashed lines.

The shifts in the x/a direction for Al_{II} and O_b were derived mainly from the $h0l$ projection of $\rho_o - \rho_c$. The rest of this map was used mainly for temperature factor correction. The $0kl$ projection indicated by its relatively low value for the R factor of 25.9% that perhaps most of the y/b values of the atoms were satisfactory. Contradicting this conclusion, however, were the relatively high R factors of the two $hk0$ projections of Stage II. The reason for the relatively low R factor for $0kl$ was that O_c occupied a position that later proved to be nearly the true position of O_b . Thus the calculations would be influenced by this fact and it would seem as though only O_b was not in its correct position. The strong electron density high at $(0\frac{11}{2}1)$ on the $0kl$ projection indicated that an atom should be placed near there, and this presently proved to be the true position of O_c .

With all of this in mind, two large shifts were made to the values of y/b for O_b and O_c as well as a large shift in x/a for O_c . New positions and temperature factors were derived from all this information, and Stage III of the refinement was carried out.

With the new atomic parameters derived from Stage II the structure factors were recalculated and the values of the reliability (R) factors for the three zones were $hk0$, 36.3%; $h0l$, 26.8%; and $0kl$, 29.0%. The R factor for the $hk0$ projection was still larger than that obtained from Hey and Taylor's parameters (34.1%) which indicated that their positions were still better than the author's. The fact that the R factor for the $0kl$ zone increased slightly suggested that much of the cause was due to the y/b coordinate shifts. The substantial drop in R from the previous value of 40.7% for the $h0l$ zone suggested that a great improvement had been made in the x/a coordinates of the atoms.

$F_0 - F_c$ syntheses were then computed along the a, b, and c axes as before and again prepared by contouring at constant values of $\rho_0 - \rho_c$. These electron density maps of Stage III are reproduced in Fig. 31, a,b,c. They still showed considerable relief with most of the atoms still lying on rather strong gradients of electron density difference. However, the situation around the two atomic positions for O_b and O_c had improved considerably. These two atoms no longer lay in regions of large negative electron density but rather on gradients from which changes in position could be calculated.

All the changes that were made to the atomic positions in Stage II appeared to have been in the right direction as may be seen from the maps at Stage III. (Fig. 31). The definite improvement in the coordinates for O_b and O_c mainly accounts for the substantial decreases in the R factors for the three zones. However, the shifts appear to be excessive for some atoms such as O_a , Si and Al_{III} . With this in mind and again considering the projection of $\rho_0 - \rho_c$ for Hey and Taylor's structure, further revision of the atomic parameters was made. Up to this point in the refinement it was felt that the z/c coordinates could not be improved upon and so no change was made to them.

It was obvious from the overcorrecting in the atomic coordinates by the use of Cochran's formula that too large values for the changes in atomic position were being made. This was probably due to the overlapping of several of the atoms as well as some incorrect temperature factors. Thus the third revision of the atomic parameters was calculated by the formula but weighted arbitrarily so that the magnitude of the change was on the low side.

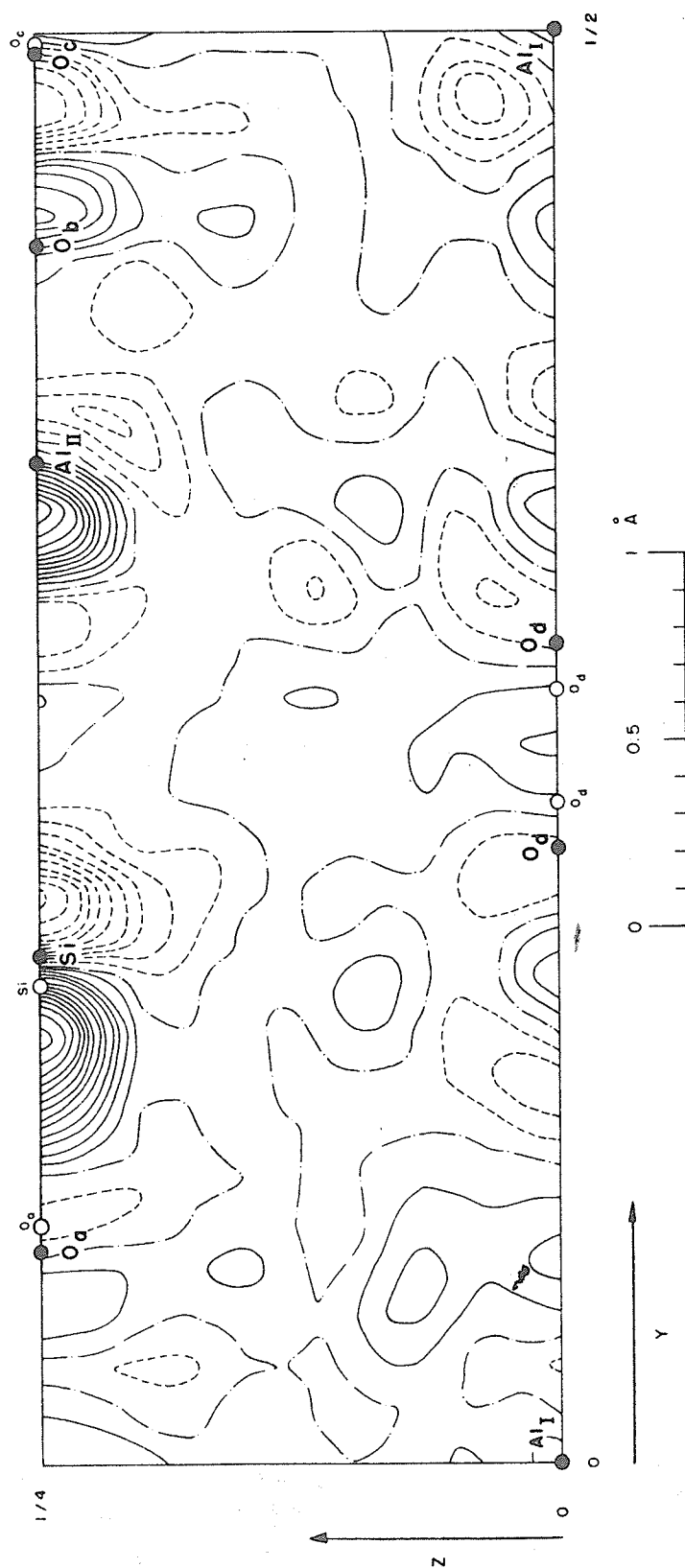


Fig. 31(a). ρ_{O-L_C} projected along the a axis at Stage III of the refinement. The contours are drawn at equal intervals of 2.0 e/Å. Zero contours are indicated by chained lines; negative contours are shown as dashed lines. Filled circles represent the atomic positions used to produce the map, open circles are the newly derived atomic positions.

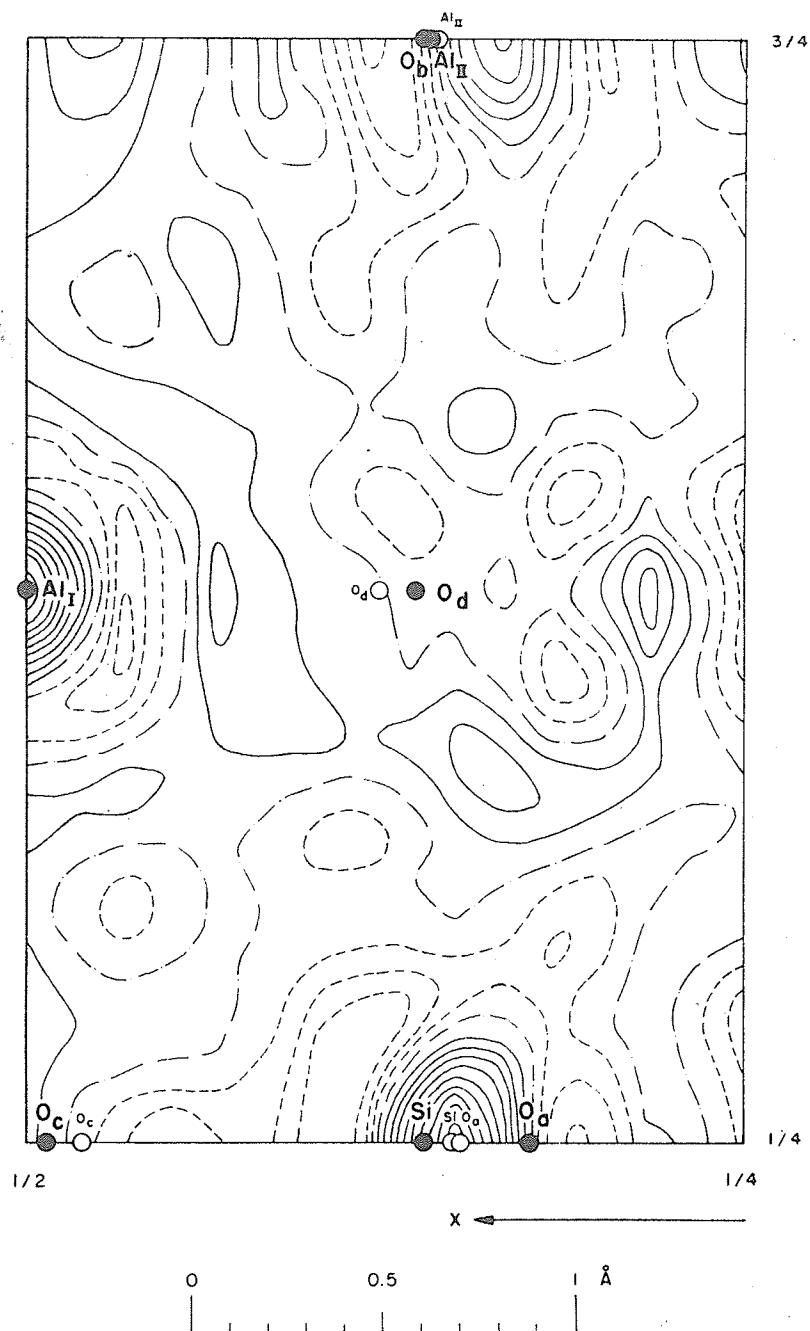


Fig. 31(b). $\rho_0 - \rho_c$ projected along the b axis at Stage III of the refinement. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are chained lines; negative contours are shown as dashed lines. Filled circles represent the atomic positions used to produce the map, open circles are the newly derived atomic positions.

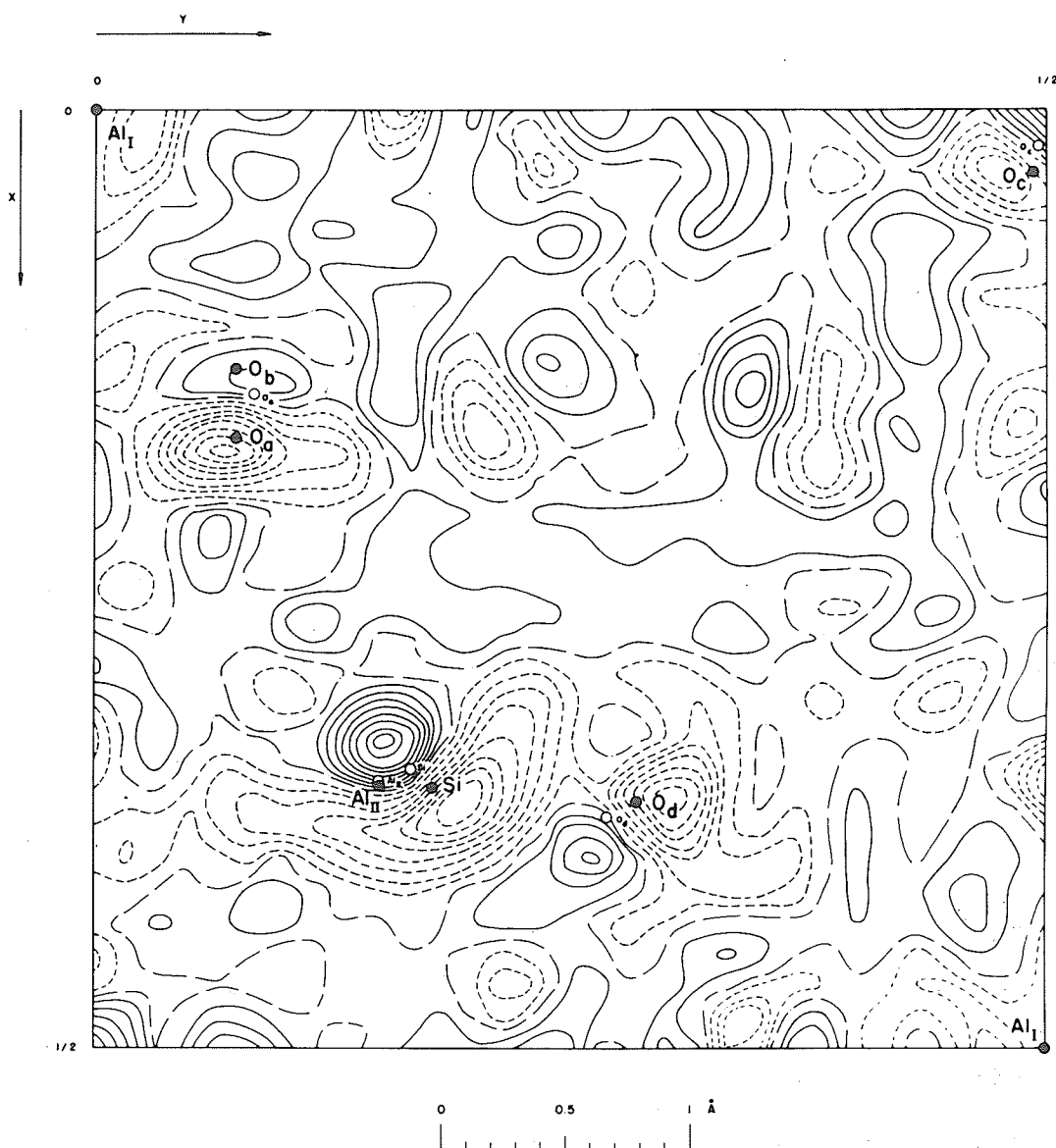


Fig. 31(c). $\ell_o - \ell_c$ projected along the c axis at Stage III of refinement₂. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are shown as chained lines; negative contours as dashed lines. Filled circles represent the atomic positions used to produce the map, open circles are the newly derived atomic positions.

F_o values were computed again from the revised set of coordinates and temperature factors derived at Stage III. At this stage of the refinement a very marked improvement in the whole structure was noted from the large decreases in the R factors. The computed values were 23.0%, 16.5% and 23.0% for the $hk0$, $h0l$ and $0kl$ reflections respectively.

$F_o - F_c$ maps were prepared along all three axes from the $F_o - F_c$ data of Stage IV. The same asymmetric units were used and the summation intervals were 1/60th of the cell edge lengths as before. The improvements in the R factor values were reflected in the marked decrease in relief of these latest maps. These maps are reproduced in Fig. 32 (a), (b), (c). The legend of representation of the atomic shifts in these maps is slightly different, but as before, closed circles represent the assumed atomic positions used to produce the maps and open circles represent the new positions that were taken directly from Stage IV of the refinement. In addition shaded circles represent the atomic positions that were derived from Stage V. This method was adopted since the author felt not much would be gained by reproducing the $F_o - F_c$ maps produced in Stage V. It is hoped that clarity is maintained in this process.

As may be seen from the maps in Fig. 32 of the Stage IV, only small shifts were made to the coordinates of the atoms. Moderate changes were made in the values of the temperature factors for some of the atoms, as shown in Table 10. Perhaps there are two significant changes that should be mentioned. It had been noticed up to this point of the refinement that persistent highs existed at the equivalent positions $(0, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$ on the $0kl$ projections. This suggested that O_c should be placed at this position. This change was made

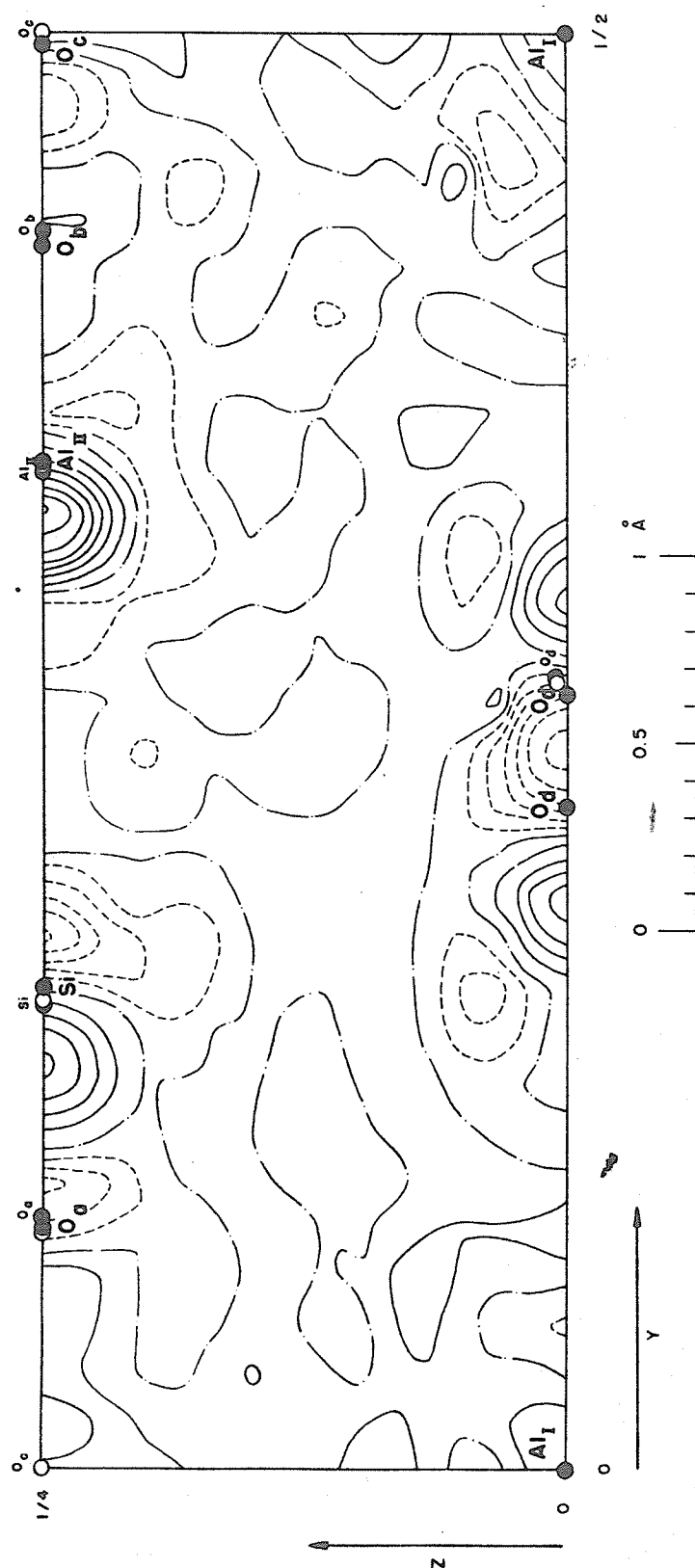


Fig. 32(a). $\rho_o - \rho_c$ projected along the a axis at Stage IV of the refinement. The contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are indicated by chained lines; negative contours are shown as dashed lines. Filled and open circles have the same meaning as on previous maps whereas shaded circles are the positions derived at Stage V.

