THE X-RAY CRYSTALLOGRAPHY OF CALCIUM PHOSPHATES: THE STRUCTURES OF DICALCIUM PHOSPHATE AND MONOCALCIUM PHOSPHATE MONOHYDRATE.

Thesis for the degree of Ph.D.

submitted by

George MacLennan, B.Sc.

University of Edinburgh

September 1955

CONTENTS

General Introduction

One of the major fields of research in modern soil chemistry is concerned with the nature and proportions of the various phosphate minerals present in the soil, and applied as fertilizers. Phosphorous is an essential plant food whose chief natural source is the calcium phosphate mineral, apatite. Unfortunately apatite itself cannot easily be absorbed by the plant roots and chemical treatment is essential to produce a suitable fertilizer. The best methods of chemical treatment, from the point of view of industrial practicability, and availability as plant foods of the treated phosphate rock, have recently been the subject of much discussion among agricultural chemists. The complex nature of many calcium phosphate precipitates and the difficulty and tedium of adequate field studies have led to a demand for detailed knowledge of the structures of certain calcium orthophosphates, in the hope that this might lead to a more exact knowledge of the phases likely to be present in fertilizers and in the soil, and, in addition, throw light on the possible ease of transformation reactions between different but related structures.

A programme of research into these structures has been undertaken in collaboration with the Research Department of Scottish Agricultural Industries. The structures of fluorapatite (1) and of dicalcium phosphate dihydrate (2) have already been determined.

This thesis describes structural determinations on two further orthophosphates of particular interest in fertilizer manufacture, namely anhydrous dicalcium phosphate, $CaHPO_4$, and monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2H_2O$. The former is the phase most likely to be present in compound fertilizers whose manufacture involves the use of free ammonia or nitric acid, such as ammoniated superphosphate and "Nitro-Phosphate". These preparations are of especial interest in view of the current world shortage of sulphur, since sulphuric acid is not necessary for their manufacture. The alternatives mentioned are expensive, however, and for economy it is desirable not to carry the conversion of apatite to dicalcium phosphate any further than is necessary to obtain a product with similar properties to the latter. Hence the structure of dicalcium phosphate, considered in relation to that of apatite, will throw light on the possible nature of the phases present in precipitated solids with Ca/P ratios between 1.66 (apatite) and 1.0 (dicalcium phosphate).
Eisenberger (3) and Arnold (4) have suggested, for

example, that there might be a series of solid solutions over part at least of this range.

Monocalcium phosphate monohydrate, on the other hand, is the phase present (5) in the ordinary superphosphate fertilizer produced by the action of sulphuric acid on apatite rock. The possibility of a structural analogy with dicalcium phosphate dihydrate has recently been pointed out (6) on morphological evidence. In any case it is to be anticipated from chemical theory and the known structures of related compounds that both calcium phosphates mentioned consist of a network of tetrahedra formed by the $PO_4^{'''}$ ion, alternating with Ca^{++} ions in the centre of a coordination shell of between six and nine oxygen atoms. The structure will be further bound by hydrogen bonds between oxygens of neighbouring tetrahedra, and with any water molecules. In dicalcium phosphate there is one hydrogen to every four oxygens, so that only half the oxygens can be linked by hydrogen bonds, but in the monocalcium phosphate there are sufficient hydrogen atoms to enable every oxygen to take part in hydrogen bonding.

The crystal structures of several ortho-phosphates have previously been determined, the phosphate ion in each being found to be tetrahedral. The mean P - O distance reported has varied slightly. In KH_2PO_4 (7) it was 1.55A; in BPO_4 (8) it was

1.54A, and in Ag_3PO_4 (9) it was 1.61A. Recently, the structure of the parent orthophosphoric acid, H_3PO_4, has been published (10), the mean P - O distance being 1.56A. Individual bond lengths and angles have usually been found to vary appreciably; some of these variations may be significant and related to packing distortions.

The structure of fluorapatite, $Ca_5F(PO_4)_3$, which is isomorphous with hydroxyapatite, $Ca_5OH(PO_4)_3$, has been determined, (11, 1). The crystal possesses hexagonal symmetry. Chains of Ca atoms lie along three-fold axes in the c direction, each coordinated by nine oxygens belonging to phosphate tetrahedra, which link the chains transversely. These linkages produce a hexagonal network, like a honeycomb, with open channels through in the c direction. Further Ca^{++} ions fit into the walls of these channels, being partly coordinated by six oxygens belonging to the columns, and partly by the F or OH ions which occupy the centre of the open channels, lying on six-fold screw axes. The total calcium coordination is thus seven, as compared to nine for the "chain" calciums.

The only other calcium orthophosphate structure fully determined is that of dicalcium phosphate dihydrate, $CaHPO_4,2H_2O$, a preliminary account of which

has been published (2). The crystals are monoclinic and the structure is similar to that of the almost isomorphous gypsum, $CaSO_4,2H_2O$ (12). It consists of sheets in the a c plane, containing parallel chains of $= PO_4 = Ca = PO_4 = Ca =$. Adjoining chains are related by centres of symmetry, and differ in height along the b axis by 2.3A to give a corrugated effect. The sheets are repeated at a distance of b/2 by vertical screw axes, and are separated by water molecules which link the sheets in the b direction. The calcium ion has a coordination of eight (six oxygens from PO_4 tetrahedra, and two water molecules).

The unit cells of both dicalcium phosphate and monocalcium phosphate monohydrate have been determined (6) and accurate intensity measurements of their respective X-ray powder patterns, using a micro-densitometer, have also been published (13).

In the present investigation, the structural determinations have been tackled, as far as possible, independently of chemical postulates. Only the numbers and scattering powers of the atoms involved, and, in the case of $CaHPO_4$, the approximate length of the PO_4 bond, were assumed.

Part 1: The Structure of Dicalcium Phosphate

1. Introduction

Calcium hydrogen orthophosphate, $CaHPO_4$, exists in the anhydrous and dihydrated forms. The crystal structure of the latter, the mineral brushite, has been determined (2). The anhydrous salt, which occurs in nature as the uncommon mineral monetite, is commonly known as dicalcium phosphate from the old double-oxide formulation $2CaO,H_2O,P_2O_5$. Its crystal morphology was first described by A. de Schulten (14), who found it to be triclinic pinacoidal. The optical properties and cell dimensions have been determined by Lehr, Smith and Brown (6).

In the presence of water below 25°C, $CaHPO_4$ is converted to the dihydrate (15), but the anhydrous crystals are not appreciably decomposed at room temperature if kept dry.

2. Unit Cell Dimensions and Space Group

Experimental

Exceptionally pure crystals of anhydrous dicalcium phosphate were kindly made available for this investigation by the Research Department of the Tennessee Valley Authority. Single prismatic crystals of maximum length 0.5 mm. were selected and mounted on glass fibres by a touch of shellac dissolved in alcohol. Their habit is shown in Figure 1. Complete sets of 20° oscillation and Weissenberg layer-line photographs were obtained, using a Newton Victor Raymax X-ray unit and a 5 cm. radius, vertical travel, normal beam Weissenberg camera. The X-ray tube was run at 25mA., 50Kv. peak voltage with Cu $K\alpha$ radiation, the $K\beta$ wavelength being absorbed by a nickel filter. The diffracted beams were recorded on Ilford Industrial G X-ray film, developed for 5 minutes in Ilford ID19 X-ray developer.

Unit Cell Dimensions

The unit cell dimensions were obtained from high-order (okl), (hol) and (hko) reflections, a weighted mean of values obtained from all the suitable reflections being taken. There were sufficient of these to enable the method of extrapolation to $\sin\theta = 1$ to be employed, but film

shrinkage errors were minimized by taking sin θ measurements from the shadow cast on the film by a knife-edge set at an accurately known value of θ near 90°. The mean value of measurements on each half of the film was used, and only reflections within 14° of the knife-edge were employed.

The reciprocal cell, obtained in this way, is tabulated below.

$a^* = 0.2301$	$\alpha^* = 83°46'$
$b^* = 0.2332$	$\beta^* = 76° 9'$
$c^* = 0.2281$	$\gamma^* = 89°44'$

The corresponding cell in crystal space, expressed in absolute Angstrom units, is:

$a = 6.90 \pm 0.01$A	$\alpha = 96°21'$
$b = 6.65 \pm 0.01$A	$\beta = 103°54'$
$c = 7.00 \pm 0.01$A	$\gamma = 88°44'$

$V = 309.5 A^3$

With four formula weights of $CaHPO_4$ in the cell, the calculated density is 2.902gm./c.c., compared to observed values of 2.928gm./c.c. (14) and 2.892gm./c.c. (16). The cell dimensions agree substantially with those previously reported (6), viz.:

a = 6.91A	$\alpha = 96°7'$
b = 6.66A	$\beta = 103°53'$
c = 7.02A	$\gamma = 89°11'$

The primitive cell has been chosen correctly to

obtain the shortest and most nearly orthogonal axes, but this has involved γ being below 90°, which is not in accordance with the arbitrary convention for the triclinic system. The corresponding "reduced primitive cell" with all angles obtuse, is:

a = 6.90A	α = 136°36'
b = 6.65A	β = 127°30'
c = 8.56A	γ = 91°16'

This, however, involves a longer c axis, and the original lattice has been retained for convenience during the present investigation.

Intensity Measurement

The intensities of diffracted beams from nearly all the planes in the reflecting sphere were estimated visually by comparison of multiple-exposure Weissenberg photographs of the zero, first, second and third layer lines. The intensities were corrected for Lorentz and polarization factors by the graphical method of Cochran (17). The small irregularly-shaped crystals precluded any correction for the rather high absorption. An attempt was made to place the intensities for the three two-dimensional zones on an absolute scale by the statistical treatment of Wilson (18), but this proved unsatisfactory, probably because of the absorption and the insufficient "randomness" of the structure. All

the curves obtained showed pronounced minima, and this was also true with $Ca(H_2PO_4)_2H_2O$. The absorption effect also prevented any reliable measurement of the temperature factor. The general intensities, $F^2(hkl)$, were therefore left on an arbitrary scale. They are listed in Table I.