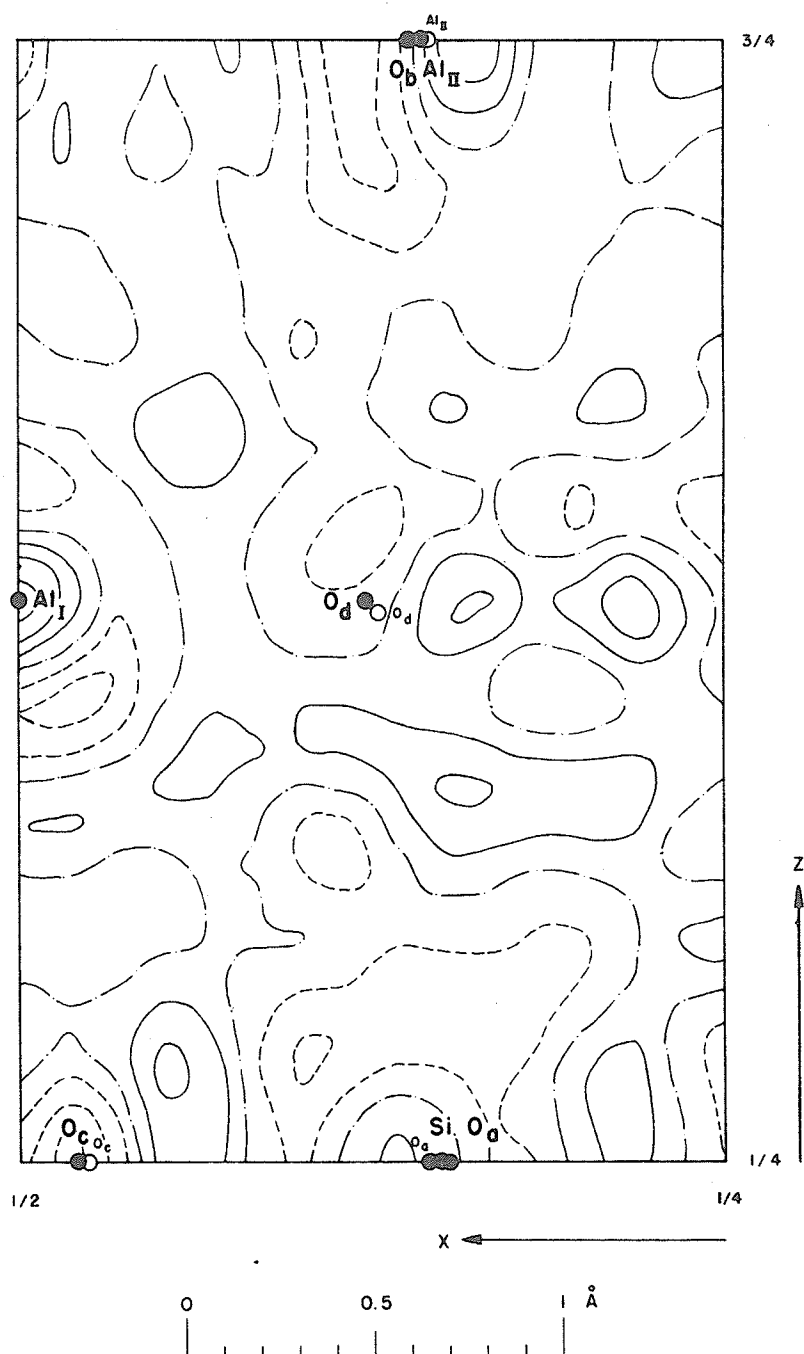


Fig. 32(b). $\rho_o - \rho_c$ projected along the b axis at Stage IV of the refinement. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are chained lines; negative contours are shown as dashed lines. Filled and open circles have the same meaning as on previous maps whereas shaded circles are the positions derived at Stage V.

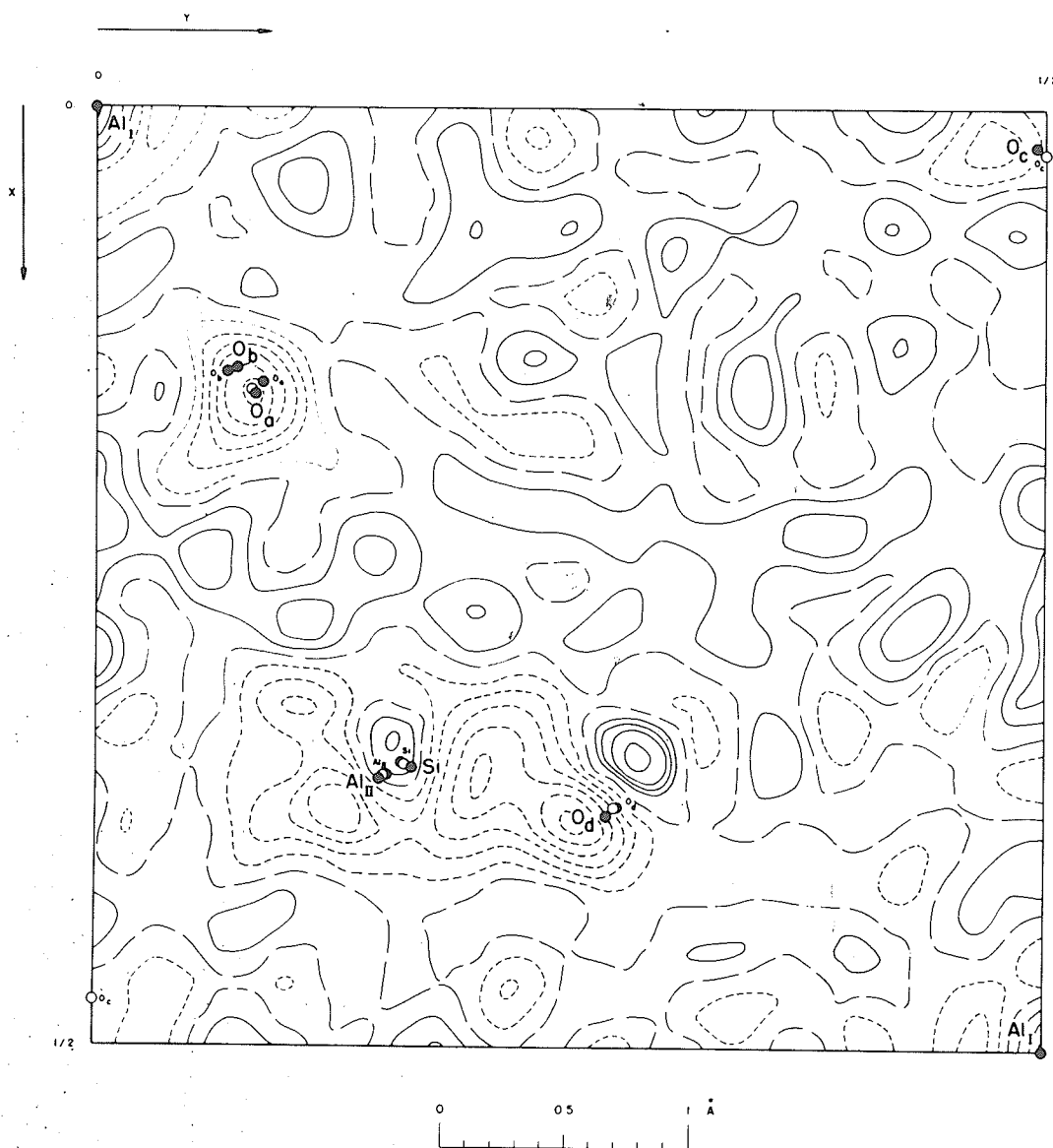


Fig. 32(c). $\rho_0 - \rho_c$ projected along the c axis at Stage IV of the refinement. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are shown as chained lines; negative contours as dashed lines. Filled and open circles have the same meaning as on previous maps whereas shaded circles are the positions derived at Stage V.

accordingly and an improvement in this region on the $\rho_o - \rho_c$ maps was noticed immediately in Stage V. Secondly, O_d was moved in the z/c direction on the basis of an indication to do so in the $\rho_o - \rho_c$ map of the $h0l$ projection Stage IV (Fig. 32 (b)). A second reason for doing so was that the bond distances would be improved, i.e., the $Si-O_d$ and $Al_{II}-O_d$ distances. The magnitudes of the revisions made to the atomic parameters in Stage IV were estimated on the basis of previous experience in earlier stages of the refinement.

The structure factors were recalculated using the parameters derived from Stage IV and the R factors were found to drop to 20.7%, 15.0% and 15.7% for the $hk0$, $h0l$ and $0kl$ reflections respectively. Quite substantial improvements were made to the y/b parameters accounting for the large drop (7.3%) in the $0kl$ zone's R factor. $F_o - F_c$ syntheses computed again for the three principal zones of reflection and the plotted values of $\rho_o - \rho_c$ so calculated were contoured. The maps of Stage V have not been included here since the change in them was not too significant. The relief had improved considerably and the changes in atomic positions derived from Stage IV were essentially correct. New and final atomic parameters (both positional and thermal) were derived from these maps at Stage V. The changes in position were becoming smaller and smaller as may be seen from Table IX so it was decided that Stage V would represent the final refinement.

The final atomic parameters were derived from the maps at Stage V of the refinement. The structure factors were recalculated on this basis and the final values of the R factors for the zones $hk0$, $h0l$ and $0kl$ were 18.9%, 12.8% and 12.9% respectively. A table of a comparison of the F_o and F_c values at this final stage of the

refinement is given at the end of this Section (Table XI). The values of F_0 for the three zones of reflection $hk0$, $h0l$ and $0kl$ have been multiplied by scale factors in order to place them on an absolute scale and it is these KF_0 values that are listed in Table XI. The values of these three scale factors are 0.9791, 1.0194 and 0.9609 respectively.

Both $\rho_0 - \rho_c$ and ρ_c maps were prepared for the three zones over the same asymmetric units, using the same summation intervals as before. These maps are reproduced in Figures 33, a,b,c and 34, a,b,c, respectively. The final projections of $\rho_0 - \rho_c$ show a much improved relief. The electron density gradients near the atomic centres are very low (compare with Fig. 29), which indicates that the refinement by 2-dimensional methods is very nearly complete. Definite shifts are indicated for some of the atoms, namely Si and Al_{III} in the $0kl$ projection (in the y/b direction). However, from past experience these changes would be very small, so it was felt that they were not significant. Some changes in thermal parameters were also indicated but not made. Since the signs of all but four of the observed structure factors had been determined at Stage VI no further changes in atomic parameters would significantly change the ρ_0 maps and so the refinement was terminated. The final atomic parameters and temperature factors are listed in Tables IX and X respectively. It is of interest to note that there is a suggestion of anisotropic thermal vibration for both O_c and O_d which may be seen in the final $hk0$ projection of $\rho_0 - \rho_c$ (Fig. 33 (c)). However, a programme to correct for anisotropy was not available so no account was taken of this effect. This anisotropy is characterized by the position of the atom occupying a region of negative electron density

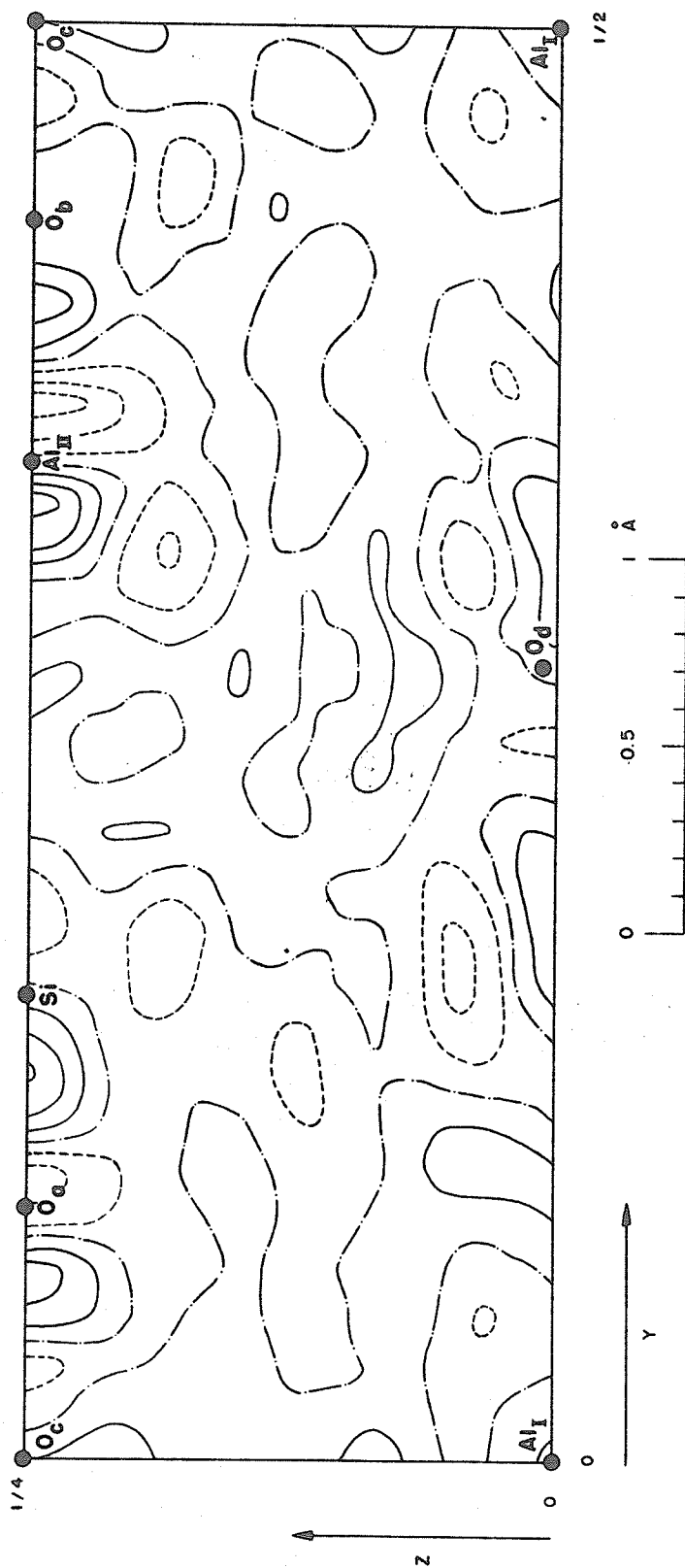


Fig. 33(a). $\rho_0 - \rho_c$ projected along the a axis at Stage VI of the refinement. The contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are indicated by chained lines; negative contours are shown as dashed lines. Filled circles represent the final atomic positions as determined in this refinement.

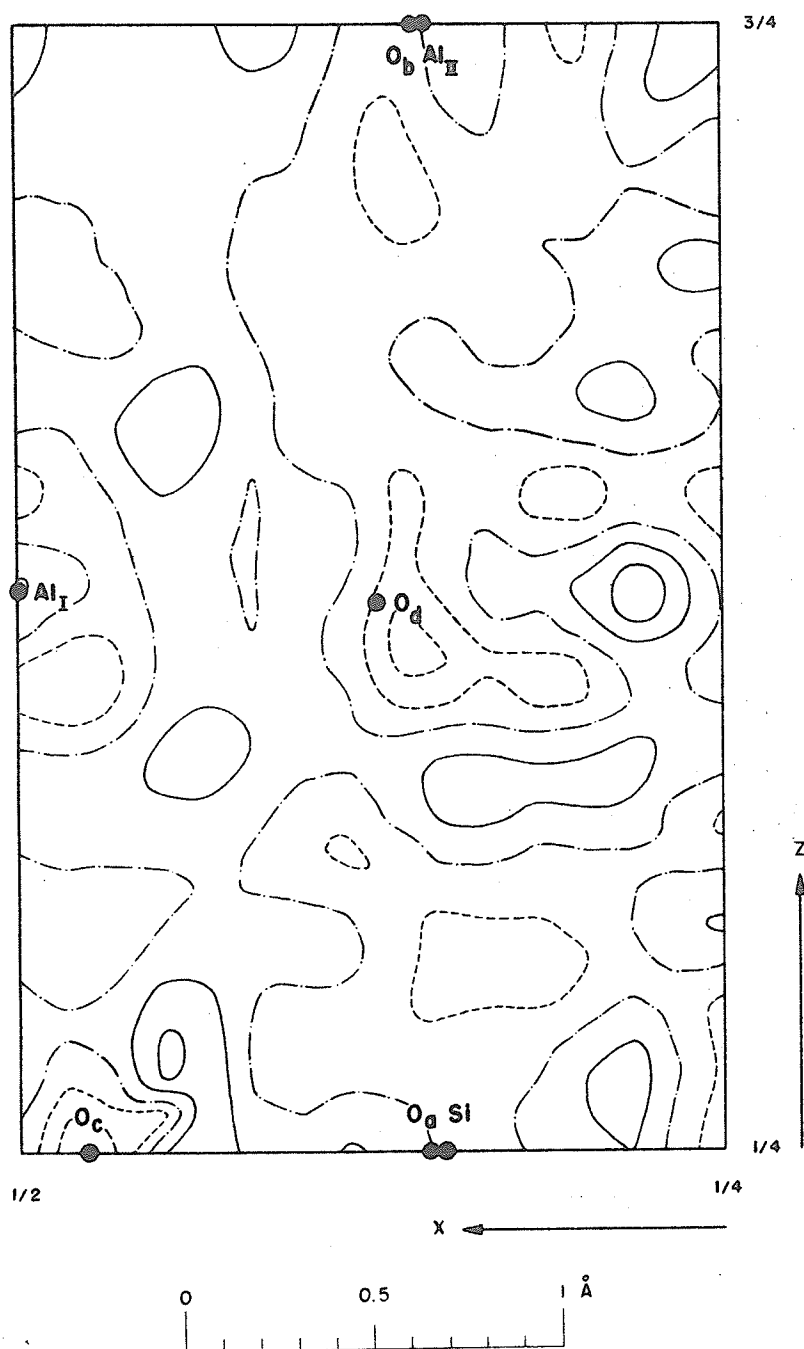


Fig. 33(b). $\rho_o - \rho_c$ projected along the b axis at Stage VI of the refinement. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are chained lines; negative contours are shown as dashed lines. Filled circles represent the final atomic positions as determined in this refinement.

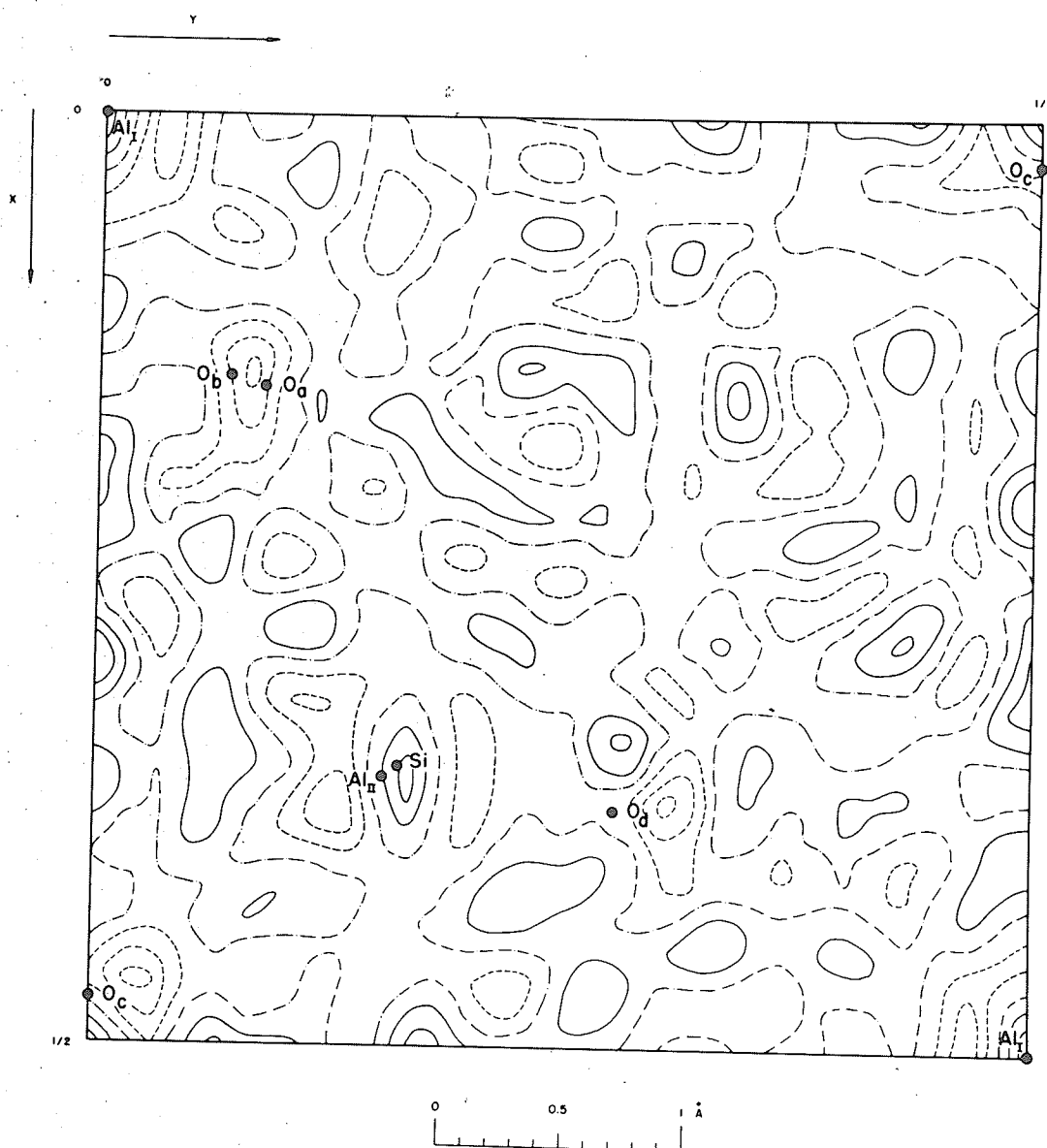


Fig. 33(c). $\rho_o - \rho_c$ projected along the c axis at Stage VI of refinement. Contours are drawn at equal intervals of $2.0 \text{ e}/\text{\AA}^2$. Zero contours are shown as chained lines; negative contours as dashed lines. Filled circles represent the final atomic positions as determined in this refinement.

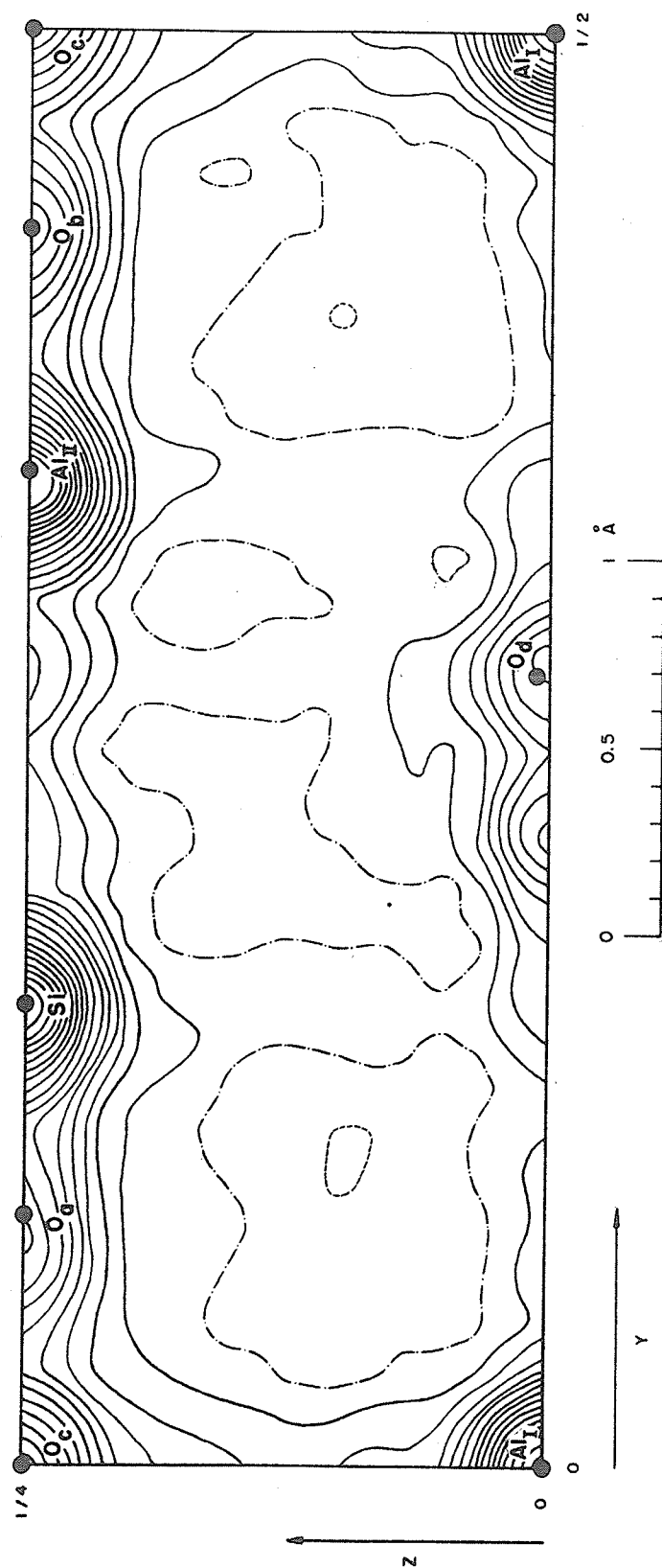


Fig. 34(a). $-\rho_0$ projected along the a axis at Stage VI of the refinement. The contours are drawn at equal intervals of $5.0 \text{ e}/\text{\AA}^2$. Zero contours are indicated by chained lines; negative contours are shown as dashed lines.

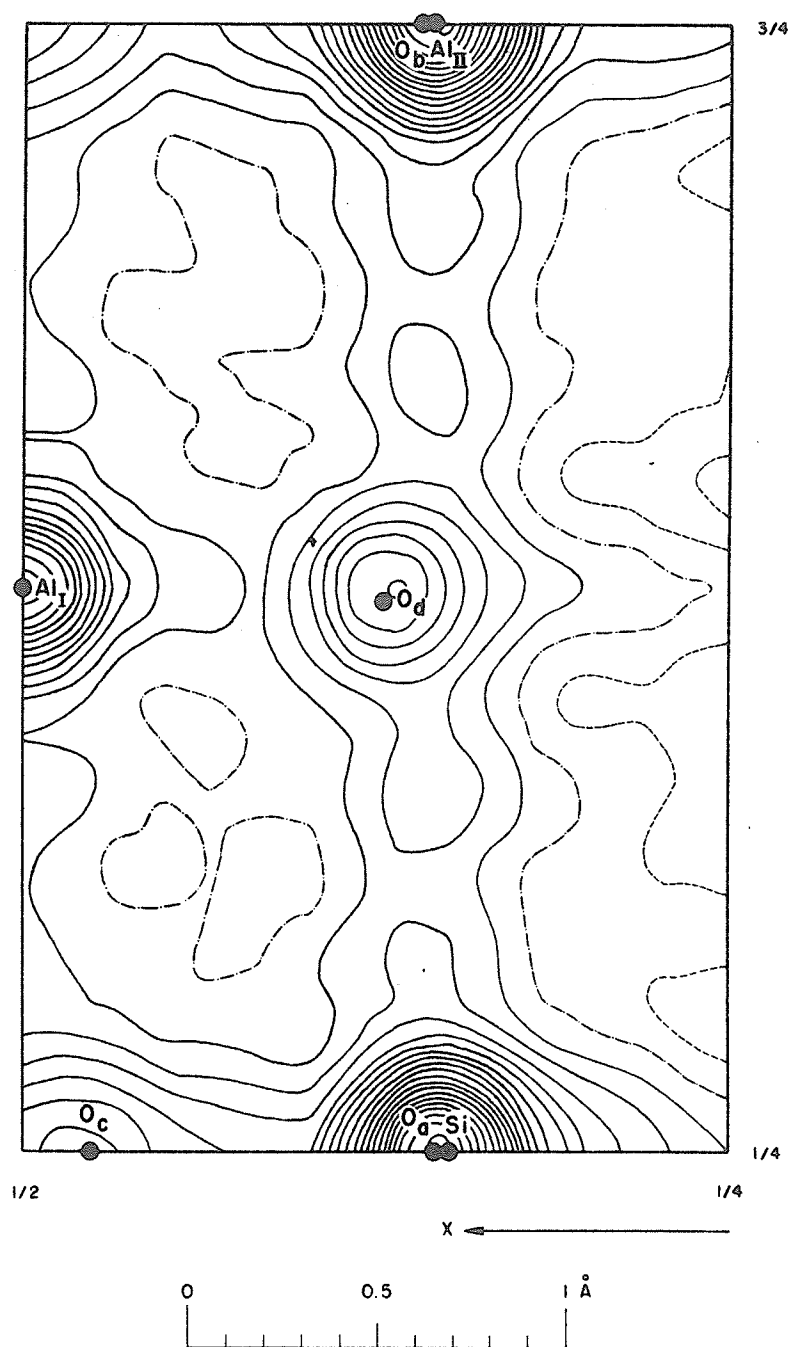


Fig. 34(b). ρ_0 projected along the b axis at Stage VI of the refinement. Contours are drawn at equal intervals of $5.0 \text{ e}/\text{\AA}^2$. Zero contours are chained lines; negative contours are shown as dashed lines.

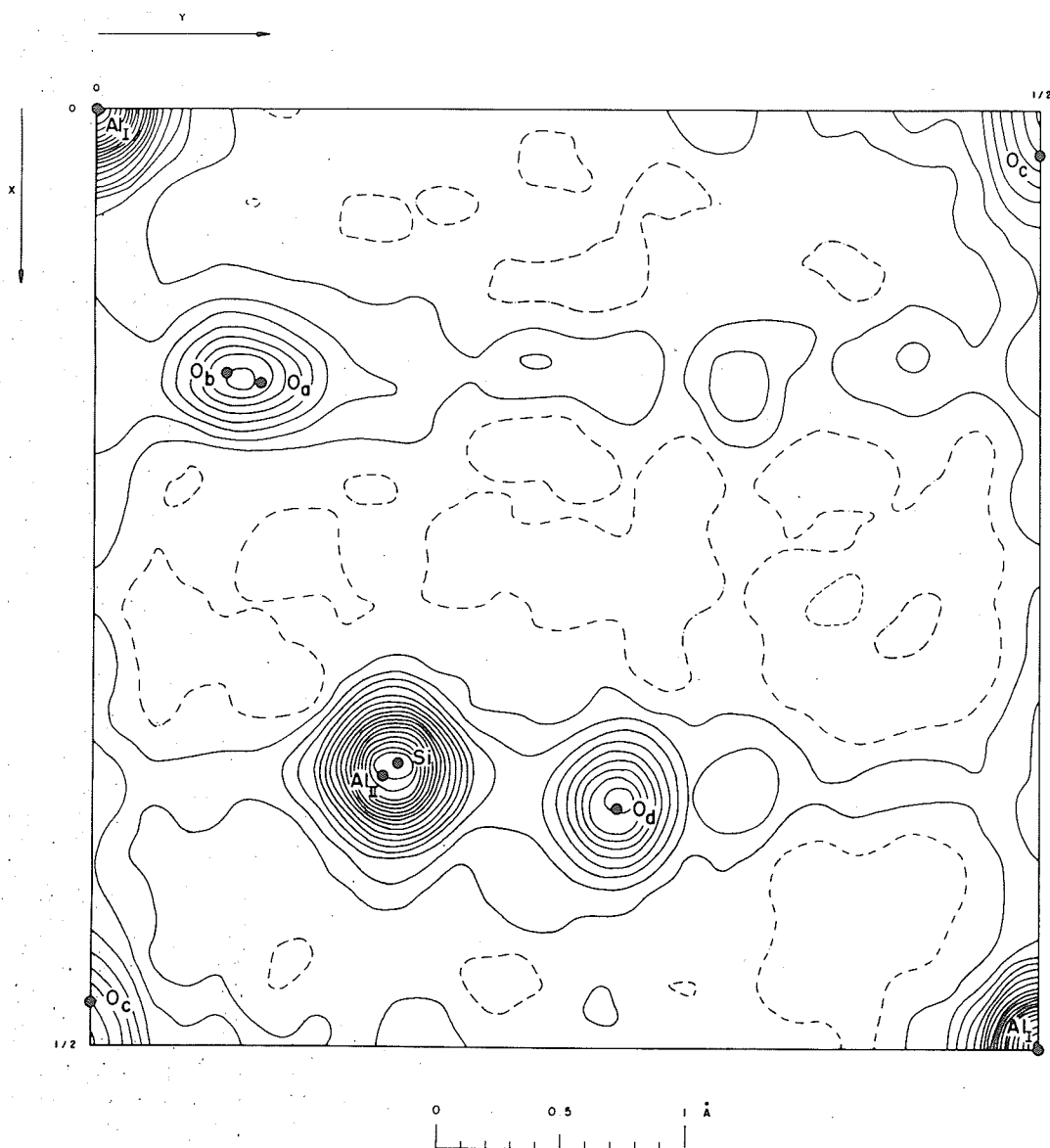


Fig. 34(c). ℓ_0 projected along the c axis at Stage VI of the refinement. Contours are drawn at equal intervals of $5.0 \text{ e}/\text{\AA}^2$. Zero contours are shown as chained lines; negative contours as dashed lines.

accompanied by two adjacent positive peaks on either side.

An error in computing was discovered after the final ρ_o maps had been prepared. It was found that the different multiplicities of the axial reflections had not been allowed for in the computation of the Fourier series. Thus the true values of the electron density were not computed and are not shown on any of the aforementioned maps. This error must be less on the difference Fourier projections than on the electron density projections for the following reason: On the former the corrections that would be necessary would be a function of certain $(F_o - F_c)$ values which are small numbers, whereas in the latter the corrections must be a function of certain F_o values, some of which may be large.

An F_o synthesis was then computed for the $0kl$ reflections, taking account of the correct multiplicities of the axial reflections, since this projection showed the greatest resolution of the atoms. This ρ_o map is shown in Fig. 35. It can be seen by comparison with Fig. 34 (a) that the shapes and positions of the peaks have not changed appreciably, but the peak heights have decreased, and much of the negative regions of Fig. 34 (a) has become positive. Since the positions and shapes of the peaks did not change in this projection, F_o syntheses were not computed on the $hk0$ or $h0l$ reflections. Also it can be seen that the atoms are not well resolved in either of these projections.