Table 1. $F^2(hkl)$ on arbitrary scale.

$l = 0$

h \ k	0	1	2	3	4	5	6	7	8
0	-	0	5	16	7	4	1	0	5
1	0	0	22	10	0	0	4	8	4
2	32	1	1	0	0	13	11	1	4
3	4	13	3	2	1	5	8	4	
4	0	2	3	2	4	0	0	6	
5	7	3	10	1	0	7	8		
6	9	0	0	3	10	1	2		
7	1	3	8	1	0				
8	10	2	0	1					
$\bar{1}$	0	0	25	4	0	4	0	8	3
$\bar{2}$	32	2	4	0	10	6	11	1	3
$\bar{3}$	4	4	48	0	16	1	0	0	
$\bar{4}$	0	2	0	1	6	0	22	2	
$\bar{5}$	7	0	0	0	5	0	6		
$\bar{6}$	9	0	0	5	3	0	36		
$\bar{7}$	1	0	3	0	3				
$\bar{8}$	10	2	3	1					

$l = 1$

h \ k	0	1	2	3	4	5	6	7	8
0	2	1	2	2	11	4	12	3	1
1	2	5	4	0	5	0	11	8	
2	24	3	22	12	14	10	6		
3	16	4	18	7					
4	30	0	2	0					
5	15	3	11	7					
6	38	5	0	0					
7	0	3	7						
8	6	2							
$\bar{1}$	0	2	12	1	11	9	18	3	10
$\bar{2}$	16	4	2	2	4	2	11	0	
$\bar{3}$	4	12	3	2	3	0	10	2	
$\bar{4}$	28	1	0	2	0	6	7	0	
$\bar{5}$	0	0	12	0	2	0	0		
$\bar{6}$	35	0	8	4	4	0	3		
$\bar{7}$	1	0	10	0	5				
$\bar{8}$	4	1	4	0					

l = 2

h \ k	0	1	2	3	4	5	6	7	8
0	25	5	12	6	2	3	0	2	3
1	14	2	12	23	10	2	12	1	
2	0	16	2	1	9	2	0	6	
3	0	0	2	1	0	5	9		
4	1	0	2	1					
5	15	5	12	4					
6	2	6	0	1					
7	8	1	4						
$\bar{1}$	5	3	17	22	0	0	0	5	
$\bar{2}$	38	2	0	2	15	8	6	0	
$\bar{3}$	2	2	55	3	16	6	7	1	
$\bar{4}$	28	3	2	5	16	3	2	2	
$\bar{5}$	4	0	12	0	0	1	10		
$\bar{6}$	1	0	0	0	6	0			
$\bar{7}$	0	0	2	1	0				
$\bar{8}$	5	0	0						

l = 3

h \ k	0	1	2	3	4	5	6	7
0	21	0	6	13	30	9	0	8
1	2	0	26	10	4	5		
2	30	22	3	8				
3	8	0	32	6				
4	14	11	0	3				
5	0	0	3	2				
6	4	7	1	0				
7	0	3						
$\bar{1}$	16	3	26	6	0	18	8	1
$\bar{2}$	0	4	8	4	7	12	0	9
$\bar{3}$	0	4	0	1	0	9	9	0
$\bar{4}$	15	3	0	0	0	0	4	
$\bar{5}$	18	0	16	0	0	0		
$\bar{6}$	48	0	0	5	6	0		
$\bar{7}$	1	0	8	0	0			
$\bar{8}$	10	0	0					

$l = 4$

h \ k	0	1	2	3	4	5	6	7
0	3	8	0	0	0	0	1	2
1	4	4	11	3	15	3		
2	0	0	0	4				
3	2	6	1	5				
4	4	5	12	1				
5	4	0	4	4				
6	2	8	3					
$\bar{1}$	14	7	4	6	2	0	0	0
$\bar{2}$	13	2	0	1	7	4	5	
$\bar{3}$	18	4	13	17	0	10	0	
$\bar{4}$	21	10	1					
$\bar{5}$	0	0	11					
$\bar{6}$	4	3						
$\bar{7}$	0	2						
$\bar{8}$	2	0						

$l = 5$

h \ k	0	1	2	3	4	5	6
0	1	17	5	0	10	12	4
1	4	5	6	15	0		
2	4	36	1	0			
3	17	1	4	6			
4	2	8	0				
5	0	0					
$\bar{1}$	2	0	12	21	2	5	2
$\bar{2}$	0	0	1	0	8	18	0
$\bar{3}$	2	1	11	2	2	6	
$\bar{4}$	4	7	0				
$\bar{5}$	21	2	4				
$\bar{6}$	4	8					
$\bar{7}$	4	0					
$\bar{8}$	7	0					

l = 6

h \ k	0	1	2	3	4	5
0	0	16	0	0	0	4
1	0	0	0	4	8	
2	0	3	0	0		
3	0	3	0			
4	0	9	1			
$\bar{1}$	1	2	0	0	2	3
$\bar{2}$	1	17	0	4	0	0
$\bar{3}$	19	5	8	21	0	
$\bar{4}$	4	17	0			
$\bar{5}$	4	4	6			
$\bar{6}$	4	2				
$\bar{7}$	0	1				
$\bar{8}$		0				

$l = 7$

h \ k	0	1	2	3	4
0	0	10	2	0	2
1	0	11	0	6	
2	0	6	0		
3	8	7			
$\bar{1}$	0	3	0	15	0
$\bar{2}$	0	8	0	0	0
$\bar{3}$	0	0	6	18	
$\bar{4}$	3	0	0		
$\bar{5}$	3	0			
$\bar{6}$	0	8			
$\bar{7}$	5				

$l = 8$

h \ k	0	1	2
0	0	1	0
1	0	1	0
2	0		
$\bar{1}$	0	0	
$\bar{2}$	0	8	0
$\bar{3}$	5	7	
$\bar{4}$	0	16	
$\bar{5}$	2	5	

$1 = \bar{1}$

h \ k	0	1	2	3	4	5	6	7	8
0	2	2	3	20	10	0	28	1	0
1	0	1	12	5	8	0	20	2	6
2	16	0	2	1	21	4	14	6	2
3	4	4	33	1	31	4	4	4	
4	28	0	2	1	15	15	9	4	
5	0	0	10	9	6	0	0	6	
6	35	2	10	0	0	5	0		
7	1	0	3	8	2	0			
8	4	6	0	2					
$\bar{1}$	2	2	0	3	1	0	7	4	10
$\bar{2}$	24	2	4	1	2	11	10	0	1
$\bar{3}$	16	3	17	0	0	7	1	1	
$\bar{4}$	30	3	7	1	7	6	0	1	
$\bar{5}$	15	4	16	1	6	0			
$\bar{6}$	38	0							
$\bar{7}$	0	0							
$\bar{8}$	6	2							

$l = \bar{2}$

h \ k	0	1	2	3	4	5	6	7	8
0	25	1	18	0	1	0	11	1	0
1	5	9	3	3	4	2	0	7	2
2	38	0	2	0	0	17	2	3	1
3	2	1	6	5	2	0	3	0	
4	28	3	2	0	4	11	10	0	
5	4	0	0	12	8	1	7		
6	1	5	2	0	4	0	2		
7	0	0	4	2	5	0			
8	5	0	0	0					
$\bar{1}$	14	0	6	2	14	0	4	5	0
$\bar{2}$	0	2	18	6	5	0	17	3	
$\bar{3}$	0	7	14	0	28	1	0		
$\bar{4}$	1	0	0	1					
$\bar{5}$	15	0	0	1					
$\bar{6}$	2	3							
$\bar{7}$	8	0							

$l = \bar{3}$

h \ k	0	1	2	3	4	5	6	7	8
0	21	13	4	17	2	2	32	0	4
1	16	6	0	1	16	2	0	0	
2	0	0	14	12	1	5	24	2	
3	0	15	18	0	26	0	0	1	
4	15	3	3	3	5	4	6	0	
5	18	1	13	0	4	0	4		
6	48	1	10	0	3	6	0		
7	1	2	5	7	0				
8	10	1	0						
$\bar{1}$	2	1	10	4	10	6	1	0	1
$\bar{2}$	30	6	9	4	0	2	4	1	
$\bar{3}$	8	10	9	7	2	0	0		
$\bar{4}$	14	0	10	9	2	0	1		
$\bar{5}$	0	29	5	10					
$\bar{6}$	4	0	0	4					
$\bar{7}$	0	4							

$l = \bar{7}$

h \ k	0	1	2	3	4	5	6	7	8
0	3	3	25	9	8	4	11	7	0
1	14	13	8	12	0	0			
2	13	0	9	2	7	4			
3	18	4	10	4	5	14			
4	21	0	3	1					
5	0	0	0	3					
6	4	0	4	4					
7	0	0	5	2					
8	2	0	5						
$\bar{1}$	4	4	3	2	17	8	2	4	
$\bar{2}$	0	3	5	14	0	8	8	0	
$\bar{3}$	2	9	0	3	19	8	0		
$\bar{4}$	4	0	0	2					
$\bar{5}$	4	0	0	0					
$\bar{6}$	2								

$l = \bar{5}$

h \ k	0	1	2	3	4	5	6	7
0	1	1	2	0	0	4	4	5
1	2	0	2	0				
2	0	5	18	1	0			
3	2	5	0	0	16			
4	4	-	13	6				
5	21	-	3	2				
6	4	-	10	3				
7	4	-	3	3				
8	7							
$\bar{1}$	4	6	0	0	0	4	8	0
$\bar{2}$	4	3	15	3	0	0		
$\bar{3}$	17	26	1	6	8			
$\bar{4}$	2	6	-	1				
$\bar{5}$	0							

$l = \bar{6}$

h \ k	0	1	2	3	4	5	6
0	0	4	11	11	0	8	6
1	1	24	0	13			
2	1	6	10	3	6	0	
3	19	14	1	10	6	4	
4	4	-	10	0			
5	4	-	6	2			
6	4	-	0	2			
7	0	-	0				
$\bar{1}$	0	15	0	2	12	2	0
$\bar{2}$	0	0	0	5	7	1	4
$\bar{3}$	0	0	0	1			
$\bar{4}$	0						