A Fourier synthesis with $F_o - F_c$ values as amplitudes was also made using the $0kl$ reflections, taking account of the correct multiplicities of the axial reflections. A comparison of the values of $\rho_o - \rho_c$ from this summation with the values of $\rho_o - \rho_c$ that were used

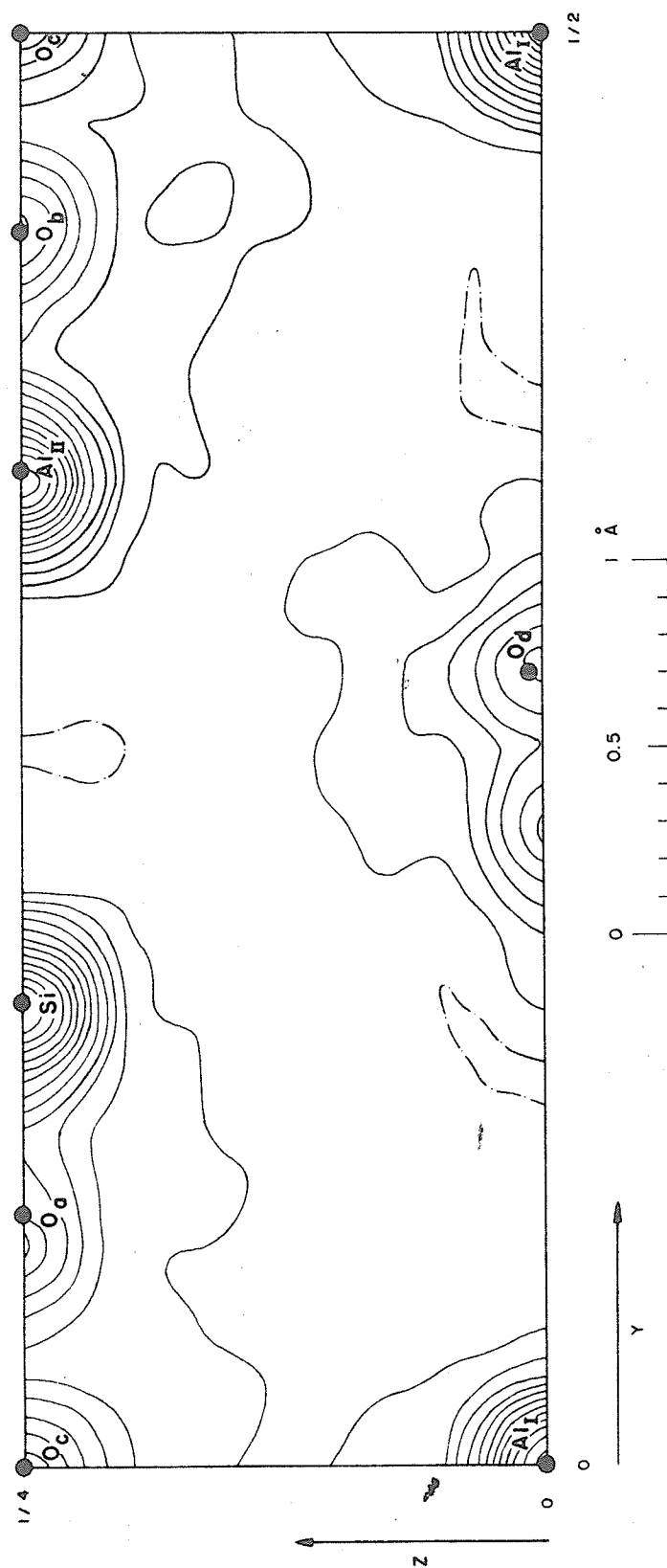


Fig. 35. ρ_0 projected along the a axis at Stage VI of the refinement taking account of the correct multiplicities of the axial reflections. Contours are drawn at equal intervals of $5.0 \text{ e}/\text{\AA}$. (Compare with electron density map shown in Fig. 34(a).)

OBSERVED AND CALCULATED STRUCTURE FACTORS

h k 0 PROJECTION

Group (1) $h + k = 2n$

h	k	l	$\sin^2 \Theta_{hkl}$	KF * o	F c
0	2	0	.0086	13.0	13.8
0	4	0	.0344	21.5	19.4
0	6	0	.0773	44.5	47.1
0	8	0	.1375	16.4	15.8
0	10	0	.2149	0	-0.8
0	12	0	.3094	29.9	23.5
0	14	0	.4211	20.4	16.9
0	16	0	.5500	0	-3.5
0	18	0	.6961	15.0	5.9
0	20	0	.8594	0	0.4
1	1	0	.0044	unobserved	24.1
1	3	0	.0216	39.0	41.3
1	5	0	.0560	8.2	7.7
1	7	0	.1075	23.6	-28.1
1	9	0	.1763	33.4	27.0
1	11	0	.2622	0	2.8
1	13	0	.3654	0	3.0
1	15	0	.4857	0	2.6
2	0	0	.0090	26.7	28.6
2	2	0	.0176	54.1	61.3
2	4	0	.0433	51.3	57.7
2	6	0	.0863	19.6	24.1
2	8	0	.1465	23.7	24.2

* All values of F_o were multiplied by 0.9791 to give the values listed in this table.

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
2	10	0	.2238	22.7	19.4
2	12	0	.3184	4.0	6.0
2	14	0	.4301	0	5.4
2	16	0	.5590	9.1	6.1
2	18	0	.7051	0	3.0
3	1	0	.0223	9.8	10.8
3	3	0	.0395	27.6	-31.7
3	5	0	.0739	25.7	27.7
3	7	0	.1254	52.3	59.4
3	9	0	.1942	20.5	-17.8
3	11	0	.2801	6.6	4.1
3	13	0	.3833	9.4	2.8
3	15	0	.5036	0	-1.8
3	17	0	.6411	0	-0.9
3	19	0	.7958	10.2	3.4
4	0	0	.0358	57.2	-72.4
4	2	0	.0444	68.3	74.5
4	4	0	.0702	45.4	52.7
4	6	0	.1132	14.1	18.2
4	8	0	.1733	21.3	23.4
4	10	0	.2507	30.4	24.0
4	12	0	.3452	0	-0.4
4	14	0	.4570	0	-2.4
4	16	0	.5859	19.4	10.7
5	1	0	.0581	10.5	11.2
5	3	0	.0753	17.9	19.0

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
5	5	0	.1097	9.1	7.8
5	7	0	.1613	20.7	21.3
5	9	0	.2300	0	0.5
5	11	0	.3160	8.4	7.4
5	13	0	.4191	0	-1.1
5	15	0	.5394	5.4	2.2
6	0	0	.0806	60.0	80.3
6	2	0	.0892	17.3	19.2
6	4	0	.1150	0	1.0
6	6	0	.1580	34.5	31.5
6	8	0	.2181	8.1	8.9
6	10	0	.2955	0	1.2
6	12	0	.3900	19.8	15.1
6	14	0	.5017	11.6	7.9
6	16	0	.6307	0	-0.1
6	18	0	.7768	7.0	2.4
7	1	0	.1119	8.8	11.0
7	3	0	.1291	40.0	42.8
7	5	0	.1634	0	2.5
7	7	0	.2150	22.0	-24.7
7	9	0	.2838	29.6	22.5
7	11	0	.3697	0	3.9
7	13	0	.4728	0	3.1
7	15	0	.5932	7.4	3.8

h	k	l	$\sin^2 \theta_{hkl}$	F_o	F_c
8	0	0	.1433	50.6	52.7
8	2	0	.1519	6.8	5.4
8	4	0	.1777	10.2	13.8
8	6	0	.2207	9.2	9.0
8	8	0	.2808	6.1	7.6
8	10	0	.3582	0	3.6
8	12	0	.4527	9.2	7.1
8	14	0	.5644	10.1	8.6
8	16	0	.6934	0	-1.1
8	18	0	.8395	7.8	3.2
9	1	0	.1835	15.5	17.2
9	3	0	.2007	0	-3.9
9	5	0	.2351	16.9	17.1
9	7	0	.2867	10.5	9.7
9	9	0	.3554	0	3.8
9	11	0	.4414	0	-0.7
9	13	0	.5445	11.1	6.0
9	15	0	.6648	0	-0.6
10	0	0	.2239	19.5	-20.4
10	2	0	.2325	17.4	14.4
10	4	0	.2583	27.7	22.9
10	6	0	.3013	4.8	1.5
10	8	0	.3614	11.7	9.8
10	10	0	.4388	17.2	9.9
10	12	0	.5333	0	-3.8
10	14	0	.6450	0	-1.2
10	16	0	.7740	9.4	4.1

h	k	l	$\sin^2 \theta_{hkl}$	F_o	F_c
11	1	0	.2731	6.5	6.7
11	3	0	.2903	0	-0.1
11	5	0	.3247	10.2	9.2
11	7	0	.3762	25.5	21.0
11	9	0	.4450	0	-2.8
11	11	0	.5309	6.9	3.7
11	13	0	.6341	0	0.2
12	0	0	.3224	0	-0.9
12	2	0	.3310	11.0	9.8
12	4	0	.3568	0	-0.9
12	6	0	.3998	16.1	9.7
12	8	0	.4600	0	2.7
12	10	0	.5373	0	1.7
12	12	0	.6318	0	3.2
13	1	0	.3806	0	4.4
13	3	0	.3978	21.1	15.6
13	5	0	.4321	0	-1.5
13	7	0	.4837	0	-0.6
13	9	0	.5525	0	4.9
13	11	0	.6384	0	6.2
13	13	0	.7415	0	0.1
13	15	0	.8619	9.0	3.3
14	0	0	.4389	23.6	16.5
14	2	0	.4475	0	1.9
14	4	0	.4733	0	-3.1

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
14	6	0	.5162	0	1.8
14	8	0	.5764	0	-1.1
14	10	0	.6537	0	-1.2
14	12	0	.7483	7.4	4.3
15	1	0	.5060	0	7.3
15	3	0	.5232	0	4.2
15	5	0	.5575	0	4.4
15	7	0	.6091	0	-2.3
15	9	0	.6779	6.4	4.9
15	11	0	.7638	0	1.2
15	13	0	.8669	0	3.8
16	0	0	.5732	0	0.6
16	2	0	.5818	0	-1.4
16	4	0	.6076	9.5	5.9
16	6	0	.6506	0	-2.3
16	8	0	.7107	0	1.6
16	10	0	.7881	0	1.4
16	12	0	.8826	0	-1.8
17	1	0	.6493	0	2.8
17	3	0	.6665	0	-1.0
17	5	0	.7008	8.7	6.8
17	7	0	.7524	9.7	5.8
18	0	0	.7255	0	-4.7
18	2	0	.7341	0	0
18	4	0	.7599	0	1.6

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
19	1	0	.8105	0	1.1
19	3	0	.8277	0	3.7

Group (2) $h + k = 2n + 1$

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
1	2	0	.0108	61.3	-76.8
1	4	0	.0366	0	-2.8
1	6	0	.0796	20.4	22.7
1	8	0	.1397	29.7	-28.3
1	10	0	.2171	21.9	21.1
1	12	0	.3116	0	3.9
1	14	0	.4234	0	-5.2
1	16	0	.5523	0	-3.1
2	1	0	.0111	64.0	87.1
2	3	0	.0283	55.1	-59.8
2	5	0	.0627	41.6	-46.9
2	7	0	.1142	17.8	19.6
2	9	0	.1830	23.3	22.7
2	11	0	.2689	14.3	-8.0
2	13	0	.3721	0	-1.3
2	15	0	.4924	8.7	5.3
2	17	0	.6299	11.5	-8.2
3	2	0	.0287	23.0	-26.1
3	4	0	.0545	6.2	-8.3

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
3	6	0	.0975	13.7	13.8
3	8	0	.1577	12.4	-14.7
3	10	0	.2350	12.8	12.4
3	12	0	.3296	0	-0.2
3	14	0	.4413	0	-0.8
3	16	0	.5702	0	-2.3
3	18	0	.7163	0	0.6
4	1	0	.0380	19.0	-23.2
4	3	0	.0552	4.2	8.0
4	5	0	.0895	24.7	27.4
4	7	0	.1411	11.8	-12.4
4	9	0	.2099	6.9	-9.8
4	11	0	.2958	5.5	5.6
4	13	0	.3989	0	-0.9
4	15	0	.5193	0	-1.2
4	17	0	.6568	0	2.6
5	2	0	.0646	45.2	61.2
5	4	0	.0904	7.0	-5.8
5	6	0	.1333	15.8	-18.2
5	8	0	.1935	29.5	24.8
5	10	0	.2708	20.8	-20.3
5	12	0	.3654	0	-4.4
5	14	0	.4771	7.5	5.7
5	16	0	.6060	0	3.3
6	1	0	.0828	33.5	-37.2
6	3	0	.0999	18.8	24.4
6	5	0	.1343	17.4	18.9

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
6	7	0	.1859	8.4	-7.3
6	9	0	.2546	13.7	-12.6
6	11	0	.3406	0	1.9
6	13	0	.4437	0	1.8
6	15	0	.5640	6.6	-3.6
6	17	0	.7016	6.8	5.7
7	2	0	.1183	7.5	-10.9
7	4	0	.1441	9.0	10.7
7	6	0	.1871	0	-3.8
7	8	0	.2472	0	1.6
7	10	0	.3246	0	-2.8
7	12	0	.4191	0	3.6
7	14	0	.5308	0	-3.4
8	1	0	.1455	18.1	20.8
8	3	0	.1626	3.8	-6.5
8	5	0	.1970	24.7	-25.2
8	7	0	.2486	13.3	11.8
8	9	0	.3173	9.7	11.1
8	11	0	.4033	6.8	-5.0
8	13	0	.5064	0	0.7
8	15	0	.6267	0	1.2
8	17	0	.7643	0	-3.3
9	2	0	.1900	22.5	-26.0
9	4	0	.2158	0	-0.3
9	6	0	.2587	11.7	9.4

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
9	8	0	.3189	15.0	-12.0
9	10	0	.3962	14.7	13.1
9	12	0	.4908	0	2.1
9	14	0	.6025	0	-2.8
10	1	0	.2261	6.2	9.2
10	3	0	.2433	10.2	-11.0
10	5	0	.2776	0	0.8
10	7	0	.3292	0	-1.6
10	9	0	.3980	0	3.5
10	11	0	.4839	0	2.1
10	13	0	.5870	0	-1.8
10	15	0	.7074	0	1.9
11	2	0	.2795	14.8	14.9
11	4	0	.3053	3.2	-7.0
11	6	0	.3483	0	0.7
11	8	0	.4085	0	1.1
11	10	0	.4858	0	-1.3
11	12	0	.5803	4.3	-4.1
11	14	0	.6921	6.9	4.1
12	1	0	.3246	9.0	-8.3
12	3	0	.3418	0	5.9
12	5	0	.3762	16.4	12.7
12	7	0	.4277	6.8	-5.9

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
12	9	0	.4965	0	-7.3
12	11	0	.5824	0	1.7
12	13	0	.6856	0	-0.2
13	2	0	.3870	0	6.6
13	4	0	.4128	0	4.4
13	6	0	.4558	0	-3.8
13	8	0	.5159	0	4.0
13	10	0	.5933	0	-6.4
13	12	0	.6878	0	-0.1
13	14	0	.7996	0	0.2
14	1	0	.4410	0	-2.2
14	3	0	.4582	0	4.6
14	5	0	.4926	0	-5.3
14	7	0	.5442	0	3.4
14	9	0	.6129	0	0.6
14	11	0	.6989	0	-2.3
15	2	0	.5124	11.9	-9.1
15	4	0	.5382	0	2.0
15	6	0	.5812	0	-0.5
15	8	0	.6413	0	0
15	10	0	.7187	0	1.8
15	12	0	.8132	0	2.8
15	14	0	.9249	6.1	-2.8
16	1	0	.5754	0	1.9
16	3	0	.5926	0	-4.0

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
16	5	0	.6270	6.6	-4.7
16	7	0	.6785	0	1.8
16	9	0	.7473	5.8	3.5
16	11	0	.8332	0	0.3
17	2	0	.6557	0	-0.1
17	4	0	.6815	0	-3.2
17	6	0	.7245	0	1.4
17	8	0	.7846	0	-1.2
18	1	0	.7276	0	1.2
18	3	0	.7448	0	-1.2
18	5	0	.7792	5.5	4.0
19	2	0	.8169	7.0	4.2
19	4	0	.8427	0	0.2

OBSERVED AND CALCULATED STRUCTURE FACTORS

h 0 l PROJECTION

Group (1) $h + l = 2n$, $h = 2n$, $l = 2n$

h	k	l	$\sin^2 \Theta_{hkl}$	KF_o^*	F_o
0	0	2	.0152	56.1	-61.0
0	0	4	.0608	105.6	148.0
0	0	6	.1369	33.6	-26.7
0	0	8	.2433	62.0	59.9
0	0	10	.3802	6.9	-10.8
0	0	12	.5475	31.9	26.0
0	0	14	.7452	0	-4.5
2	0	0	.0090	31.2	28.6
2	0	2	.0242	40.7	42.4
2	0	4	.0698	16.5	15.9
2	0	6	.1458	25.7	24.7
2	0	8	.2523	0	6.3
2	0	10	.3891	9.9	9.7
2	0	12	.5564	0	2.4
2	0	14	.7541	0	4.1
4	0	0	.0358	70.1	-74.2
4	0	2	.0510	54.5	64.6
4	0	4	.0967	46.6	-44.8
4	0	6	.1727	41.4	37.0
4	0	8	.2791	21.7	-21.2
4	0	10	.4160	20.2	15.0
4	0	12	.5833	10.0	-10.6
4	0	14	.7810	11.2	6.7

*All values of F_o were multiplied by 1.0194 to give the values listed in this table.

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
6	0	0	.0806	79.2	85.0
6	0	2	.0958	28.8	-28.3
6	0	4	.1414	57.8	60.7
6	0	6	.2175	20.3	-15.9
6	0	8	.3239	31.4	30.0
6	0	10	.4608	0	-7.7
6	0	12	.6281	15.4	13.7
8	0	0	.1433	53.1	58.3
8	0	2	.1585	5.1	6.0
8	0	4	.2041	44.9	45.0
8	0	6	.2802	6.3	3.7
8	0	8	.3866	27.9	25.5
8	0	10	.5235	0	1.9
8	0	12	.6908	12.9	13.0
10	0	0	.2239	24.9	-23.5
10	0	2	.2391	45.1	42.7
10	0	4	.2848	15.9	-19.1
10	0	6	.3608	32.1	28.4
10	0	8	.4672	10.2	-11.8
10	0	10	.6041	17.9	15.3
10	0	12	.7714	4.6	-6.3
12	0	0	.3224	0	0.3
12	0	2	.3377	0	0.3
12	0	4	.3833	0	-0.3
12	0	6	.4593	0	0
12	0	8	.5658	0	-1.1

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
14	0	0	.4389	27.1	23.4
14	0	2	.4541	10.1	-8.1
14	0	4	.4997	20.4	20.2
14	0	6	.5758	10.0	-6.3
14	0	8	.6822	14.6	13.8
14	0	10	.8191	0	-4.1
16	0	0	.5732	0	1.6
16	0	2	.5884	15.7	16.5
16	0	4	.6341	0	1.6
16	0	6	.7101	12.6	12.7
16	0	8	.8166	7.5	1.3
16	0	10	.9534	6.5	8.0
18	0	0	.7255	0	-5.9
18	0	2	.7407	10.6	9.6
18	0	4	.7863	0	-5.4
18	0	6	.8624	10.3	7.8

Group (2) $h = 2n + 1, l = 2n + 1$

1	0	1	.0060	unobserved	-7.9
1	0	3	.0365	0	1.4
1	0	5	.0973	8.5	-5.4
1	0	7	.1885	0	-0.4
1	0	9	.3102	0	-3.2
1	0	11	.4623	0	-1.3

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
3	0	1	.0240	6.7	-4.8
3	0	3	.0544	0	-0.3
3	0	5	.1152	0	-2.9
3	0	7	.2064	0	-1.5
3	0	9	.3281	0	-2.2
3	0	11	.4802	0	-1.4
5	0	1	.0598	4.8	-6.2
5	0	3	.0902	7.4	6.6
5	0	5	.1510	0	-1.1
5	0	7	.2423	0	4.2
5	0	9	.3639	0	0.3
5	0	11	.5160	0	3.0
7	0	1	.1135	14.5	-14.1
7	0	3	.1439	15.6	13.2
7	0	5	.2048	8.0	-7.9
7	0	7	.2960	12.8	8.2
7	0	9	.4177	0	-3.2
7	0	11	.5698	0	4.4
9	0	1	.1852	0	-3.4
9	0	3	.2156	0	1.8
9	0	5	.2764	0	-3.7
9	0	7	.3677	0	0.2
9	0	9	.4893	0	-2.8

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
11	0	1	.2747	0	0.5
11	0	3	.3052	0	-1.2
11	0	5	.3660	0	-0.4
11	0	7	.4572	0	-1.1
13	0	1	.3822	0	-6.2
13	0	3	.4126	0	6.6
13	0	5	.4735	0	-4.0
15	0	1	.5076	0	-2.9
15	0	3	.5380	0	3.2
15	0	5	.5989	0	-1.9

OBSERVED AND CALCULATED STRUCTURE FACTORS

0 k l PROJECTION

Group (1) $k = 2n$, $l = 2n$

h	k	l	$\sin^2 \Theta_{hkl}$	$K_F^*_{\circ}$	$F_{\circ}$
0	0	2	.0152	58.9	-61.7
0	0	4	.0608	119.0	151.0
0	0	6	.1369	30.9	-29.1
0	0	8	.2433	65.1	65.0
0	0	10	.3802	13.6	-13.6
0	0	12	.5475	35.6	30.5
0	0	14	.7452	0	-6.5
0	0	16	.9733	13.8	14.8
0	2	0	.0086	14.7	13.9
0	2	2	.0238	21.9	-21.7
0	2	4	.0694	8.6	8.2
0	2	6	.1455	6.6	6.3
0	2	8	.2519	0	4.0
0	2	10	.3888	0	0.8
0	2	12	.5561	0	2.7
0	2	14	.7538	0	-0.1
0	4	0	.0344	22.9	19.4
0	4	2	.0496	84.4	91.8
0	4	4	.0952	3.6	7.4
0	4	6	.1712	47.2	49.4
0	4	8	.2777	0	3.1
0	4	10	.4146	26.0	23.0

* All values of $F_{\circ}$ were multiplied by 0.9609 to give the values listed in this table.

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
0	4	12	.5819	0	2.0
0	4	14	.7796	12.2	11.1
0	6	0	.0773	48.3	53.9
0	6	2	.0926	23.2	-23.8
0	6	4	.1382	40.3	42.6
0	6	6	.2142	13.3	-14.0
0	6	8	.3207	24.4	20.8
0	6	10	.4575	0	-6.0
0	6	12	.6248	10.9	9.4
0	6	14	.8225	0	-2.3
0	8	0	.1375	19.3	18.9
0	8	2	.1527	23.5	25.7
0	8	4	.1983	12.7	14.6
0	8	6	.2744	17.5	16.6
0	8	8	.3808	0	8.0
0	8	10	.5177	6.8	9.1
0	8	12	.6850	4.8	4.2
0	8	14	.8827	0	5.0
0	10	0	.2149	0	-2.9
0	10	2	.2301	34.2	31.7
0	10	4	.2757	0	-1.9
0	10	6	.3517	25.9	20.9
0	10	8	.4582	0	-0.4
0	10	10	.5951	14.2	11.5
0	10	12	.7623	0	0.2
0	10	14	.9600	7.1	6.6

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
0	12	0	.3094	34.2	33.4
0	12	2	.3246	17.5	-18.9
0	12	4	.3702	29.4	28.3
0	12	6	.4463	14.7	-14.2
0	12	8	.5527	20.1	18.7
0	12	10	.6896	8.3	-8.7
0	12	12	.8569	12.0	11.1
0	14	0	.4211	25.8	24.3
0	14	2	.4363	0	0.4
0	14	4	.4820	20.9	21.3
0	14	6	.5580	5.0	0
0	14	8	.6644	12.9	15.1
0	14	10	.8013	0	-0.2
0	14	12	.9686	7.2	9.3
0	16	0	.5500	6.7	-6.8
0	16	2	.5652	7.3	8.7
0	16	4	.6109	6.6	-5.9
0	16	6	.6869	0	6.9
0	16	8	.7934	0	-3.9
0	16	10	.9302	5.0	5.1
0	18	0	.6961	16.9	12.1
0	18	2	.7114	0	4.7
0	18	4	.7570	15.9	10.8
0	18	6	.8330	0	3.9
0	18	8	.9395	9.6	8.0

Group (2) $k = 2n$, $l = 2n + 1$

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
0	2	1	.0124	0	-1.5
0	2	3	.0428	5.6	2.9
0	2	5	.1036	0	-0.4
0	2	7	.1949	0	2.2
0	2	9	.3165	0	0.1
0	2	11	.4686	0	1.1
0	2	13	.6511	0	0.8
0	4	1	.0382	6.1	7.2
0	4	3	.0686	11.2	-8.5
0	4	5	.1294	0	3.5
0	4	7	.2207	6.8	-5.6
0	4	9	.3423	0	1.0
0	4	11	.4944	0	-3.2
0	4	13	.6769	0	-0.2
0	6	1	.0812	7.7	1.3
0	6	3	.1116	0	1.4
0	6	5	.1724	7.0	2.1
0	6	7	.2636	0	1.8
0	6	9	.3853	5.1	2.5
0	6	11	.5374	0	1.4
0	6	13	.7199	0	1.8
0	8	1	.1413	0	2.9
0	8	3	.1717	0	-4.3
0	8	5	.2326	0	0.5

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
0	8	7	.3238	0	-4.1
0	8	9	.4455	0	-0.2
0	8	11	.5975	0	-3.6
0	8	13	.7800	0	-0.1
0	10	1	.2187	0	5.7
0	10	3	.2491	0	-3.6
0	10	5	.3099	0	5.3
0	10	7	.4012	0	-0.8
0	10	9	.5228	0	3.6
0	10	11	.6749	0	0.5
0	10	13	.8574	0	2.1
0	12	1	.3132	6.2	-9.6
0	12	3	.3436	0	7.9
0	12	5	.4044	5.1	-8.8
0	12	7	.4957	0	5.1
0	12	9	.6174	8.7	-6.7
0	12	11	.7694	0	2.9
0	12	13	.9519	0	-4.4
0	14	1	.4249	0	-5.8
0	14	3	.4553	0	6.1
0	14	5	.5162	0	-4.1
0	14	7	.6074	5.9	4.8
0	14	9	.7291	0	-2.1
0	14	11	.8812	0	3.1

h	k	l	$\sin^2 \Theta_{hkl}$	F_o	F_c
0	16	1	.5538	0	4.4
0	16	3	.5843	0	-4.4
0	16	5	.6451	0	3.3
0	16	7	.7363	0	-3.6
0	16	9	.8580	0	2.1
0	18	1	.6999	0	1.5
0	18	3	.7304	0	-1.4
0	18	5	.7912	0	1.3
0	18	7	.8824	0	-0.9

to prepare the map in Fig. 33 (a) showed an almost negligible change at each summation point. Therefore this $\rho_o - \rho_c$ map has not been included in this dissertation. The corrected ρ_o map projected along a in conjunction with the corrected values of $\rho_o - \rho_c$ for the same projection were used to assess the accuracy of this refinement as discussed in Section F of this Chapter.

At this point in the discussion of the electron density maps, it should be noted that a particularly striking feature on the $hk0$ projection and the $h0l$ projection persisted throughout the refinement. The feature on the $hk0$ maps (both ρ_o and $\rho_o - \rho_c$) was a ridge of peaks parallel to the x axis in a line passing through the peaks of 0_a and 0_b . The persisting feature on the $h0l$ projections was a single maximum of electron density just to the right of 0_d at $\frac{1}{2} c$. The anomalous peaks on the $hk0$ projections could not be explained by the author but it was noticed that as the refinement progressed the maximum values of the electron density at the peaks slowly decreased. The anomaly on the $h0l$ projection may be explained as anisotropic thermal vibration of 0_d , since 0_d lies in a slightly negative region with an accompanying very small maximum area to the left.

E Calculation of Interatomic Distances and Bond Angles

The general equation for the calculation of an interatomic distance from the fractional coordinates of two atoms (x_1, y_1, z_1) and (x_2, y_2, z_2) in a triclinic crystal is given by:

$$d_{12}^2 = \left\{ (x_2 - x_1)^2 a^2 + (y_2 - y_1)^2 b^2 + (z_2 - z_1)^2 c^2 \right. \\ + 2 (x_2 - x_1) (y_2 - y_1) ab \cos \gamma \\ + 2 (z_2 - z_1) (x_2 - x_1) ca \cos \beta \\ \left. + 2 (y_2 - y_1) (z_2 - z_1) bc \cos \alpha \right\}$$

where d_{12} is the required distance in $\overset{\circ}{\text{\AA}}$ units,

a, b, c are the cell dimensions in $\overset{\circ}{\text{\AA}}$,

and α, β, γ are the angles between the cell edges,

b and c ; a and c ; a and b respectively.

If the unit cell has orthogonal axes as in the present orthorhombic case, then $\cos\alpha = \cos\beta = \cos\gamma = 0$ and the expression simplifies to:

$$d_{12} = \left\{ (x_2 - x_1)^2 a^2 + (y_2 - y_1)^2 b^2 + (z_2 - z_1)^2 c^2 \right\}^{\frac{1}{2}}.$$

In the orthorhombic system the expression for the angle between the bonds which link an atom at (x_2, y_2, z_2) to atoms at

(x_1, y_1, z_1) and (x_3, y_3, z_3) is

$$\cos \theta_2 = \frac{1}{d_{2-1} d_{2-3}} \left\{ (x_1 - x_2)(x_3 - x_2) a^2 + (y_1 - y_2)(y_3 - y_2) b^2 + (z_1 - z_2)(z_3 - z_2) c^2 \right\}$$

where θ_2 is the required angle and d_{2-1}, d_{2-3} are the bond lengths between atoms (1) and (2) and between atoms (2) and (3) respectively.

This expression is applicable to crystals with orthogonal axes but cross-product terms including the interaxial angles are necessary in the general triclinic case.

A list of the bond lengths for the Si-O and Al-O tetrahedra and for the Al-O octahedra calculated from the final atomic parameters (Stage VI) is given in Table XII. Table XIII lists the interbond angles within the tetrahedra and octahedra as well as angles at which tetrahedra and octahedra are linked. All these calculations were done by hand due to the simplicity and number of them.

The mean value of the Si-O distance in the silicon tetrahedron is $1.630 \overset{\circ}{\text{\AA}}$ and the mean Al-O distance in the Al tetrahedron is $1.742 \overset{\circ}{\text{\AA}}$.

The average value for the Al-O distance in the aluminum octahedron is $1.916 \overset{\circ}{\text{\AA}}$. The mean O-X-O angle in Si and Al tetrahedra was $109^\circ 2'$ which

CALCULATED INTERATOMIC DISTANCES FOR SILLIMANITE (Stage VI)

Silicon-Oxygen Tetrahedron	Aluminum-Oxygen Tetrahedron	Aluminum-Oxygen Octahedron
Si - O _a 1.62 ₂ ^Å	Al _{II} - O _b 1.73 ₀ ^Å	x2 Al _I - O _a 1.92 ₆ ^Å
Si - O _c 1.55 ₇ ^Å	Al _{II} - O _c 1.72 ₅ ^Å	x2 Al _I - O _b 1.86 ₁ ^Å
Si - O _d 1.67 ₁ ^Å	Al _{II} - O _d 1.75 ₆ ^Å	x2 Al _I - O _d 1.96 ₁ ^Å
Si - O _d [†] 1.67 ₁ ^Å	Al _{II} - O _d [†] 1.75 ₆ ^Å	
Mean 1.63 ₀ ^Å	Mean 1.74 ₂ ^Å	Mean 1.91 ₆ ^Å
O _a - O _c 2.56 ₁ ^Å	O _b - O _c 2.91 ₆ ^Å	O _a - O _b 2.88 ₅ ^Å
O _a - O _d 2.63 ₈ ^Å	O _b - O _d 2.77 ₆ ^Å	O _a - O _b [†] 2.45 ₄ ^Å
O _c - O _d 2.65 ₉ ^Å	O _c - O _d 2.82 ₃ ^Å	O _a - O _d 2.77 ₁ ^Å
O _d - O _d [†] 2.81 ₂ ^Å	O _d - O _d [†] 2.95 ₁ ^Å	O _a - O _d [†] 2.73 ₄ ^Å
Mean 2.66 ₁ ^Å	Mean 2.84 ₄ ^Å	O _b - O _d 2.68 ₉ ^Å
		O _b - O _d [†] 2.72 ₇ ^Å
		Mean 2.71 ₀ ^Å

TABLE XIII

CALCULATED INTERBOND ANGLES FOR FINAL PARAMETERS (STAGE VI)

Silicon-Oxygen Tetrahedron	Aluminum-Oxygen Tetrahedron	Aluminum-Oxygen Octahedron
O_a-Si-O_c 107° 17'	$O_b-Al_{II}-O_c$ 115° 11'	$O_a-Al_I-O_b$ 99° 15'
x2 O_a-Si-O_d 106° 22'	x2 $O_b-Al_{II}-O_d$ 105° 35'	$O_a-Al_I-O_d$ 90° 56'
x2 O_c-Si-O_d 110° 51'	x2 $O_c-Al_{II}-O_d$ 108° 12'	$O_a-Al_I-O_d$ 89° 4'
O_d-Si-O_d 114° 35'	$O_d-Al_{II}-O_d$ 114° 21'	$O_a-Al_I-O_b$ 80° 45'
Mean 109° 3'	Mean 109° 1'	$O_b-Al_I-O_d$ 89° 24'
		$O_b-Al_I-O_d$ 90° 36'
Bridging Oxygens between Al_I-O_6 chains		
$Al_I-O_a-Al_I$ 96° 51'		Common Oxygen between Tetrahedra
$Al_I-O_b-Al_I$ 101° 29'		$Si-O_c-Al_{II}$ 170° 36'
		$Si-O_d-Al_{II}$ 114° 29'

is very close to the expected tetrahedral angle of $109^{\circ}28'$.

F Assessment of the Accuracy

The reliability factor (R) as discussed in Section C of this chapter gives one a general indication of the progress of a refinement. However, R is not directly related to the probable errors of the determination, and no estimation of the standard deviation of the final parameters can be obtained from it. The accuracy of this 2-dimensional refinement of sillimanite has been determined by a method shown in Lipson and Cochran (1953). The standard deviation ($\sigma(x_n)$) of the atomic parameters was determined in the y direction only from the final 0kl projections of ℓ_o and $\ell_o - \ell_c$, on the assumption that $\sigma(x_n) = \sigma(y_n) = \sigma(z_n)^*$. The 0kl maps were used because the atoms were best resolved in this projection. (See Fig. 35)

Lipson and Cochran have reproduced Cruickshank's formula for the determination of the standard deviation as

$$\sigma(y_n) = \frac{2\pi \left\{ \sum_q k^2 (F_o - F_c)^2 \right\}^{\frac{1}{2}}}{b A C_n}$$

for a 2-dimensional refinement, where C_n is the central curvature at the n^{th} atom, b is the cell edge length in the y direction, A is the area of the projection used to determine $\sigma(y_n)$, and $\sum_q$ is the summation over all the reflections in the limiting sphere (or circle in a 2-dimensional case). Account was taken in this summation for the orthorhombic symmetry of sillimanite by multiplying $(F_o - F_c)$ for the

* This relation may hold for a 3-dimensional refinement but it is not necessarily true for a 2-dimensional refinement.