$l = \bar{7}$

h \ k	0	1	2	3	4	5
0	0	3	6	0	5	0
1	0	1	3	1		
2	0	0	0	3	6	
3	0	6	6	7	2	
4	3	-	0	4		
5	3	-	0	4		
6	0	-	5			
7	5					
$\bar{1}$	0	11	0	7	3	0
$\bar{2}$	0	10	1	0	0	
$\bar{3}$	8					

$l = \bar{8}$

h \ k	0	1	2	3	4
0	0	9	0	0	7
1	0	4	0	6	
2	0	8	0		
3	5	18	2		
4	0	-	2		
5	2				
$\bar{1}$	0	0	0	0	0
$\bar{2}$	0				
$\bar{3}$	0				

Space Group

The crystals of $CaHPO_4$ belong to the triclinic system, and the choice of space group depends only upon the presence or absence of a centre of symmetry. The crystal morphology (Figure 1) suggests the presence of a centre, and this was confirmed by an application to the (hko) zone of the statistical analysis of reflection intensities described by Howells, Phillips and Rogers (19). The method consists in tabulating the fractions N(z) of reflections whose intensities are equal to or less than a fraction z of the local average. The graph of N(z) against z differs considerably for centred and non-centred distributions, especially where z is small. Comparison (Figure 2) of the observed values with the calculated curves clearly indicates that a centre of symmetry is present. The space group of $CaHPO_4$, therefore, is $P\bar{1}$.

3. Structure Determination

Interpretation of Patterson Synthesis

In the space group $P\bar{1}$, the general positions are twofold, and since there are two $CaHPO_4$ molecules in the unique volume of the cell, all the atoms can be in general positions. Apart from hydrogen atoms, which are unlikely to be discoverable by X-ray methods in the presence of Ca and P atoms, there are 12 independent atoms whose positions are defined by 36 parameters. However since there are only four unique heavy atoms, giving rise to 16 interatomic vectors, Patterson syntheses seemed promising. This well-known method involves computing a Fourier series whose coefficients are the squares of the moduli of the structure factors, the resulting function representing the interatomic vectors in the crystal. Since all the vectors are erected from the origin, interpretation in terms of atomic arrangement is normally difficult; but if the structure contains a minority of heavy atoms, the vectors due to their interactions are easily distinguishable since the vector peak height is proportional to the product of the scattering powers of the atoms involved.

Two-dimensional Patterson functions projected down each of the three axes were computed (see Appendix for equations used). Unfortunately no useful information was gained from these maps, the heavy atom vectors being obscured by the large number of other interatomic vectors superposed on them in the relatively small areas of projection. This difficulty was not unexpected, and it was decided that in order to interpret the structure by vector methods it would be necessary to resolve all the vectors in three dimensions. This meant the computation of the general Patterson function, using all the (hkl) intensities. The function was expanded for computation as shown in the Appendix, and the work proceeded in three stages, the summations being taken in turn over h, k and l, and expressed as a function of X, Y and Z, at intervals of $^{1}/_{30}$th of each of these. The function P(X, Y, Z) was therefore evaluated at just over 15,000 points contained in the unique half of the unit cell. It was drawn out in 16 sections parallel to the b c plane, contours being drawn at arbitrary levels. The sections at X = 2, 6 and 8 are reproduced here. (Figures 3, 4 and 5).

A list was drawn up of the principal vectors, and a preliminary attempt made to recover the fundamental set of heavy atoms from them by trial

and error methods. This failed, as in many previous instances, principally because the vector peaks are not sharply enough defined to permit their being treated as points, in order to reconstruct their fundamental set graphically, as described, for example, by Lipson and Cochran (20).

The vector convergence method (21) was therefore adopted. This is based on the principle that the Patterson function can be regarded as n patterns of the electron distribution within the crystal, superimposed with each in turn of the n atoms at the origin, and having weight proportional to the atomic number of the nth atom. If there is a minority of heavy atoms in the structure, a particularly high vector peak can be chosen on the assumption that it corresponds to the distance between two heavy atoms. If two Patterson functions are superimposed with their origins at either end of this vector, the images of other atoms in each of the heavy atoms are brought into coincidence on atomic sites. Another vector may then be chosen in a similar way from those not eliminated by the superposition, and the process repeated to eliminate any chance coincidences. There is, however, always the danger that the second chosen vector is itself present in the superposition function only by chance.

In the present case, heavy atoms were assumed to lie at the Patterson origin and at the two outstandingly heavy peaks at (6, 5, 33) and (8, 36, 37). The Patterson function was superposed over the entire cell with these three positions in turn as origin. The coincidence of vectors at once revealed five other heavy atoms at (2, 31, 4), (28, 18, 56), (30, 49, 0), (35, 23, 28) and (36, 54, 33), and a centre of symmetry at (18, 27, 17), showing that the original two vectors had been correctly chosen. Moreover it was possible, by comparing the peak heights carefully, to separate unambiguously the Ca and P atoms. Transferring the origin to the centre of symmetry, the unique Ca atoms are at (42, 33, 43) and (50, 9, 20) and the P atoms at (44, 4, 47) and (48, 38, 16). (All coordinates are quoted in 60ths of the cell edges.) A table is given below comparing the observed peak heights of all the vectors involved with their calculated heights on a roughly equivalent scale.

Peak			Vectors	Theoretical Height	Actual Height
26	37	30	Ca+P	60	70
30	11	59	Ca+P	60	75
28	18	57	(Ca+Ca)+(P+P)	125	120
26	47	53	Ca+P	60	60
22	13	24	Ca+P	60	85
2	31	4	2(Ca-P)	120	110
6	5	33	2(Ca-P)	120	120
8	36	37	Ca-Ca	80	102
4	34	29	P-P	45	60
24	6	26	2Ca	40	43
28	8	34	2P	22	34
24	44	28	2P	22	30
20	42	20	2Ca	40	52

It yet remained to discover the sixteen oxygen atoms. Further study of the superposition function, which had been transferred to tracing paper as a "minimum function" (22), showed that the number of recorded coincidences of medium height was confusingly large. A further superposition, using the P at (2, 31, 4), failed to simplify the choice significantly. The fact was therefore used that the P-O distance in a PO_4 tetrahedron is approximately 1.6A. Spheres of this radius were constructed round the four P atomic positions on the superposition maps, and all coincident

vectors within about 0.2A of the spheres were noted. Pairs of these which were related by the previously-found centre of symmetry were then picked out. Nine pairs were in fact found, of which one corresponded to an atom in a sterically unlikely position near the centre, at (28, 25, 18). The remaining eight gave convincing PO_4 tetrahedra with no gross packing difficulties. All the vectors between the heavy atoms and the oxygens chosen were then calculated and compared with the original Patterson function to ensure, not only that all the vectors were present, but that no significant peaks on the map remained unaccounted for.

Since the agreement between the calculated vectors and the observed distribution was satisfactory, small alterations were then applied to the postulated atomic positions to obtain the best possible overall fit. Shifting the origin to the centre of symmetry at (18, 27, 17), the parameters thus chosen, now in 360ths of the cell edges, were:

Ca_1	108	162	102
Ca_2	66	306	240
P_1	72	132	264
P_2	102	336	78
O_1	120	126	330

O_2	120	174	216
O_3	48	66	210
O_4	18	198	270
O_5	114	300	6
O_6	156	42	114
O_7	42	30	60
O_8	96	282	126

Refinement of Structure

The atomic positions obtained by the vector convergence method were used to calculate structure factors for the (okl) zone. The equations used and methods employed are detailed in the Appendix. An encouraging degree of agreement between observed and calculated structure factors was obtained, the residual error R, defined as

$$R = \frac{\Sigma \| F_{obs.} | - | F_{calc.} \|}{\Sigma | F_{obs.} |}$$

being 0.40. A fourier projection of the electron density down the a axis, using the 77 F_o(okl) terms which could be given signs, showed satisfactory detail and only small shifts. When these were applied, R fell to 0.35. At this stage it was felt desirable to scale F_o to fit F_c over five ranges of sin θ , since the Wilson scaling curve was not felt to be reliable.

Further refinement was carried out by the use of $\Delta F_o - F_c \Delta$ "difference syntheses" as described by Cochran (23). Refinement is accomplished by shifting those atoms which lie on gradients in the synthesis. The atoms are moved up the steepest gradient by an amount given by

$$\Delta x = \frac{\partial \rho}{\partial x} \Big/ 2p\rho_{(o)}$$

where p is an empirical constant for a particular atom. It may be derived from the peak height ρ (o) of the atom in a Fourier synthesis by the equation

$$\rho\ (o) = N(p/\pi)^{3/2}$$

The values derived for p on this basis, from the earlier Fourier map, approximated to 5, and this value was used.

Four successive stages of refinement by difference syntheses were carried out, the residual error being thereby reduced to 0.203. As there were several pairs of atoms not completely resolved in this projection, it was then decided to refine the x parameters using the data for the (hko) zone. Structure factors calculated using the x parameters from the Patterson superposition and the already refined y parameters gave R = 0.51. This is a high figure even for an approximate structure, but a Fourier projection using 82 signed F_o terms gave an encouraging amount of detail (Figure 6). Five

cycles of refinement by difference syntheses improved the agreement to a satisfactory level with R = 0.20. There were, as frequently occur, minor differences in the y parameter of some atoms between the two zones.

Finally, structure factors for the (hol) zone, using the already refined x and z parameters, were calculated, giving an R = 0.23. After one refinement by a difference synthesis, the mean parameters for all atoms from the three refined zones were taken and structure factors using these final parameters recalculated for each zone. The residual errors were then:

R(hko) = 0.193
R(hol) = 0.216
R(okl) = 0.193
Average R = 0.201

These figures include reflections of observed zero intensity, and no corrections have been applied for extinction nor for a temperature factor. It is, however, considered that secondary extinction has been responsible for lessening the observed intensity of several of the strongest reflections, namely (120), ($1\bar{2}0$), (200), (002), (201) and ($0\bar{2}2$).