0kℓ reflections by four and for the 0k0 reflections by two.

The above expression may be written as

$$\sigma(y_n) = \left\{ \overline{\left(\frac{\partial D}{\partial y} \right)^2} \right\}^{\frac{1}{2}} / c_n$$

as shown in Lipson and Cochran. In this formula, $D = \rho_o - \rho_c$ and

$\partial D / \partial y$ is the slope of D in the y direction on a $\rho_o - \rho_c$ map.

The average is taken over the whole unit cell or projected area of the cell. By taking this average over the whole unit cell, the calculated experimental error includes errors due to the residual gradients which might be removed by further small shifts.

Errors other than these random errors of measurement were neglected. Errors due to scale of the F_o synthesis were not considered since the electron densities were not rigidly required in this project. Series termination errors and computational errors discussed in Lipson and Cochran (1953) and Cruickshank (1949) have also been ignored since their effects were assumed to be negligible compared to the random errors.

In assessing the accuracy of this refinement use was made of both the above expressions for the standard deviation. If these equations are written so that C_n is the only denominator such as:

$$\sigma(y_n) = \left\{ \frac{2\pi \left\{ \sum_a k^2 (F_o - F_c)^2 \right\}}{b A} \right\}^{\frac{1}{2}} \cdot \frac{1}{C_n} = \left\{ \overline{\left(\frac{\partial D}{\partial y} \right)^2} \right\}^{\frac{1}{2}} \cdot \frac{1}{C_n}$$

then both bracketed terms should have the same value since C_n is the only variable for any particular atom. The first bracketed term was evaluated from the $F_o - F_c$ data for the 0kℓ reflections and was found to be $14.21 \text{ e } \text{\AA}^{-3}$. The expression $\left\{ \overline{\left(\partial D / \partial y \right)^2} \right\}^{\frac{1}{2}}$ was evaluated

over 240 points distributed evenly over the $\rho_o - \rho_c$ map projected along a. Its value was found to be $13.24 \text{ e } \text{\AA}^{-3}$ giving good agreement with the value determined by the first method.

In order to evaluate the standard deviation it is necessary to determine the curvature for each atom. This was done in the case of sillimanite for Si, Al_{II}, O_b and O_c using the final Okl ρ_o map (Fig. 35). The curvature C_n , at an atomic centre is the same as $(\partial^2 \rho_o / \partial y^2)$ in the y direction. The atoms were assumed to be spherically symmetrical, so the curvature was evaluated in several directions across the Si, Al_{II}, O_b and O_c peaks. Assuming that the electron density at a point r Å from the atomic centre is given by

$$\rho(r) = \rho(0) \exp(-pr^2)$$

$$\text{or } \ln(\rho(r)/\rho(o)) = -pr^2$$

where $\rho(o)$ is the observed electron density at $r=0$, then the straight line for $\ln(\rho(r)/\rho(o))$ against r^2 has as its slope $-p$. The curvature may be written simply as

$$|C_n| = |-2p \rho(o)|$$

The values of p were determined by the above methods from a straight line plot fit to the data by least squares. Using these values of p and the observed electron densities at the peak maxima, the values of the central curvature at each atom were calculated. Calculations of the standard deviation of error in the final atomic parameters were performed using both values of the numerator in these equations.

The averages of these two calculations were used as the final result.

The following tabulation lists the values of ρ_o , p , c_n and $\sigma(y)$ for the atoms Si, Al_{II}, O_b and O_c.

	$\rho(o) (e \text{ \AA}^{-2})$	$p (\text{\AA}^{-2})$	$c_n (e \text{ \AA}^{-4})$	$\sigma(y) (\text{\AA})$
Si	62.5	24.0	3,000.0	0.005
Al _{II}	59.5	21.2	2,523.0	0.006
O _b	35.0	17	1,190.0	0.012
O _c	32.6	14.8	965.0	0.014

The average of the two values for O_b and O_c is 0.013 and this value was used in further calculations to represent the standard deviation in atomic parameters for all the oxygen atoms in the unit cell of sillimanite.

These standard deviations agree fairly closely with those obtained by 2-dimensional methods from similar structures, for example Low and High Albite by Ferguson, Traill and Taylor (1958) in which they report $\sigma(y) \text{ O} = 0.018$ and $\sigma(y) \text{ Si} = 0.006$. There is perhaps a slight underestimate on the part of Si and Al_{II} but it is felt that these numbers represent the true values very closely.

The standard deviation of the length of a bond, A-B, between two atoms, A and B, is given by the relation,

$$\sigma^2(A-B) = \sigma^2(A) + \sigma^2(B)$$

or by $\sigma(A-B) = \sqrt{2} \sigma(A)$ when the two atoms are the same. The present standard deviations of error in the atomic positions of Si, Al_{II} and Oxygen were substituted into this expression, and the following standard deviations of error in Si-O, Al_{II}-O, and O-O distances

were found to be,

$$\sigma(\text{Si} - \text{O}) = 0.014 \text{ \AA}$$

$$\sigma(\text{Al}_{\text{II}} - \text{O}) = 0.014 \text{ \AA}$$

$$\sigma(\text{O} - \text{O}) = 0.018 \text{ \AA}$$

Cruickshank (1949) has suggested a test to determine the significance of differences in bond lengths which are subject to error. If a bond of length C with standard deviation $\sigma(C)$ is determined as greater than a bond of length D with standard deviation $\sigma(D)$ by an amount δl then;

if $\delta l / \sigma \leq 1.645$, the difference is not significant,

if $2.327 > \delta l / \sigma > 1.645$, the difference is possibly significant,

and if $3.090 > \delta l / \sigma > 2.327$, the difference is significant.

In these inequalities the quantity σ is given by

$$\sigma = \{\sigma^2(C) + \sigma^2(D)\}^{1/2}$$

This test was applied to the bonds Si-O of the silicon tetrahedron, $\text{Al}_{\text{II}}-\text{O}$ of the aluminum tetrahedron and the O-O distances in both of these tetrahedra. Since the standard deviation of error is the same for each bond length of the Si and Al_{II} tetrahedra, the overall standard deviation, σ , is $\sqrt{2} (0.014) \text{ \AA}$ or $0.020 \text{ \AA}$, and for the O-O distances is $\sqrt{2} (0.018) \text{ \AA}$ or $0.0255 \text{ \AA}$.

For the examination of the differences of the bond lengths from the mean values of the Si-O and $\text{Al}_{\text{II}}-\text{O}$ distances, a different overall standard deviation σ is employed. This standard deviation is given by:

$$\sigma = \{\sigma^2(C) + \sigma_{\text{mean}}^2\}^{1/2},$$

where $\sigma(C)$ is the standard deviation of the bond length C and $\sigma_{\text{mean}} = \sigma(l)/N^{1/2}$. $\sigma(l)$ is the overall standard deviation of the Si-O and $\text{Al}_{\text{II}}-\text{O}$ distances and N is the number of bonds involved in deriving the mean length. In the present case since the standard deviations of the bond lengths in the Si and Al_{II} tetrahedra were the same, the value of the overall standard deviation was the same as the above σ for the comparison of two bonds of lengths C and D. (i.e., $\sigma = 0.020 \text{ \AA}$.)

The deviation of each bond length in the Si-O and Al_{II}-O tetrahedra from the mean was determined and then these significance tests were applied. It was found that in the Si-O tetrahedron, the bond length differences from the mean of Si-O_c, O_a-O_c and O_d-O_d' were significant and the differences of Si-O_d from the mean were possibly significant. In the Al_{II}-O tetrahedron all the Al_{II}-O differences from the mean were not significant whereas the differences of O_b-O_c, O_b-O_d and O_d-O_d' from the mean were all significant. The difference between the mean values for the Si-O distance and the Al_{II}-O distance in these two tetrahedra is highly significant.

When the curvatures for the different atoms in the unit cell of sillimanite were calculated, it was felt that the values were excessively large. A comparison of the author's values with the curvatures for silicon and oxygen obtained by Ferguson, Traill and Taylor (1958) in a refinement of low- and high-temperature albites revealed this to be the case. The curvatures reported in the above paper were $303 \text{ e}\text{\AA}^{-3}$ for oxygen and $845 \text{ e}\text{\AA}^{-3}$ for silicon. Both these values are approximately one-quarter the size of the curvatures for oxygen and silicon obtained in this study. In order to provide an explanation for this, a comparison was made of the number of terms that were used as amplitudes in the F_o syntheses of both refinements. In the present work, 63 observed reflections were used to calculate the ρ_o map projected along a, whereas 125 observed reflections were used in the same projection in the low-albite refinement. The large value of the curvature in this refinement represents a high narrow peak with steep slopes on the sides. Thus the large curvature may be attributed to a series termination effect due to the fewer number of terms used in the Fourier summation.

CHAPTER VIII

SUMMARY, COMPARISON AND DISCUSSION OF THE RESULTS

A Introduction

The crystal structure of sillimanite has been refined by 2-dimensional Fourier techniques. An X-ray determination of the centrosymmetric nature of sillimanite confirms Taylor's (1928) result that the space group is Pbnm. The essential structural features of sillimanite determined by Hey and Taylor (1931) have been confirmed by this refinement through the agreement between 268 observed and calculated structure factors, although the values of the interatomic distances and interbond angles have been obtained more accurately.

The structure of sillimanite is characterized by chains of aluminum octahedra parallel to the c axis linked by parallel double chains of alternating silicon and aluminum tetrahedra formed into 4-membered rings. This linkage suggests that sillimanite should be placed in the chain or ino-silicate group in the silicate classification, with the pyroxenes and the amphiboles. However the very close structural and mineralogical relationship of sillimanite to andalusite and kyanite probably justifies the customary inclusion of sillimanite with these two minerals.

In this Chapter comparison is made with the work of other authors on sillimanite, but it should be pointed out that since much of this work was well underway before any of these refinements had appeared in detail, this constitutes a completely independent refinement of the structure. The first refinement that appeared was that of Durovic and Davidova (1962). This was a short note in *Acta Crystallographica* containing only the R factor for 72 unspecified planes, the measured density and a list of the refined atomic coordinates.

Burnham's refinement appeared in 3 different publications (1962a, 1962b and 1963) in November 1962, December 1962, and May 1963. The present refinement had been completed by the time the full account (Burnham 1963) had been published, but the data given in the two earlier shorter publications were purposely ignored in order to insure the independence of the author's refinement.

B Cell Dimensions and Specific Gravity

Table XIV (a) contains a list of the measured specific gravities and cell dimensions of this work, Burnham (1963) and Durovic and Davidova (1962). Burnham's paper contains no specific gravity determination whereas the cell dimensions are absent in the paper by Durovic and Davidova. There is no appreciable difference in the specific gravities measured by the two different authors. The differences between the two sets of measured cell dimensions are probably significant since the present author's values are all slightly smaller for all three axes than Burnham's refined values. The standard deviations of the author's values are not sufficiently large to include the ranges reported by Burnham.

C Comparison of Atomic Parameters

A list of the final atomic parameters in sillimanite determined in this work is given in Table XIV (b). This table compares the atomic parameters determined by Taylor (1928), Hey and Taylor (1931), Burnham (1963) and Durovic and Davidova (1962) with those of the present refinement. Since the R factors relative to Hey and Taylor's structure

TABLE XIV a
COMPARISON OF SPECIFIC GRAVITIES AND
CELL DIMENSIONS OF VARIOUS AUTHORS

	This Work	Burnham (1962b)	D. and D. (1962)
Measured Sp. Gravity (gm.cm. ⁻³)	3.240	-	3.226
a_o (Å)	$7.476 \pm .003$ *	$7.4856 \pm .0006$	-
b_o (Å)	$7.666 \pm .005$	$7.6738 \pm .0003$	-
c_o (Å)	$5.763 \pm .003$	$5.7698 \pm .0008$	-
V (Å ³)	330.28	331.43	-

* The $\pm$ values listed here are the estimated standard deviations, not the probable errors.

were improved upon in the present work a definite improvement has been made to their structure. Durovic and Davidova report a final R factor of 7.1% for 72 independent reflections. Since so few planes were used in their refinement it is felt that the present work is more accurate and this is also suggested by their reported accuracies of the atomic parameters which are larger than the ones in this work. The very small value of the R factor (5.6%) for a large number of 3-dimensional data reported by Burnham shows definitely that his parameters are much more accurate than the present author's.

Table XIV (b) requires an explanation of the notation used in it. The parameters that are subscripted by T (x_T , y_T , z_T) are referred to Taylor's original setting and choice of prototype in the unit cell. The parameters for "This Work" include all of the atoms in the unit cell and the headings of the columns give the equivalent positions in the space group Pbnm referred to Taylor's setting. The parameters with a subscript B are those listed by Burnham (1963). In order to facilitate a comparison with andalusite he has moved the origin to $\frac{1}{2} \frac{1}{2} 0$ in the Taylor cell which corresponds to a transformation of $x_B \longrightarrow x_T$; $y_B \longrightarrow \overline{y_T}$; $z_B \longrightarrow \overline{z_T}$. The atomic parameters of This Work that correspond to the transformed parameters of Burnham have been singly underlined. The doubly underlined parameters in This Work and Durovic and Davidova (1962) are the prototype atoms referred to Taylor's original setting with coordinates all positive. These parameters are the ones that were used in the computations during this refinement and they are contained in Table IX.

The largest discrepancy in atomic parameters reported by Burnham and the author occurs in the parameter of O_d . The difference is 0.0104 which is most definitely significant. However there was little indication from the $\rho_o - \rho_c$ maps during this refinement that

TABLE XIV b

COMPARISON OF ATOMIC PARAMETERS DERIVED BY DIFFERENT AUTHORS

Notes:

1. x_T, y_T, z_T are the parameters given in the original setting of Taylor (1928).
2. x_B, y_B, z_B are the parameters given in the setting of Burnham (1962).
3. $x_B \rightarrow x_T$ etc., under Burnham gives the transformation from Burnham's to Taylor's parameters.
4. Singly underlined parameters of This Work correspond to the singly underlined parameters of Burnham.
5. Doubly underlined parameters of This Work are those in Taylor's setting with all positive values which designate the atoms used as prototypes in this Thesis. (Durovic's and Davidova's parameters are doubly underlined for the same reason.)

Hey and
Taylor
(1931)

This Work (Stage VI - Final)														Burnham (1962)				Durovic and Davidova (1962)				
y_T	z_T	x_T	y_T	z_T	$\frac{1}{2}-x_T$	$\frac{1}{2}+y_T$	$\frac{1}{2}-z_T$	$\bar{x}_T$	$\bar{y}_T$	$\frac{1}{2}+z_T$	$\frac{1}{2}+x_T$	$\frac{1}{2}-y_T$	$\bar{z}_T$	x_B	y_B	z_B	$x_B \rightarrow x_T$	$y_B \rightarrow y_T$	$z_B \rightarrow z_T$	x_T	y_T	z_T
0	0	0	0	0	1/2	1/2	1/2	0	0	1/2	1/2	1/2	0	0	0	0	0	0	0	0	0	0
0.35	1/4	-0.144 ₉	0.346 ₆	1/4	0.644 ₉	0.846 ₆	1/4	0.144 ₉	-0.346 ₆	3/4	0.355 ₁	0.153 ₄	3/4	0.1419	0.3447	1/4	0.1419	-0.3447	3/4	0.352	0.158	3/4
0.35	3/4	-0.151 ₀	0.339 ₀	3/4	0.651 ₀	0.839 ₀	3/4	0.151 ₀	-0.339 ₀	1/4	0.349 ₀	0.161 ₀	1/4	0.1535	0.3404	3/4	0.1535	-0.3404	1/4	0.352	0.158	1/4
0.07	1/4	0.145 ₅	0.087 ₅	1/4	0.354 ₅	0.587 ₅	1/4	-0.145 ₅	-0.087 ₅	3/4	0.645 ₅	0.412 ₅	3/4	0.3599	0.4078	3/4	0.3599	0.5922	1/4	0.139	0.079	1/4
0.07	3/4	0.140 ₄	0.069 ₅	3/4	0.359 ₆	0.569 ₅	3/4	-0.140 ₄	-0.069 ₅	1/4	0.640 ₄	0.430 ₅	1/4	0.3576	0.4352	1/4	0.3576	0.5648	3/4	0.139	0.079	3/4
0.47	1/4	0.024 ₀	0.500 ₀	1/4	0.476 ₀	1.000 ₀	1/4	-0.024 ₀	-0.500 ₀	3/4	0.524 ₀	0	3/4	0.4753	0.0008	3/4	0.4753	0.9992	1/4	0.025	0.490	1/4
0.22	0	-0.127 ₅	0.223 ₅	-0.006 ₀	0.627 ₅	0.723 ₅	0.506 ₀	0.127 ₅	-0.223 ₅	0.494 ₀	0.372 ₅	0.276 ₅	0.006 ₀	0.1248	0.2237	0.5164	0.1248	-0.2237	0.4836	0.374	0.275	0

0_d 0.127₅ -0.223₅ 0.006₀ 0.372₅ 0.276₅ 0.494₀ -0.127₅ 0.223₅ 0.506₀ 0.627₅ 0.723₅ -0.006₀

$\bar{x}_T$ $\bar{y}_T$ $\bar{z}_T$ $\frac{1}{2}+x_T$ $\frac{1}{2}-y_T$ $\frac{1}{2}+z_T$ x_T y_T $\frac{1}{2}-z_T$ $\frac{1}{2}+x_T$ $\frac{1}{2}-y_T$ $\bar{z}_T$

TABLE XIV b

COMPARISON OF ATOMIC PARAMETERS DERIVED BY DIFFERENT AUTHORS

Notes:

1. x_T, y_T, z_T are the parameters given in the original setting of Taylor (1928).
2. x_B, y_B, z_B are the parameters given in the setting of Burnham (1962).
3. $x_B \rightarrow x_T$ etc., under Burnham gives the transformation from Burnham's to Taylor's parameters.
4. Singly underlined parameters of This Work correspond to the singly underlined parameters of Burnham.
5. Doubly underlined parameters of This Work are those in Taylor's setting with all positive values which designate the atoms used as prototypes in this Thesis. (Durovic's and Davidova's parameters are doubly underlined for the same reason.)

Taylor (1928)			Hey and Taylor (1931)			This Work (Stage VI - Final)										Burnham (1962)			
x_T	y_T	z_T	x_T	y_T	z_T	$\frac{1}{2}-x_T$	$\frac{1}{2}+y_T$	$\frac{1}{2}-z_T$	$\bar{x}_T$	$\bar{y}_T$	$\frac{1}{2}+z_T$	$\frac{1}{2}+x_T$	$\frac{1}{2}-y_T$	$\bar{z}_T$	x_B	y_B	z_B	$x_B \rightarrow x_T$	$y_B \rightarrow y_T$
Al _I	0	0	0	0	0	1/2	1/2	1/2	0	0	1/2	1/2	1/2	0	0	0	0	0	0
Al _{II}	-0.14	0.33	1/4	0.35	1/4	0.644 ₉	0.846 ₆	1/4	0.144 ₉	-0.346 ₆	3/4	0.355 ₁	0.153 ₄	3/4	0.1419	0.3447	1/4	0.1419	-0.3447
Si	-0.18	0.35	3/4	0.35	3/4	0.651 ₀	0.839 ₀	3/4	0.151 ₀	-0.339 ₀	1/4	0.349 ₀	0.161 ₀	1/4	0.1535	0.3404	3/4	0.1535	-0.3404
O _a	0.11	0.12	1/4	0.07	1/4	0.354 ₅	0.587 ₅	1/4	-0.145 ₅	-0.087 ₅	3/4	0.645 ₅	0.412 ₅	3/4	0.3599	0.4078	3/4	0.3599	0.5922
O _b	0.10	0.16	3/4	0.07	3/4	0.359 ₆	0.569 ₅	3/4	-0.140 ₄	-0.069 ₅	1/4	0.640 ₄	0.430 ₅	1/4	0.3576	0.4352	1/4	0.3576	0.5648
O _c	0.08	0.46	1/4	0.03	1/4	0.476 ₀	1.000 ₀	1/4	-0.024 ₀	-0.500 ₀	3/4	0.524 ₀	0	3/4	0.4753	0.0008	3/4	0.4753	0.9992
O _d	-0.15	0.18	0	-0.11	0.22	0.627 ₅	0.723 ₅	0.506 ₀	0.127 ₅	-0.223 ₅	0.494 ₀	0.372 ₅	0.276 ₅	0.006 ₀	0.1248	0.2237	0.5164	0.1248	-0.2237
						$\frac{1}{2}+x_T$	$\frac{1}{2}-y_T$	$\frac{1}{2}+z_T$	x_T	y_T	$\frac{1}{2}-z_T$	$\frac{1}{2}-x_T$	$\frac{1}{2}+y_T$	z_T					
						0.372 ₅	0.276 ₅	0.494 ₀	-0.127 ₅	0.223 ₅	0.506 ₀	0.627 ₅	0.723 ₅	-0.006 ₀					

O_d should be moved any further from the (001) plane. This large difference in the position of O_d accounts for the large differences in interatomic distances $Si-O_d$ and $Al_{III}-O_d$ which are shown in Table XIV (c) (Next section). This difference in the position of O_d is half as much again as great in distance as the difference in position of any other atom, the largest being the X parameter of O_a (0.0054). No definite indication of any of these differences in atomic position were indicated by the $\rho_o - \rho_c$ maps so this refinement may be considered to be complete.

D Comparison of Temperature Factors

The final temperature factors B for the individual atoms in the three zones $hk0$, $h0l$ and $0kl$ are given in Table XIV (c) where they are compared with Burnham's (1963) equivalent isotropic temperature factors. Since the present author used different temperature factors for the atoms in the three zones they appear as anisotropic temperature factors, whereas because of the overlapping of certain atoms in projection some of these differences may not be real. The final temperature factors, especially those in the $hk0$ projection, are significantly different from the isotropic temperature factors of Burnham.

In the final $\rho_o - \rho_c$ projections (Fig. 33, a,b,c) there are indications that the temperature factors could also be improved upon. However due to the overlapping of many of the atoms, especially in the $hk0$ and $h0l$ zones, the work required to make these changes in temperature factor was not warranted. It can be seen in Table XIV (c) that the best overall agreement with Burnham's values is obtained in

TABLE XIV c

COMPARISON OF TEMPERATURE FACTORS B IN $\text{\AA}^2$:
 FINAL STAGE VI WITH THOSE OF BURNHAM (1963)

Atom	This Work (projections)			Burnham (1963) (isotropic)
	hk0	h0l	0kl	
Al _I	1.07	0.60	0.38	0.238
Al _{II}	1.07	0.60	0.40	0.370
Si	1.25	0.90	0.52	0.339
O _a	0.83	0.40	0.58	0.355
O _b	0.73	0.63	0.53	0.500
O _c	0.87	0.95	0.65	0.857
O _d	0.92	0.62	0.65	0.407

the $0k\ell$ projection which is probably due to the fact that the resolution is best in this zone. The anisotropy of O_c as reported by Burnham (1963) is suggested in the present study by the variation in the values of B for this atom in the three projections. However, differences between the values for the other atoms observed by the author are even greater than those for O_c whereas Burnham observed no appreciable anisotropism for these atoms. Therefore little reliance should be placed on the differences in the B values of individual atoms between the three projections as a measure of anisotropism. The large values of B for Si and Al in the $hk0$ zone may be significantly reduced since both of these atoms are in electron density highs on the final $\rho_o - \rho_c$ maps. Since O_a and O_b are in negative electron density regions on the $hk0$ $\rho_o - \rho_c$ map a contrary increase in their temperature factors is indicated.

E Comparison of Interatomic Distances and Interbond Angles

The bond distances and interbond angles from the parameters of the refinement by Durovic and Davidova were not calculated so no comparison was made with them, since it was felt that nothing would be gained from this. Table XIV (d) gives a comparison of the interatomic distances and interbond angles of this work with those of Burnham (1963). The atom pairs that have asterisks fall outside the accuracy range of both authors. It also can be noted that $Si-O_d$ and $Al_{II}-O_d$ distances differ appreciably from those of Burnham's. This is due to the fact that O_d is placed farther from the (001) planes in Burnham's structure thus decreasing the $Si-O_d$ distance and increasing the $Al_{II}-O_d$ distance since these O_d atoms are related by the mirror planes. The author's $Al_{II}-O_b$ distance is also much smaller than

TABLE XIV (d)

COMPARISON OF INTERATOMIC DISTANCES AND INTERBOND ANGLES
BETWEEN THIS WORK AND BURNHAM (1963)

Interatomic Distances ($\text{\AA}$)

Atom Pair	This Work	Burnham (1963)
Si-O _a	1.622±0.014*	1.629±0.007
Si-O _c	1.557±0.014	1.564±0.006
x2 Si-O _d	* 1.671±0.014	1.633±0.004
	1.630±0.014*	1.615
O _a -O _c	* 2.561±0.018	2.608±0.007
x2 O _a -O _d	2.638±0.018	2.628±0.005
x2 O _c -O _d	* 2.659±0.018	2.627±0.006
O _d -O _{d'}	* 2.812±0.018	2.696±0.007
	2.661±0.018	2.636
Al _{II} -O _b	* 1.730±0.014	1.758±0.005
Al _{II} -O _c	1.725±0.014	1.721±0.006
x2 Al _{II} -O _d	* 1.756±0.014	1.800±0.004
	1.742±0.014	1.770
O _b -O _c	2.916±0.018	2.903±0.007
x2 O _b -O _d	* 2.776±0.018	2.834±0.005
x2 O _c -O _d	2.823±0.018	2.843±0.006
O _d -O _{d'}	* 2.951±0.018	3.074±0.007
	2.844±0.018	2.889

* The ± values for the bond distances of This Work are the estimated standard deviations (σ) not the probable errors.

Atom Pair	This Work	Burnham (1963)
x2 Al _I -O _a	1.926±0.013	1.919±0.003
x2 Al _I -O _b	1.861±0.013	1.861±0.003
x2 Al _I -O _d	1.961±0.013	1.957±0.003
	1.916±0.013	1.912
x2 O _a -O _b	2.885±0.018	2.893±0.001
x2 O _a -O _b '	2.454±0.018	2.434±0.006
x2 O _a -O _d	2.771±0.018	2.776±0.005
x2 O _a -O _d '	* 2.734±0.018	2.705±0.005
x2 O _b -O _d	2.689±0.018	2.698±0.005
x2 O _b -O _d '	* 2.727±0.018	2.703±0.005
	2.710±0.018	2.702

Interbond Angles

	This Work	Burnham (1963)
O _a -Si-O _c	107° 17'	109.6°
x2 O _a -Si-O _d	106° 22'	107.4°
x2 O _c -Si-O _d	110° 51'	110.5°
O _d -Si-O _d '	114° 35'	111.3°
O _b -Al _{II} -O _c	115° 11'	113.2°
x2 O _b -Al _{II} -O _d	105° 35'	105.6°
x2 O _c -Al _{II} -O _d	108° 12'	107.7°
O _d -Al _{II} -O _d '	114° 21'	117.3°

x2 $O_a-Al_I-O_b$	99° 15'	99.8°
x2 $O_a-Al_I-O_b'$	80° 45'	80.2°
x2 $O_a-Al_I-O_d$	90° 56'	91.5°
x2 $O_a-Al_I-O_d'$	89° 4'	88.5°
x2 $O_b-Al_I-O_d$	89° 24'	89.9°
x2 $O_b-Al_I-O_d'$	90° 36'	90.1°
$Si-O_c-Al_{II}$	170° 36'	171.6°
$Si-O_d-Al_{II}$	114° 29'	114.4°

Burnham's corresponding distance. This is due to a disagreement in the y parameter of O_b and the x parameter of Al_{II} between the two authors. The significant differences in the values of the average interatomic distances for tetrahedral silicon and aluminum is due mainly to the value of the z parameter of O_d . The table of the comparison of the bond angles also shows these trends in the differences of the atomic position of O_d .

F Discussion of Electrostatic Charge Distribution in the Sillimanite Structure

There is good reason to believe that in silicate structures the atoms exist as ions and therefore it is profitable to discuss the electrostatic charge distribution in the sillimanite structure. In an ionic structure the balance of the electrostatic charges may determine the stability of the structure. If one assumes a completely ionic character of the atoms in sillimanite (Al^{+3} , Si^{+4} and O^{-2}) then the bond strengths of the positive ions contributed to the four oxygen atoms constituting a tetrahedral AlO_4 or SiO_4 group should total 8 and the bond strengths contributed to the six oxygens constituting an AlO_6 group should total 12. Care must be taken in drawing conclusions from the results of applying Paulings Rules (1961) since it is possible that the Si-O bonds may possess a partial covalent character. In applying these rules to the sillimanite structure several different approaches are described below. The structure was first assumed to be fully ordered but with the Al_{II} in two possible coordinations, 4 and 5. Two impossible situations which will be shown presently, rule out the possibility of AlO_5 coordination for Al_{II} . In addition, for 4-coordinated Al_{II} cases of partial disorder, complete disorder, and complete interchange of Si^{+4} and Al^{+3} between the two sites are

examined.

Table XV shows the charge distribution for 4 and 5-coordinated Al_{II} . The charge on the silicon atom is assumed to be +4 and is divided among four oxygens, whereas the charge on the aluminum atoms is +3 and it is divided among 4 and 6 oxygens for the tetrahedra and octahedra respectively.

It can be seen from Table XV that 4-coordinated Al_{II} gives perfect agreement for the $\text{Al}_{\text{II}}\text{-O}_4$ groups and the $\text{Al}_{\text{I}}\text{-O}_6$ groups but an excess of 0.25 e on the Si-O_4 groups. In the case of 5-coordinated Al_{II} only the $\text{Al}_{\text{II}}\text{-O}_5$ group gives perfect agreement whereas both the SiO_4 and $\text{Al}_{\text{I}}\text{-O}_6$ groups have excess charge on them. One reason for discarding the possibility of 5-coordinated Al_{II} in sillimanite is this poor value of the charge balance. Another is the impossible situation that occurs in the $\text{Al}_{\text{I}}\text{-O}_6$ group of oxygens. The whole group has an excess of 0.6 electrons. This cannot be lowered by disorder considerations since there are no ions with a positive charge less than 3 that could be placed there on a statistical basis to lower the effective charge on the Al_{I} site. Also Si is not known to exist in six fold coordination. The final reason for discarding the $\text{Al}_{\text{II}}\text{-O}_5$ group is the fact that the oxygen atom (O_a) that is the closest to Al_{II} other than the four atoms to which it is definitely bonded is 2.942 Å from Al_{II} , and this distance is approximately 1.20 Å larger than the sum of the ionic radii of Al^{+3} and O^{-2} .

Table XV also shows that there is a local charge unbalance on the individual oxygen atoms. Both O_c and O_b have a deficiency of 0.25 e while O_d has an excess of 0.25 e. With O_d being present in

TABLE XV

CHARGE BALANCES FOR TETRAHEDRAL AND OCTAHEDRAL GROUPS

BASED ON $\text{Al}_{\text{II}}\text{-O}_4$ AND ON $\text{Al}_{\text{II}}\text{-O}_5$ COORDINATION

Group	$\text{Al}_{\text{II}}\text{-O}_4$ Total ($\bar{e}$)	$\text{Al}_{\text{II}}\text{-O}_5$ Total ($\bar{e}$)
O_a	2.00	2.60
O_c	1.75	1.60
Si O_d	2.25	2.10
O_d'	2.25	2.10
Group Total	8.25	8.40
O_a	-	2.60
O_b	1.75	1.60
O_c	1.75	1.60
$\text{Al}_{\text{II}} \text{O}_d$	2.25	2.10
O_d'	2.25	2.10
Group Total	8.00	10.00
O_a	2.00	2.60
O_a'	2.00	2.60
O_b	1.75	1.60
$\text{Al}_I \text{O}_b'$	1.75	1.60
O_d	2.25	2.10
O_d'	2.25	2.10
Group Total	12.00	12.60

twice the number compared with O_c in the unit cell there results an excess of charge on the SiO_4 tetrahedral group since O_a has a perfect charge balance and O_b is not coordinated to Si.

It can be shown that it is not possible to vary the charges contributed to the two tetrahedral groups of oxygens for a given silicon-aluminum distribution by dividing the charges on the cations in amounts that are inversely proportional to the cation-oxygen distances in the tetrahedra. However, it is possible to vary the charges on the tetrahedral groups of oxygens by varying the Si-Al distribution and some possibilities of this kind are shown in Table XVI. So in attempting to provide an explanation for the charge distribution two disordered structures were considered. The results of the calculations are given in Table XVI. This table also shows the result occurring when Si and Al are completely interchanged in their sites. Notice that when this is done the excess charge on the Si site is changed to the Al_{II} site whereas no excess charge is observed on the Al_I octahedral site. Also throughout the different approaches, except in the $Al_{II}-O_5$ case, the charge distribution to the oxygens surrounding Al_I has remained nearly perfect.

Table XVI along with the results of Table XV suggests that the fully disordered structure of sillimanite ($Al_{0.5}-Si_{0.5}$) provides the best overall charge distribution with an equal excess of $0.13 e^-$ on each of the tetrahedral groups of oxygens. However this is contradicted by the size of these two tetrahedral sites. In this work the average Si-O distance is $1.630 \text{ \AA}$ and the average $Al_{II}-O$ distance is $1.742 \text{ \AA}$ and Burnham's more accurate values are $1.615 \text{ \AA}$ and $1.770 \text{ \AA}$.

TABLE XVI
CHARGE DISTRIBUTIONS FOR
DIFFERENT Al-Si ARRANGEMENTS

Group	Partial Disorder Si _{0.9} -Al _{0.1} in Si site	Full Disorder Si _{0.5} -Al _{0.5} in both sites	Interchange Si & Al _{II} in tetrahedral sites
Si	$\left\{ \begin{array}{l} O_a \\ O_c \\ O_d \\ O_d' \end{array} \right.$	$\left\{ \begin{array}{l} 1.98 \\ 1.75 \\ 2.25 \\ 2.25 \end{array} \right.$	$\left\{ \begin{array}{l} 1.88 \\ 1.75 \\ 2.25 \\ 2.25 \end{array} \right.$
	Group total	8.23	8.13
			8.00
Al _{II}	$\left\{ \begin{array}{l} O_b \\ O_c \\ O_d \\ O_d' \end{array} \right.$	$\left\{ \begin{array}{l} 1.78 \\ 1.75 \\ 2.25 \\ 2.25 \end{array} \right.$	$\left\{ \begin{array}{l} 1.88 \\ 1.75 \\ 2.25 \\ 2.25 \end{array} \right.$
	Group total	8.03	8.13
			8.25
Al _I	$\left\{ \begin{array}{l} O_a \\ O_a' \\ O_b \\ O_b' \\ O_d \\ O_d' \end{array} \right.$	$\left\{ \begin{array}{l} 1.98 \\ 1.98 \\ 1.78 \\ 1.78 \\ 2.25 \\ 2.25 \end{array} \right.$	$\left\{ \begin{array}{l} 1.88 \\ 1.88 \\ 1.88 \\ 1.88 \\ 2.25 \\ 2.25 \end{array} \right.$
	Group total	12.02	12.02
			12.00

respectively. When these values are taken into account with the values given by Smith (1954; see also Smith 1962) for the pure Si-O and Al-O distances, $1.60 \pm 0.01 \text{ \AA}$ and $1.78 \pm 0.02 \text{ \AA}$ respectively, it appears that the silicon and aluminum atoms must be completely ordered or nearly so in sillimanite.