As a final check on the validity of the structure, it was thought advisable to calculate structure factors for a randomly chosen set of general planes (hkl). For this purpose, the general structure factor equation given in the Appendix must be used, and the calculations are considerably more tedious. A satisfactory degree of agreement was obtained, using the (hk3) intensities, the value of R being 0.285 after the arbitrary F_o values had been scaled directly against F_c. Tables listing observed and calculated F values for the planes (hko), (hol), (okl) and (hk3) are given on a separate page (Table 2).

It was considered that refinement was unlikely to proceed to any further significant extent, in view of the various errors present for which no adequate correction could be made. Apart from the effects of absorption, extinction and temperature, the principal source of error is the inaccurate estimation of intensity by purely visual examination of photographs. It is generally agreed that deviations of at least 5% in the value of F are likely using this method. The only satisfactory alternative is to measure the intensity of each reflection individually using a Geiger counter spectrometer, but this is

Table 2. Values of F_o and F_c for the (h k 0), (h 0 l), (0 k l) and (h k 3) planes of $CAHPO_4$

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
010	0	$\bar{1}$	$2\bar{3}0$	0	1	500	29	$\bar{30}$	810	14	20	207	4	8	$40\bar{6}$	19	$\bar{15}$	$70\bar{7}$	28	$\bar{17}$	$06\bar{2}$	38	38	055	34	$\bar{43}$	213	64	65	$\bar{3}33$	13	$\bar{7}$
020	32	25	$24\bar{0}$	39	41	510	21	$\bar{20}$	820	3	7	208	0	1	$40\bar{7}$	16	15	801	28	$\bar{13}$	$07\bar{2}$	10	$\bar{12}$	065	20	17	313	0	1	$\bar{4}33$	0	7
030	51	$\bar{51}$	$25\bar{0}$	27	$\bar{20}$	520	37	$\bar{38}$	830	10	15	$20\bar{1}$	54	$\bar{64}$	$40\bar{8}$	5	2	$80\bar{1}$	20	17	$08\bar{2}$	7	$\bar{4}$	$01\bar{5}$	11	6	413	42	$\bar{36}$	$\bar{5}33$	0	0
040	33	$\bar{31}$	$26\bar{0}$	35	32	530	12	$\bar{6}$	$81\bar{0}$	12	$\bar{12}$	$20\bar{2}$	78	77	501	36	$\bar{33}$	$80\bar{2}$	23	28	013	0	0	$02\bar{5}$	19	$\bar{16}$	513	0	$\bar{5}$	$\bar{6}33$	28	$\bar{34}$
050	23	14	$27\bar{0}$	12	$\bar{8}$	540	8	$\bar{9}$	$82\bar{0}$	16	$\bar{18}$	$20\bar{3}$	0	2	502	35	30	$80\bar{3}$	33	$\bar{37}$	023	30	$\bar{31}$	$03\bar{5}$	0	$\bar{6}$	613	32	27	$\bar{7}33$	0	8
060	10	7	$28\bar{0}$	15	12	550	28	27	$83\bar{0}$	7	$\bar{3}$	$20\bar{4}$	38	$\bar{37}$	503	7	6	$80\bar{4}$	16	$\bar{19}$	033	44	$\bar{37}$	$04\bar{5}$	6	6	713	20	18	143	24	$\bar{18}$
070	6	$\bar{6}$	300	24	18	560	27	29	001	21	$\bar{20}$	$20\bar{5}$	0	$\bar{1}$	504	20	$\bar{20}$	$80\bar{5}$	30	31	043	67	$\bar{57}$	$05\bar{5}$	21	20	$\bar{1}13$	24	$\bar{31}$	$\bar{1}43$	6	8
080	16	$\bar{24}$	310	47	$\bar{44}$	$51\bar{0}$	0	3	002	62	$\bar{89}$	$20\bar{6}$	8	9	505	0	$\bar{6}$	011	10	10	053	33	29	$06\bar{5}$	21	$\bar{16}$	$\bar{2}13$	27	$\bar{35}$	$\bar{2}43$	35	$\bar{19}$
100	0	2	320	21	$\bar{23}$	$52\bar{0}$	8	$\bar{9}$	003	53	63	$20\bar{7}$	0	$\bar{3}$	$50\bar{1}$	0	7	021	14	$\bar{14}$	063	5	$\bar{5}$	$07\bar{5}$	23	$\bar{21}$	$\bar{3}13$	29	18	$\bar{3}43$	0	3
110	0	3	330	16	14	$53\bar{0}$	6	8	004	20	20	$20\bar{8}$	0	3	$50\bar{2}$	18	$\bar{22}$	031	15	8	073	29	34	016	46	52	$\bar{4}13$	21	20	$\bar{4}43$	0	$\bar{4}$
120	64	83	340	12	12	$54\bar{0}$	25	$\bar{27}$	005	9	$\bar{10}$	301	46	47	$50\bar{3}$	40	30	041	40	32	$01\bar{3}$	40	$\bar{41}$	026	0	2	$\bar{5}13$	0	5	$\bar{5}43$	6	7
130	42	$\bar{40}$	350	25	$\bar{15}$	$55\bar{0}$	0	$\bar{9}$	006	0	$\bar{1}$	$30\bar{2}$	0	$\bar{4}$	$50\bar{4}$	0	5	051	24	$\bar{15}$	$02\bar{3}$	23	$\bar{14}$	036	0	2	$\bar{6}13$	0	$\bar{6}$	$\bar{6}43$	30	$\bar{27}$
140	5	0	360	30	$\bar{27}$	$56\bar{0}$	24	20	007	0	7	303	28	$\bar{22}$	$50\bar{5}$	42	$\bar{39}$	061	39	46	$03\bar{3}$	50	$\bar{47}$	046	0	$\bar{9}$	$\bar{7}13$	0	0	$\bar{7}43$	0	3
150	5	3	370	19	$\bar{11}$	600	30	34	008	0	$\bar{2}$	304	11	9	$50\bar{6}$	17	14	071	16	$\bar{17}$	$04\bar{3}$	16	22	056	22	24	$\bar{8}13$	0	$\bar{1}$	153	29	$\bar{19}$
160	23	18	$31\bar{0}$	28	$\bar{29}$	610	0	7	101	19	$\bar{19}$	305	38	36	$50\bar{7}$	18	12	081	9	$\bar{12}$	$05\bar{3}$	18	12	$01\bar{6}$	24	23	123	69	69	$\bar{1}53$	53	50
170	29	20	$32\bar{0}$	88	93	620	0	$\bar{5}$	102	49	$\bar{45}$	306	0	$\bar{6}$	$50\bar{8}$	14	$\bar{10}$	$01\bar{1}$	15	16	$06\bar{3}$	62	61	$02\bar{6}$	38	$\bar{39}$	223	23	20	$\bar{2}53$	44	$\bar{43}$
180	19	19	$33\bar{0}$	0	$\bar{4}$	630	18	$\bar{13}$	103	18	24	307	28	$\bar{38}$	601	55	53	$02\bar{1}$	19	20	$07\bar{3}$	0	0	$03\bar{6}$	37	$\bar{37}$	323	74	$\bar{66}$	$\bar{3}53$	37	$\bar{21}$
$1\bar{1}0$	0	$\bar{6}$	$34\bar{0}$	47	54	640	32	$\bar{36}$	104	21	25	$30\bar{1}$	22	22	$60\bar{2}$	14	$\bar{16}$	$03\bar{1}$	50	60	$08\bar{3}$	12	14	$04\bar{6}$	0	$\bar{8}$	423	0	4	$\bar{4}53$	0	6
$1\bar{2}0$	69	$\bar{93}$	$35\bar{0}$	11	$\bar{10}$	650	11	11	105	20	$\bar{13}$	$30\bar{2}$	17	18	603	19	$\bar{17}$	$04\bar{1}$	39	$\bar{45}$	014	34	$\bar{38}$	$05\bar{6}$	27	$\bar{27}$	523	20	14	$\bar{5}53$	0	$\bar{8}$
$1\bar{3}0$	24	23	$36\bar{0}$	5	$\bar{5}$	660	12	$\bar{13}$	106	5	$\bar{5}$	$30\bar{3}$	0	$\bar{3}$	604	16	11	$05\bar{1}$	8	$\bar{7}$	024	8	$\bar{11}$	$06\bar{6}$	24	22	623	10	$\bar{16}$	$\bar{6}53$	0	3
$1\bar{4}0$	7	$\bar{6}$	$37\bar{0}$	0	$\bar{1}$	$61\bar{0}$	0	0	107	4	5	$30\bar{4}$	42	39	$60\bar{1}$	53	$\bar{70}$	$06\bar{1}$	60	$\bar{60}$	034	0	$\bar{2}$	017	31	$\bar{33}$	$\bar{1}23$	70	$\bar{81}$	$\bar{1}63$	35	25
$1\bar{5}0$	25	15	400	5	4	$62\bar{0}$	8	$\bar{8}$	108	0	$\bar{3}$	$30\bar{5}$	12	15	$60\bar{2}$	9	6	$07\bar{1}$	6	8	044	0	5	027	14	$\bar{12}$	$\bar{2}23$	36	42	$\bar{2}63$	0	0
$1\bar{6}0$	6	2	410	17	$\bar{16}$	$63\bar{0}$	23	$\bar{26}$	$10\bar{1}$	9	$\bar{5}$	$30\bar{6}$	40	$\bar{38}$	$60\bar{3}$	61	75	$08\bar{1}$	0	2	054	0	$\bar{6}$	037	0	5	$\bar{3}23$	0	$\bar{2}$	$\bar{3}63$	37	$\bar{35}$
$1\bar{7}0$	29	$\bar{20}$	420	20	22	$64\bar{0}$	18	18	$10\bar{2}$	31	25	$30\bar{7}$	4	$\bar{15}$	$60\bar{4}$	19	$\bar{18}$	012	26	25	064	9	$\bar{7}$	047	15	$\bar{13}$	$\bar{4}23$	0	$\bar{12}$	$\bar{4}63$	24	$\bar{27}$
$1\bar{8}0$	16	$\bar{17}$	430	19	22	$65\bar{0}$	0	0	$10\bar{3}$	48	$\bar{47}$	$30\bar{8}$	23	22	$60\bar{5}$	17	$\bar{13}$	022	39	$\bar{32}$	074	16	$\bar{10}$	$01\bar{7}$	17	$\bar{17}$	$\bar{5}23$	51	64	$\bar{1}73$	10	$\bar{26}$
200	78	$\bar{88}$	440	23	22	$66\bar{0}$	56	59	$10\bar{4}$	40	$\bar{25}$	401	55	$\bar{55}$	$60\bar{6}$	19	22	032	29	19	$01\bar{4}$	20	$\bar{16}$	$02\bar{7}$	25	26	$\bar{6}23$	0	$\bar{3}$	$\bar{2}73$	34	$\bar{13}$
210	13	8	450	8	11	700	10	19	$10\bar{5}$	14	13	402	10	4	$60\bar{7}$	0	$\bar{8}$	042	17	15	$02\bar{4}$	60	66	$03\bar{7}$	0	$\bar{8}$	$\bar{7}23$	34	$\bar{43}$			
220	16	$\bar{17}$	460	7	13	710	18	27	$10\bar{6}$	9	12	403	34	32	701	4	7	052	21	$\bar{15}$	$03\bar{4}$	37	36	$04\bar{7}$	22	$\bar{16}$	$\bar{8}23$	0	10			
230	6	4	470	22	$\bar{15}$	720	30	39	$10\bar{7}$	0	0	404	18	11	702	28	$\bar{22}$	062	0	7	$04\bar{4}$	34	$\bar{25}$	$05\bar{7}$	8	$\bar{13}$	133	42	$\bar{43}$			
240	0	$\bar{8}$	$41\bar{0}$	19	$\bar{19}$	730	9	$\bar{10}$	$10\bar{8}$	0	5	405	16	$\bar{11}$	703	0	4	072	15	13	$05\bar{4}$	22	20	018	10	$\bar{14}$	233	38	42			
250	41	$\bar{31}$	$42\bar{0}$	0	6	740	0	$\bar{3}$	201	62	72	406	0	$\bar{2}$	$70\bar{1}$	9	$\bar{14}$	082	18	27	$06\bar{4}$	34	$\bar{39}$	028	8	10	333	30	40			
260	35	$\bar{35}$	$43\bar{0}$	11	11	$7\bar{1}0$	0	1	202	6	$\bar{4}$	$40\bar{1}$	55	59	$70\bar{2}$	0	$\bar{9}$	$01\bar{2}$	9	8	$07\bar{4}$	25	25	$01\bar{8}$	30	$\bar{30}$	433	20	17			
270	10	11	$44\bar{0}$	28	$\bar{29}$	$72\bar{0}$	18	$\bar{25}$	203	58	$\bar{61}$	$40\bar{2}$	55	$\bar{43}$	$70\bar{3}$	8	$\bar{12}$	$02\bar{2}$	47	$\bar{61}$	015	50	47	$02\bar{8}$	5	8	533	15	$\bar{12}$			
280	19	20	$45\bar{0}$	0	$\bar{2}$	$73\bar{0}$	5	$\bar{10}$	204	0	9	$40\bar{3}$	39	$\bar{38}$	$70\bar{4}$	4	8	$03\bar{2}$	6	$\bar{6}$	025	26	27	$03\bar{8}$	0	10	633	0	$\bar{8}$			
$2\bar{1}0$	21	21	$46\bar{0}$	47	$\bar{48}$	$74\bar{0}$	16	15	205	18	13	$40\bar{4}$	44	44	$70\bar{5}$	20	21	$04\bar{2}$	12	17	035	0	1	$04\bar{8}$	30	26	$\bar{1}33$	35	35			
$2\bar{2}0$	25	19	$47\bar{0}$	15	14	800	33	$\bar{42}$	206	0	$\bar{6}$	$40\bar{5}$	17	$\bar{20}$	$70\bar{6}$	0	$\bar{2}$	$05\bar{2}$	0	1	045	33	40	113	7	6	$\bar{2}33$	27	18			

in practice a tedious proceeding that is adopted only when fine details of structure, e.g. bond lengths and electron distributions, are required. As the present determination had as its object merely the elucidation of the chemical structure, and as the crystals are, by their small, irregular dimensions, low symmetry and preponderance of heavy atoms, unsuited for more detailed work, the structure determination was regarded as complete at this stage.

A fourier projection on (hko), Figure 7, was computed for the final structure. Unfortunately, since all the signed F_o terms were used for this synthesis, the oxygen atomic peaks appear badly distorted and displaced by the diffraction rings around the heavy atoms, compared to Figure 6, in which mainly low-order F_o terms were used. This effect is to be expected in a Fourier series for heavy atoms with no modification for heat motion, when the series is terminated abruptly at $\sin\theta = 1$. However, the introduction of an artificial temperature factor to lessen the diffraction would render the oxygen (and, of course, the heavy atom) peaks blurred and diffuse. The difficulty lies primarily in the high proportion of the total molecular scattering power concentrated in the heavy atoms. A similar Fourier projection, (Figure 16), for the $Ca(H_2PO_4)_2H_2O$ crystal, whose

oxygens have a higher proportion of the total scattering power, shows much improved resolution even without a temperature factor.

The final atomic parameters, in 360ths of the cell edges, are:

Ca_1	106	157	98
Ca_2	63	302	240
P_1	74	135	259
P_2	107	339	75
O_1	114	120	336
O_2	123	177	222
O_3	48	66	213
O_4	15	192	270
O_5	120	300	6
O_6	165	39	108
O_7	39	27	57
O_8	105	285	126

Comparison of these parameters with the original values, obtained from the superposition of the three-dimensional Patterson function, shows that the latter gave surprisingly good approximations to the final atomic positions, even for the oxygen atoms. The maximum error in any one parameter is nine 360ths, corresponding to about 0.12A, and most are considerably smaller than this, which was hardly to be anticipated for the reasons

mentioned above. It is generally held that structures most favourable to solution by "heavy atom" methods are those in which the sums of the squares of the atomic numbers of the heavy and light atoms present are equal. In the present case,

$$\Sigma N^2(Ca+P) = 1098$$
$$\Sigma N^2(O+H) = 514$$

a ratio of two to one in favour of the heavy atoms. This implies that the accuracy in the oxygen positions will be relatively low.

Standard Deviations

The actual accuracy of the determination cannot be quantitatively judged from the residual error R alone. Methods of estimating the probable errors in electron density and atomic coordinates have been described by Cruikshank (24). He shows that the standard deviation in electron density, $\sigma(\rho_o)$, in the two-dimensional case, can be expressed

$$\sigma(\rho_o) = \frac{1}{A}\left[\sum_q (F_o - F_c)^2\right]^{1/2},$$

the summation being taken over the whole reciprocal plane.

Similarly the standard deviation in atomic coordinates, $\sigma(x_n)$, is expressed

$$\sigma(x_n) = \frac{2\pi\left[\sum_q h^2 (Fo-Fc)^2\right]^{1/2}}{a\, A\, C_n}$$

where C_n is the central curvature, $\frac{\partial^2 \rho_c}{\partial x^2}$, at the centre of the nth atom.

Using these equations on a typical projection in $CaHPO_4$, the standard deviation in electron density, $\sigma(\rho_o) = 1.1\ e/A^2$ on the (okl) projection. The standard deviation in atomic coordinates along the c axis, $\sigma(z_n) = 0.006A$ for Ca, 0.011A for P, and 0.039A for O. Hence the standard deviations in bond lengths, which are equal to

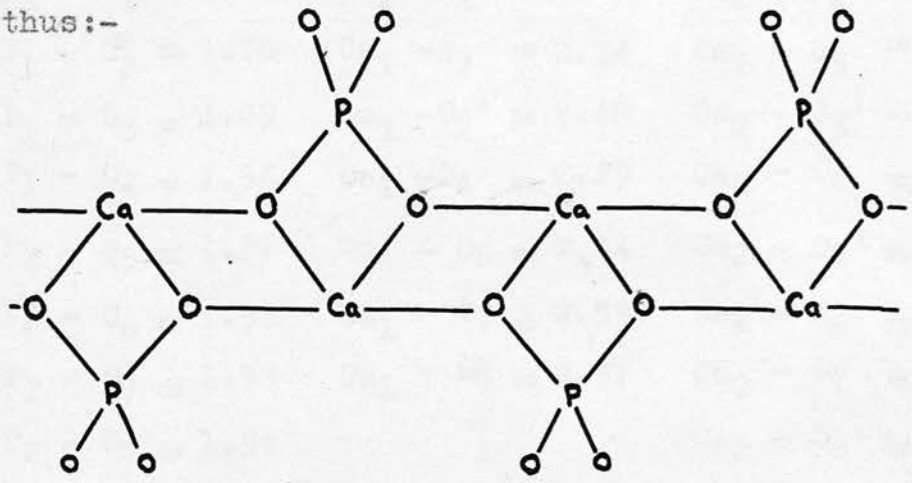
$$\sigma(d_{12}) = \left[\sigma(z_1)^2 + \sigma(z_2)^2\right]^{1/2},$$

have the values:

Ca-O = 0.039A
P -O = 0.040A
O -O = 0.055A
O -O = 0.078A (if related by a centre of symmetry, when $\sigma(d_{12}) = 2\sigma(z_1)$.)