APPENDIX I

PROCEDURE FOR TAKING WEISSENBERG PHOTOGRAPHS

A Zero Level

1. Affix Weissenberg screen in position. Make sure screen setting and horizontal angular settings are reading zero.
2. Slide direct beam trap to extreme left and check for emission of X-ray beam.
3. Record central streak in the film as follows:
 - (a) Place direct beam trap to extreme left, turn off X-rays and have the brass drive pin for the carriage aligned with the collimator.
 - (b) Insert camera on carriage, free carriage from drive, and have camera and carriage to the extreme left of its traverse.
 - (c) Turn on X-rays and immediately slide the camera and the carriage fairly quickly to the extreme right and at once turn off the X-rays.
4. Lock the carriage to the drive pin, remove the camera from carriage, replace the direct beam trap in line with the collimator and return camera to the carriage making sure the camera setting is zero.
5. Make sure the circular scale piece (drum) is linked to the drive by the lock pin (as distinguished from the pressure pin). Fix the traverse stops for the appropriate traverse lengths.
6. Start Weissenberg motor and turn on the X-rays.

B Upper Level

1. Set the Weissenberg instrument at the appropriate horizontal angular setting and affix the Weissenberg screen in the appropriate position.
2. Same as for the zero level.

3. Same as for the zero level.
4. Lock the carriage to the drive pin, remove the camera from the carriage, replace the direct beam trap at the required setting and return the camera to the carriage making sure the camera is at its appropriate setting for the upper level.
5. Same as for the zero level noting that in general, the traverse stops will be in slightly different position from those required for the zero level, and their positions will be determined by the position of the camera and carriage relative to the collimator.
6. Same as for the zero level.

APPENDIX II

STRUCTURE FACTOR COMPUTATION FOR SPACE

GROUP Pbnm ON THE I.B.M. "1620"

A programme was prepared to compute crystallographic structure factors for the space group Pbnm on the I.B.M. "1620" at the University of Manitoba using the simplified coding system of FORTRAN. A familiarity with the FORTRAN system on the part of the reader is assumed in this section*. The programme prepared by the author is admittedly simple and can only be applied to the special case of sillimanite. However, since it was prepared in the course of this M.Sc Thesis, it was felt that it should be included in this report.

A The Problem Statement

Crystallographic structure factors of the type $F_{(hkl)}$ for the space group Pbnm as required in the present investigation can be represented by the relation

$$F_{(hkl)} = 8 \sum_j f_j \exp (-B_j \sin^2 \theta / \lambda^2) \\ \times \cos 2\pi(hx_j + \frac{h+k}{4}) \\ \times \cos 2\pi(ky_j - \frac{h+k+l}{4}) \\ \times \cos 2\pi(lz_j + l/4).$$

In this expression, the summation is over the j atoms in the unit cell, f_j is the scattering factor of the j^{th} atom, B_j is the temperature

* Reference: General Information Manual FORTRAN, I.B.M. (1961)

factor of the j^{th} atom, θ is the Bragg angle of reflection from the lattice planes with Miller indices hkl , λ the wave-length of the X-radiation and x_j , y_j and z_j are the coordinates of the j^{th} atom expressed as fractions of the cell edges. The factor 8 applies only for the case of O_d which is the only atom in the unit cell that is in the general position of the space group. For all the other atoms in special positions the factor is 4. Since this was a 2-dimensional refinement and structure factors of the type $F(hkl)$ were not required, this expression was modified slightly to calculate structure factors for the reflections of the types $(hk0)$, $(h0l)$ and $(0kl)$ by preparing three separate programmes, one for each zone. The same equation was used for each zone but provision was made for keeping one of the Miller indices constantly zero. The scattering factors f_j of the atoms were computed from a sixth degree polynomial expansion of the scattering factor in terms of $\sin \theta / \lambda$. The coefficients of the terms in these equations were obtained by using a polynomial curve fitting programme also run on the "1620" (W.R. Graves, I.B.M. file number 7.0.001).

B Description of the Programme

In order to facilitate explanation of this programme reference should be made to the Flow Chart given in Fig. 36. This description closely follows this block diagram so that correlation between the chart and the programme listed at the end of this Appendix is easily made.

The constants that were stored at the beginning of the programme were 2π , the squares of the cell dimensions, and the coefficients

of the sixth degree polynomials used to calculate the scattering factors for Si^{+4} , Al^{+3} and O^{-2} . These constants were as follows:

	Si ⁺⁴	Al ⁺³	O ⁻²
2 = 6.283186	A0 = 9.99543	B0 = 9.98324	C0 = 10.0393
a ² = 55.8906	A1 = 0.195043	B1 = 0.95214	C1 = -16.8775
b ² = 58.7676	A2 = -23.3760	B2 = -36.9209	C2 = -65.1891
c ² = 33.2122	A3 = 7.25941	B3 = 38.9954	C3 = 287.178
	A4 = 31.4735	B4 = 0.757586	C4 = -427.181
	A5 = -32.0954	B5 = -18.32297	C5 = 286.020
	A6 = 9.22637	B6 = 6.87218	C6 = -72.6295

The temperature factors of the atoms were read into the computer first. These were punched onto paper tape along with the atomic coordinates since they were all entered at the same place in the programme. Allowance was made for possible differences in temperature factors for Si , Al_I , Al_II and O . Only isotropic temperature corrections were incorporated into this programme. The atomic coordinates for one prototype of each structurally different atom were entered since the use of the general structure factor equation from the International Tables of X-ray Crystallography (Vol. I) allows for the symmetry of the related positions in the space group Pbnm .

At this point of the programme, depending upon which zone of structure factors was being calculated ($hk0$, $h0l$ or $0kl$), provision was made to keep one of the Miller Indices constantly zero. The example shown in the listing at the end of the appendix is for the calculation of F_{hk0} so that $l = 0$. Throughout the programme, in order to keep all calculations in the floating point system, h , k and l have been replaced by P , Q and R respectively.

The indices h, k, l are generated by "DO" statements. The index that varies least is designated by "H" while the one varying most is designated by "K" in the flow chart. This double looping generated by two "DO" statements caused the computations of all structure factors up to the arbitrarily imposed limit of $\sin \theta / \lambda = 1.2$. The test for the limit of $\sin \theta / \lambda$ was done by first calculating $\sin \theta / \lambda$ from the indices and the orthorhombic spacing formula $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$ and then testing whether its value was greater than 1.2. If the value of $\sin \theta / \lambda$ was less than 1.2, the structure factor for that plane was computed but if the value was greater than 1.2 the computations were bypassed and the "K" index incremented by 1 and the test applied again.

Having already determined the value of $\sin \theta / \lambda$ for the particular plane that had been generated by the looping, the next section of the programme computed the scattering factors for the 3 chemical atoms Si^{+4} , Al^{+3} and O^{-2} . Following the evaluation of these three polynomials of the sixth degree, the scattering factor values were then corrected for the thermal motion by multiplying each scattering factor by $1/e^{-B(\sin \theta / \lambda)^2}$.

Using these thermally corrected values of the scattering factors of the atoms the contribution of each atom to the structure factor for the particular plane was calculated by the equation given at the beginning of this appendix. After all contributions were calculated the total structure factor was computed by summing these seven terms. Finally, the indices of the plane, $\sin \theta / \lambda$ and the structure factor for that plane were printed on the typewriter. When

the value of "H" had reached its maximum, the computations were stopped and the programme was terminated.

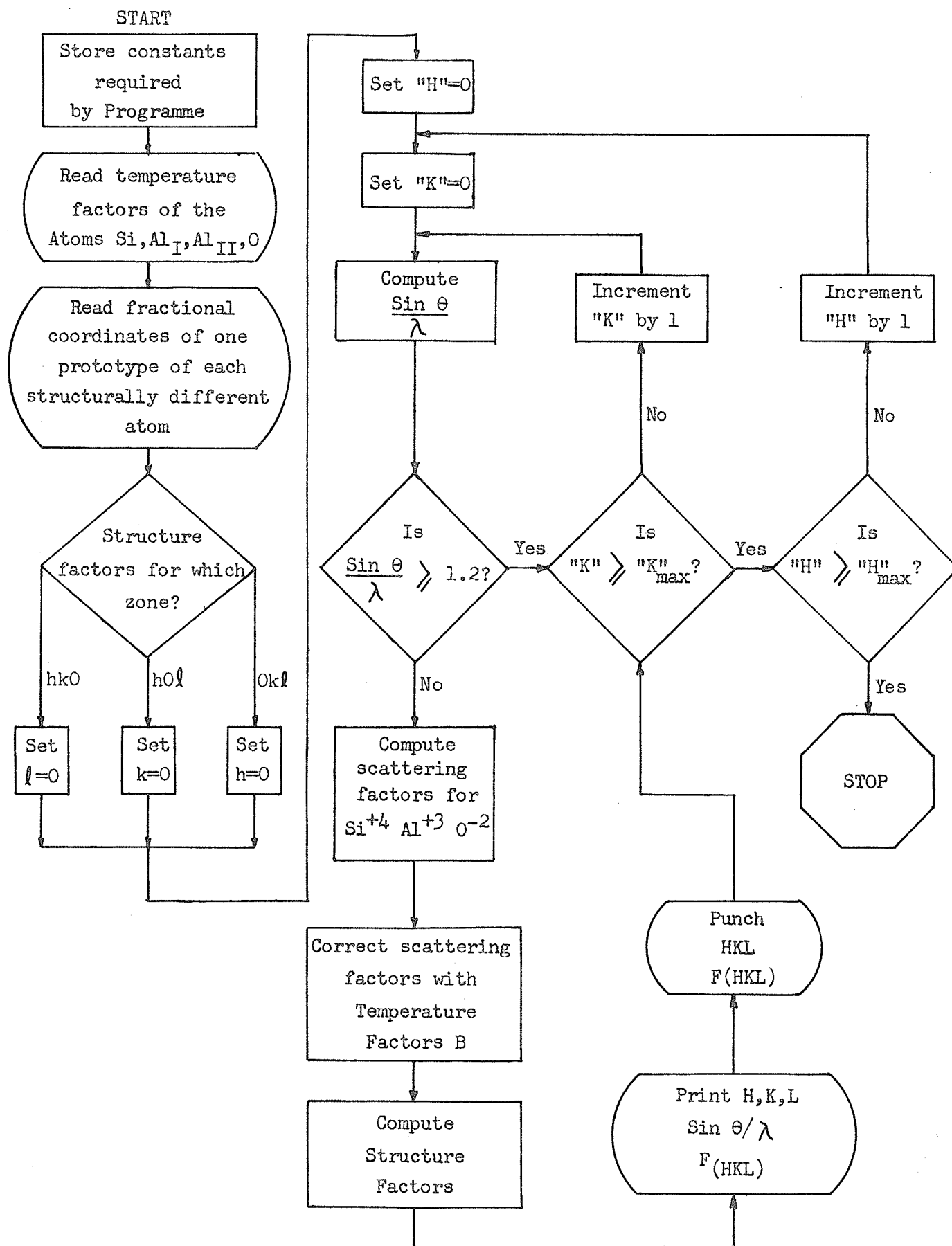
During the compilation of the source programme into machine language a trace feature was incorporated into the object programme. This factor allowed the operator to follow a complete cycle in the calculation of a single structure factor so that each step was typed and any error in the programme could be detected. "FORTRAN" sub-routines were also incorporated into the object programme so that the different arithmetic and trigonometric commands could be executed by the computer.

This programme was run successfully for the three zones $hk0$, $h0l$ and $0kl$. A representative number of structure factors computed for the three zones were checked by hand calculation by the author and the computed values were found to be correct. The computing time for each structure factor was approximately seven seconds. No provision was made to omit the printing of the structure factors of the systematically extinct reflections of the space group. A typical out-put for the $hk0$ reflections has been included following the listing of the programme in FORTRAN language at the end of this appendix. The atomic parameters for this calculation were those of Taylor (1928).

Fig. 36

FLOW CHART OF IBM 1620 PROGRAMME FOR STRUCTURE FACTORS

FOR SPACE GROUP Pbnm



FORTRAN LANGUAGE LISTING OF PROGRAMME
TO COMPUTE F_{hk0} VALUES FOR SILLIMANITE

```

READ, BSI, BAL1,BAL2,BOX
READ,XSI,YSI,ZSI,XAL1,YAL1,ZAL1,XAL2,YAL2,ZAL2
READ,XOX1,YOX1,ZOX1,XOX2,YOX2,ZOX2,XOX3,YOX3,ZOX3
READ,XOX4,YOX4,ZOX4

1 R=0.0
DO 10 I=1,21
P=I-1
DO 10 J=1,21
Q=J-1
GO TO 99
99 ASPAC=((P**2)/55.8906)+((Q**2)/58.7676)+((R**2)/33.2122)
SNTL2=(1./4.)*ASPAC
SINTL=SQR(SNTL2)
ZZ=1.2001-SINTL
IF(ZZ)10,10,89
89 CONTINUE
Z1=SINTL
Z2=Z1**2
Z3=Z2*Z1
Z4=Z2**2
Z5=Z2*Z3
Z6=Z3**2
SF5I=9.99543+A1*Z1+A2*Z2+A3*Z3+A4*Z4+A5*Z5+A6*Z6
SFAL=9.98324+B1*Z1+B2*Z2+B3*Z3+B4*Z4+B5*Z5+B6*Z6
SFOX=10.0393+C1*Z1+C2*Z2+C3*Z3+C4*Z4+C5*Z5+C6*Z6

```

```

SSFSI=SFBI*(1./(EXP(BSI*SNTL2)))
S1FAL=SFAL*(1./(EXP(BAL1*SNTL2)))
S2FAL=SFAL*(1./(EXP(BAL2*SNTL2)))
SSFOX=SFOX*(1./(EXP(BOX*SNTL2)))
X=(P+Q)/4.
Y=(P+Q+R)/4.
Z=R/4.
RRSI=4.*SSFSI*COS(PI*(P*XSI+X))
SSSI=COS(PI*(Q*YSI-Y))
TTSI=COS(PI*(R*ZSI+Z))
FSI=RRSI*SSSI*TTSI
RRAL1=4.*S1FAL*COS(PI*(P*XAL1+X))
SSAL1=COS(PI*(Q*YAL1-Y))
TTAL1=COS(PI*(R*ZAL1+Z))
FAL1=RRAL1*SSAL1*TTAL1
RRAL2=4.*S2FAL*COS(PI*(P*XAL2+X))
SSAL2=COS(PI*(Q*YAL2-Y))
TTAL2=COS(PI*(R*ZAL2+Z))
FAL2=RRAL2*SSAL2*TTAL2
RROX1=4.*SSFOX*COS(PI*(P*XOX1+X))
SSOX1=COS(PI*(Q*YOX1-Y))
TTOX1=COS(PI*(R*ZOX1+Z))
FOX1=RROX1*SSOX1*TTOX1
RROX2=4.*SSFOX*COS(PI*(P*XOX2+X))
SSOX2=COS(PI*(Q*YOX2-Y))
TTOX2=COS(PI*(R*ZOX2+Z))
FOX2=RROX2*SSOX2*TTOX2
RROX3=4.*SSFOX*COS(PI*(P*XOX3+X))
SSOX3=COS(PI*(Q*YOX3-Y))

```

```
TTOX3=COS(PI*(R*ZOX3+Z))
FOX3=RROX3*SSOX3*TTOX3
RROX4=8.*SSFOX*COS(PI*(P*XOX4+X))
SSOX4=COS(PI*(Q*YOX4-Y))
TTOX4=COS(PI*(R*ZOX4+Z))
FOX4=RROX4*SSOX4*TTOX4
FHKL=FSI+FAL1+FAL2+FOX1+FOX2+FOX3+FOX4
L=P
M=Q
N=R
PRINT, L,M,N,SINTL,FHKL
PUNCH,L,M,FHKL
10 CONTINUE
END
```

EXAMPLE OF OUTPUT FROM PROGRAMME TO COMPUTE F_{hk0}

h	k	l	$\sin \Theta / \lambda$	$F_{(hk0)}$	
0	0	0	.00000000	320.63364	
0	1	0	6.52E-02	-9.44E-06	extinct
0	2	0	.1304	9.95	
0	3	0	.1957	-1.79E-05	extinct
0	4	0	.2609	-44.15	
0	5	0	.3261	-8.28E-06	extinct
0	6	0	.3913	96.89	
0	7	0	.4566	-2.96E-05	extinct
0	8	0	.5218	7.30	
0	9	0	.5870	1.99E-05	extinct
0	10	0	.6522	-21.20	
0	11	0	.7174	2.69E-06	extinct
0	12	0	.7827	34.84	
0	13	0	.8479	-3.31E-05	extinct
0	14	0	.9131	8.34	
0	15	0	.9783	4.43E-07	extinct
0	16	0	1.044	-15.23	
0	17	0	1.109	1.65E-05	extinct
0	18	0	1.174	6.17	

h	k	l	$\sin \theta / \lambda$	$F_{(hkl)}$	
1	0	0	6.688E-02	1.27E-05	extinct
1	1	0	9.342E-02	42.86	
1	2	0	.1466	-46.27	
1	3	0	.2068	10.99	
1	4	0	.2693	27.53	
1	5	0	.3329	11.54	
1	6	0	.3970	9.96	
1	7	0	.4614	16.56	
1	8	0	.5261	-13.86	
1	9	0	.5908	23.67	
1	10	0	.6557	16.69	
1	11	0	.7206	17.50	
1	12	0	.7855	1.73	
1	13	0	.8505	16.57	
1	14	0	.9156	-8.76	
1	15	0	.9806	8.23	
1	16	0	1.046	1.85	
1	17	0	1.111	2.87	
1	18	0	1.176	-1.50	
2	0	0	.1338	17.17	
2	1	0	.1488	57.84	
2	2	0	.1868	61.55	
2	3	0	.2370	-13.42	
2	4	0	.2932	60.76	
2	5	0	.3525	-72.94	

h	k	l	$\sin \theta/\lambda$	$F_{(hkl)}$
2	6	0	.4136	6.92
2	7	0	.4758	25.21
2	8	0	.5387	15.00
2	9	0	.6021	19.26
2	10	0	.6658	23.29
2	11	0	.7298	-23.33
2	12	0	.7940	2.26
2	13	0	.8584	-1.83
2	14	0	.9229	0.16
2	15	0	.9874	7.80
2	16	0	1.052	8.14
2	17	0	1.117	-4.52
2	18	0	1.182	3.83

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