4. Description of Structure

The structure of $CaHPO_4$ consists of discrete $PO_4^{'''}$ tetrahedra and Ca^{++} ions, the latter coordinated by a shell of oxygen atoms. Figure 8 shows a projection of the structure down the c axis, four unit cells being shown. In the a direction Ca_1 is bonded to O_2 and O_4 attached to P_1, while Ca_2 is bonded to O_6 and O_7, attached to P_2. In the b direction Ca_1 is bonded to O_6 and O_7, and Ca_2 to O_2 and O_4, so that a double chain of Ca - PO_4 - Ca extends along the a axis thus:-



Bonds from Ca_1 to O_8 and Ca_2 to O_3 link these chains transversely in the b direction, forming a distorted sheet of atoms roughly in the (0 0 1) plane. The centre of symmetry produces a similar sheet below the first in the c direction, further bonds from Ca_1 to O_1 'and O_2', and from Ca_2 to O_3', O_5' and O_8' linking the sheets. Ca_1 thus has seven and Ca_2 eight nearest oxygen neighbours in its coordination shell. This

variation in the calcium coordination is not unexpected. The highly electropositive nature of the metallic ion results in an unusually great ionic character in its coordination, so that no definite allocation of shared electrons from the oxygens is possible. Ca - O coordinations of all values from 6 to 9 have been reported (25) and different values in the same structure have been noted where the symmetry permits (26, 1).

The bond lengths and angles obtained are:

$P_1 - O_1 = 1.53A$	$Ca_1 - O_1' = 2.44A$	$Ca_2 - O_2 = 2.58A$
$P_1 - O_2 = 1.58$	$Ca_1 - O_2 = 2.34$	$Ca_2 - O_3 = 2.40$
$P_1 - O_3 = 1.49$	$Ca_1 - O_2' = 2.48$	$Ca_2 - O_3' = 2.43$
$P_1 - O_4 = 1.56$	$Ca_1 - O_4 = 2.29$	$Ca_2 - O_4 = 2.44$
$P_2 - O_5 = 1.52$	$Ca_1 - O_6 = 2.44$	$Ca_2 - O_5' = 2.44$
$P_2 - O_6 = 1.56$	$Ca_1 - O_7 = 2.59$	$Ca_2 - O_6 = 2.51$
$P_2 - O_7 = 1.55$	$Ca_1 - O_8 = 2.37$	$Ca_2 - O_7 = 2.58$
$P_2 - O_8 = 1.54$		$Ca_2 - O_8' = 2.51$
$O_1P_1O_2 = 116.5^\circ$		$O_5P_2O_6 = 111.0^\circ$
$O_1P_1O_3 = 113.5^\circ$		$P_5P_2O_7 = 109.0^\circ$
$O_1P_1O_4 = 105.5^\circ$		$O_5P_2O_8 = 107.0^\circ$
$O_2P_1O_5 = 108.5^\circ$		$O_6P_2O_7 = 100.0^\circ$
$O_2P_1O_4 = 103.5^\circ$		$O_6P_2O_8 = 108.5^\circ$
$O_3P_1O_4 = 116.0^\circ$		$O_7P_2O_8 = 112.0^\circ$

The average P - O bond length is 1.54A, the average Ca - O bond length is 2.46A, and the average distance O - O within the PO_4 group is 2.51A.

The two hydrogen atoms probably lie between oxygens of neighbouring PO_4 groups. It is not feasible to identify their positions by a reduction in the O - O distance between non-bonded atoms, since in this case with a standard deviation of 0.055A in the bond length, only differences in O - O bonds greater than 0.18 are significant. This uncertainty, caused primarily by the swamping effect of the heavy atoms, is sufficient to obscure any evidence of hydrogen bonding. In fact, the shortest measured O - O contact is 2.48A between O_7 and its symmetry-related atom, where the standard deviation is higher and where a hydrogen bond is not possible by space-group considerations. The next shortest contacts observed are

$$O_1 - O_5 = 2.60A$$
$$O_6 - O_{8'} = 2.62$$
$$O_4 - O_7 = 2.71.$$

The structure of $CaHPO_4$ is thus a three-dimensional network of $PO_4^{'''}$ tetrahedra with Ca^{++} ions in the interstices, holding the anions together by highly ionic bonds with the oxygens. There seems to be no close resemblance to the structure of chemically related compounds, though $CaSO_4$, which is orthorhombic, has very similar cell dimensions (27). In particular, the structure

of apatite (11, 1) is quite different, so that profound alterations in the crystal lattice must be necessary as the Ca/P ratio is reduced from 1.66, and a continuous series of solid solutions between hydroxyapatite and anhydrous dicalcium phosphate seems unlikely.

Publication. A paper embodying the results of this investigation has been accepted for publication (28).

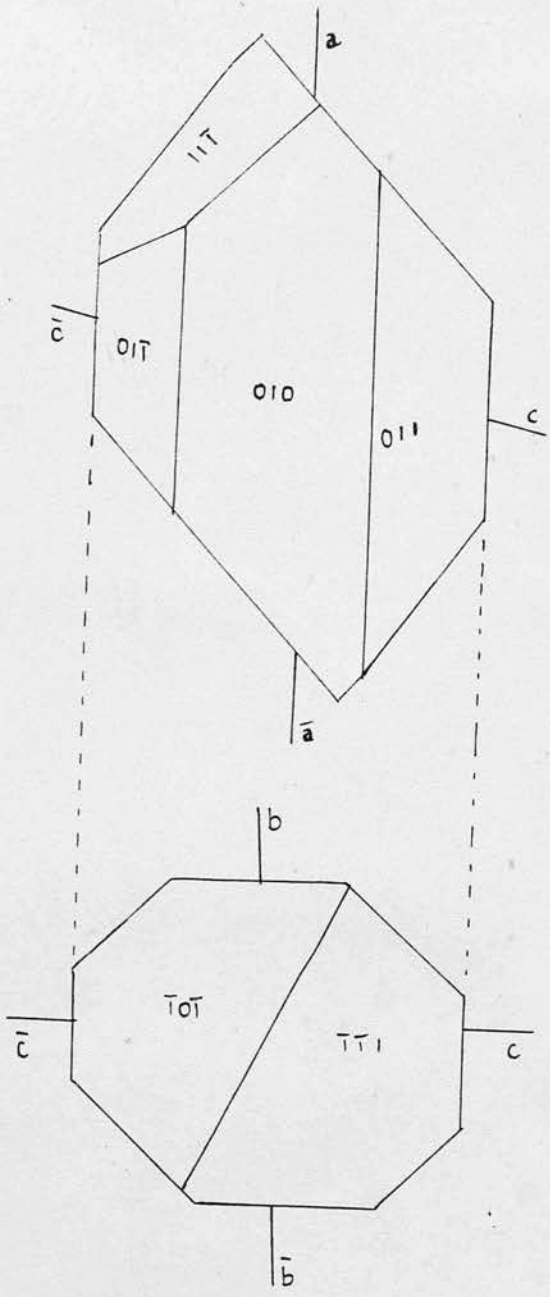


Fig. 1. Crystal habit of $CaHPO_4$, after Lehr et al.[6].

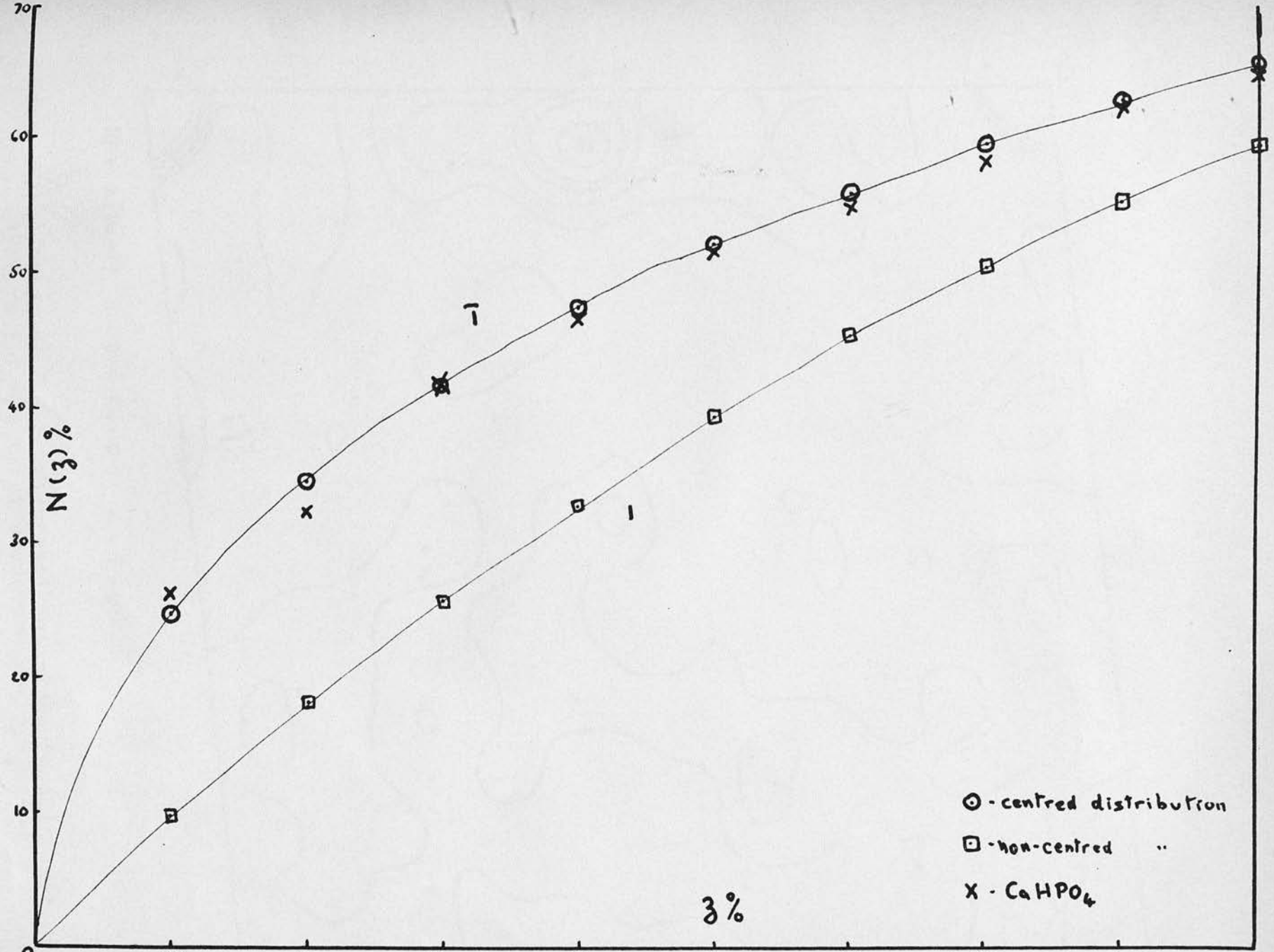

70
60
50
40
30
20
10
0
N(3)%
10
20
30
40
50
60
70
80
90
3%
⊙ - centred distribution
⊡ - non-centred ..
X - CaHPO4

FIGURE 2.

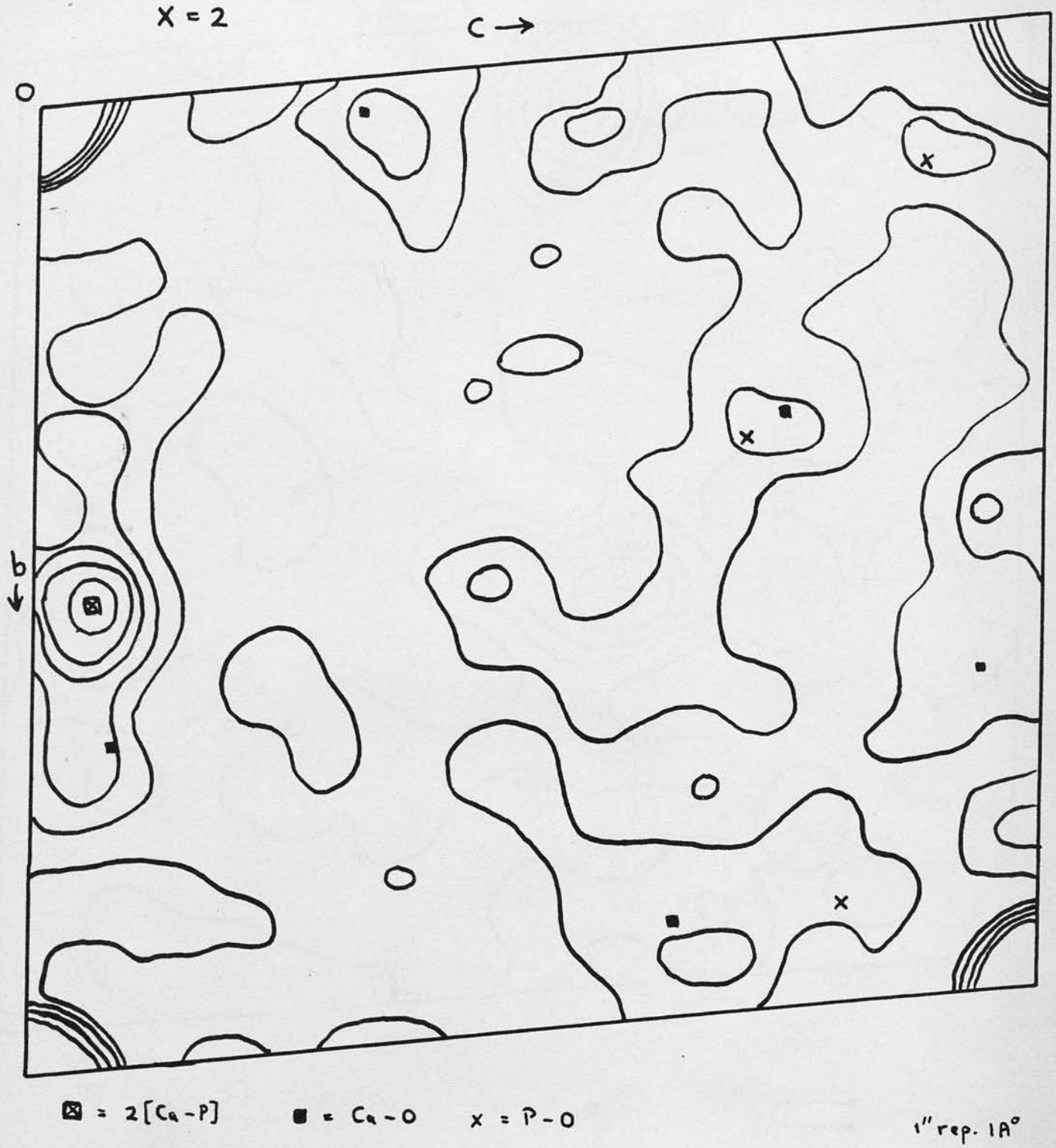


Fig. 3. Section at X = 2 of general Patterson function for $CaHPO_4$. Vectors for the trial structure are indicated.

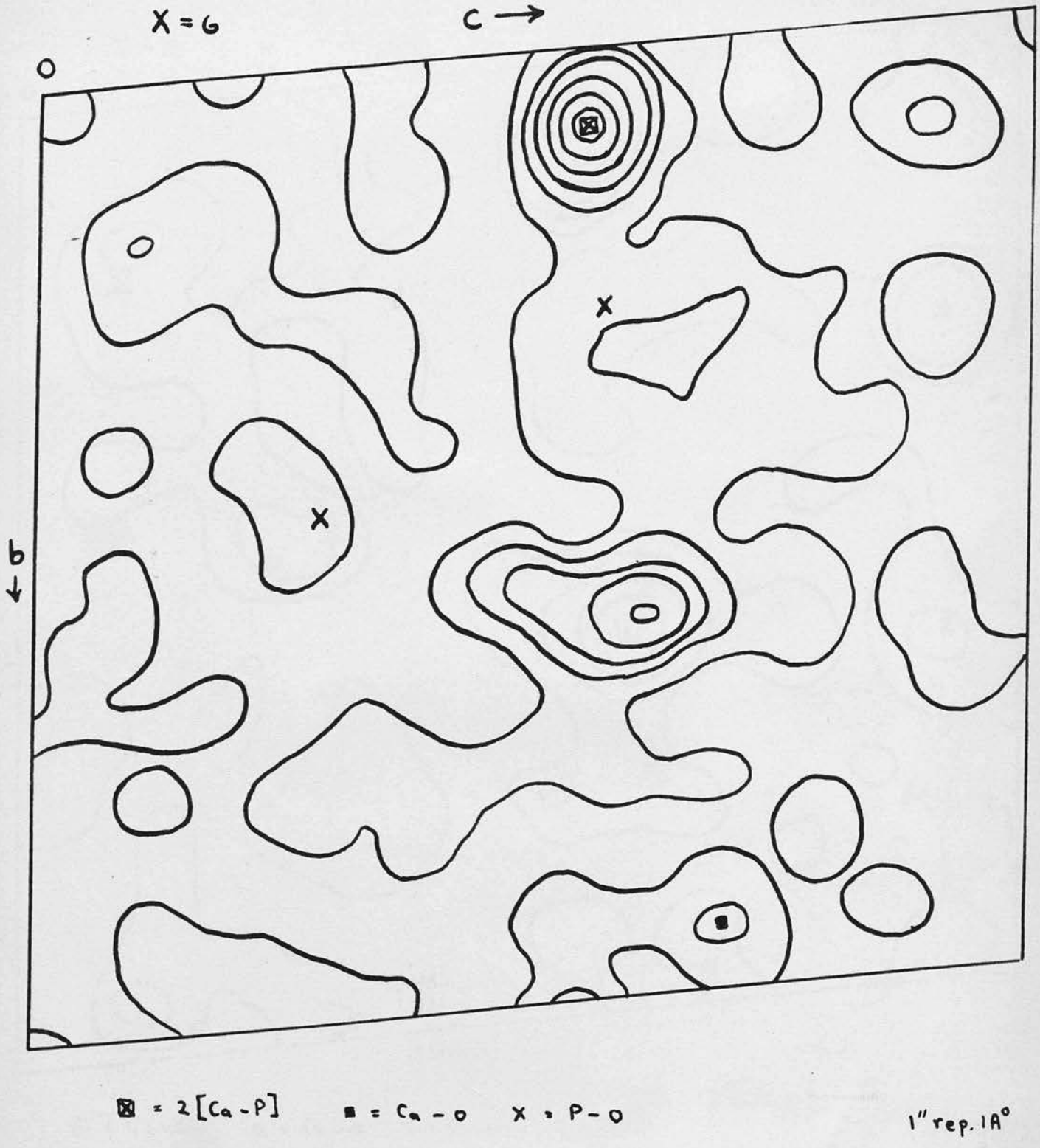


Fig. 4. Section at X = 6 of general Patterson function for $CaHPO_4$.

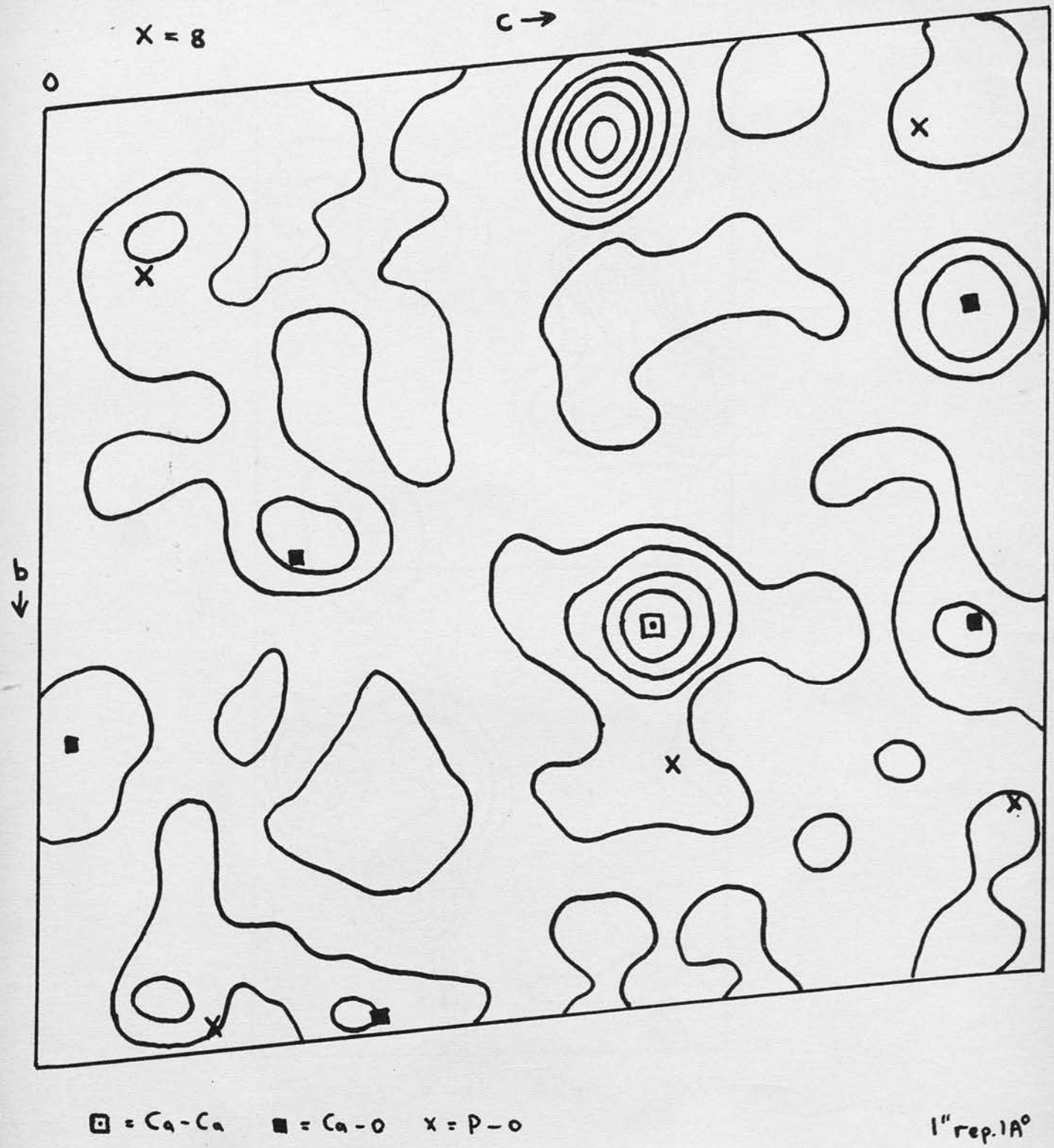


Fig. 5. Section at X = 8 of general Patterson function for $CaHPO_4$.

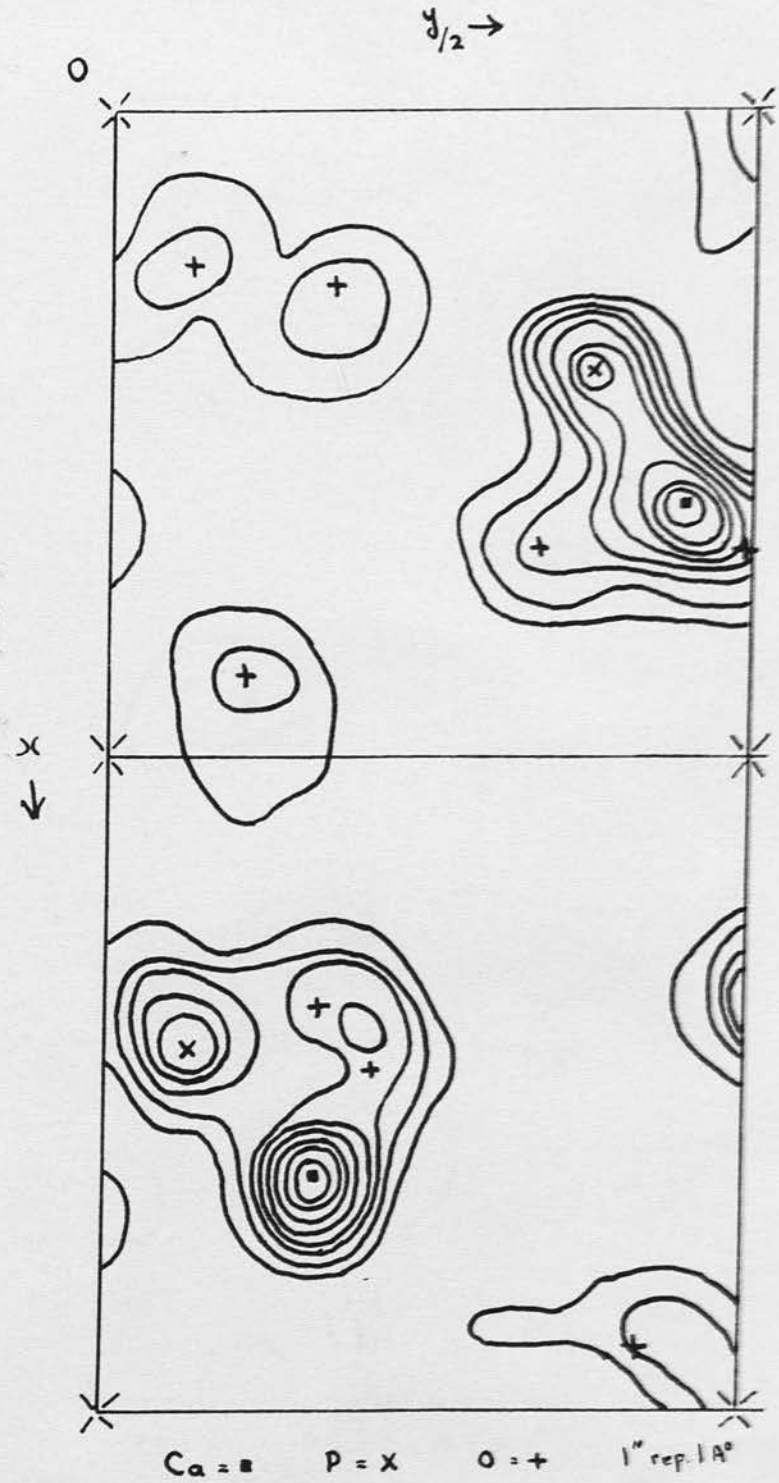


Fig. 6. Fourier projection down C axis of $CaHPO_4$, using only 82 terms from approximate structure. Contours at 6, 12, 18 . . . . . 48 e/A^2.

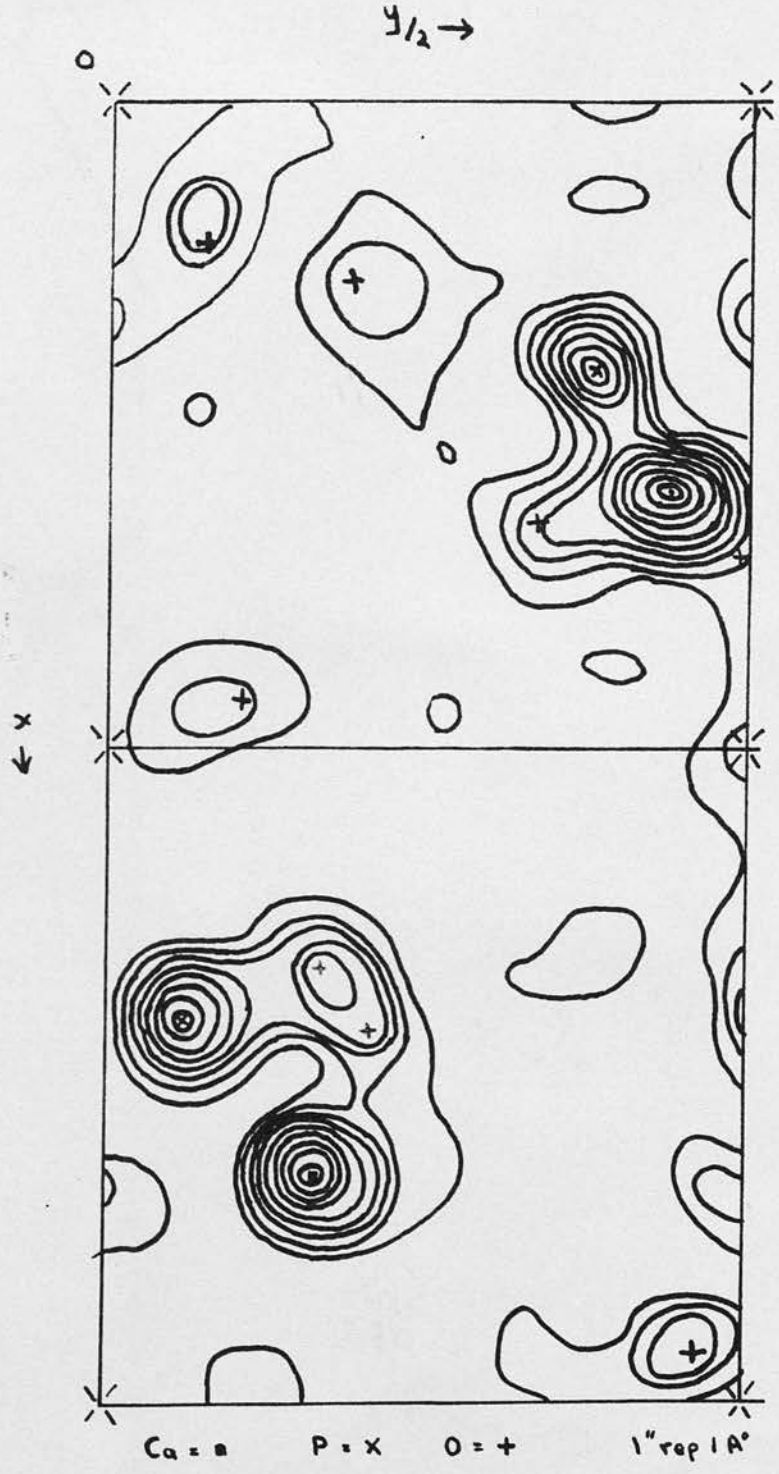


Fig. 7. Fourier projection down C axis of $CaHPO_4$ for final structure. Contours at 6, 12, 18 . . . . 54 e/A^2.

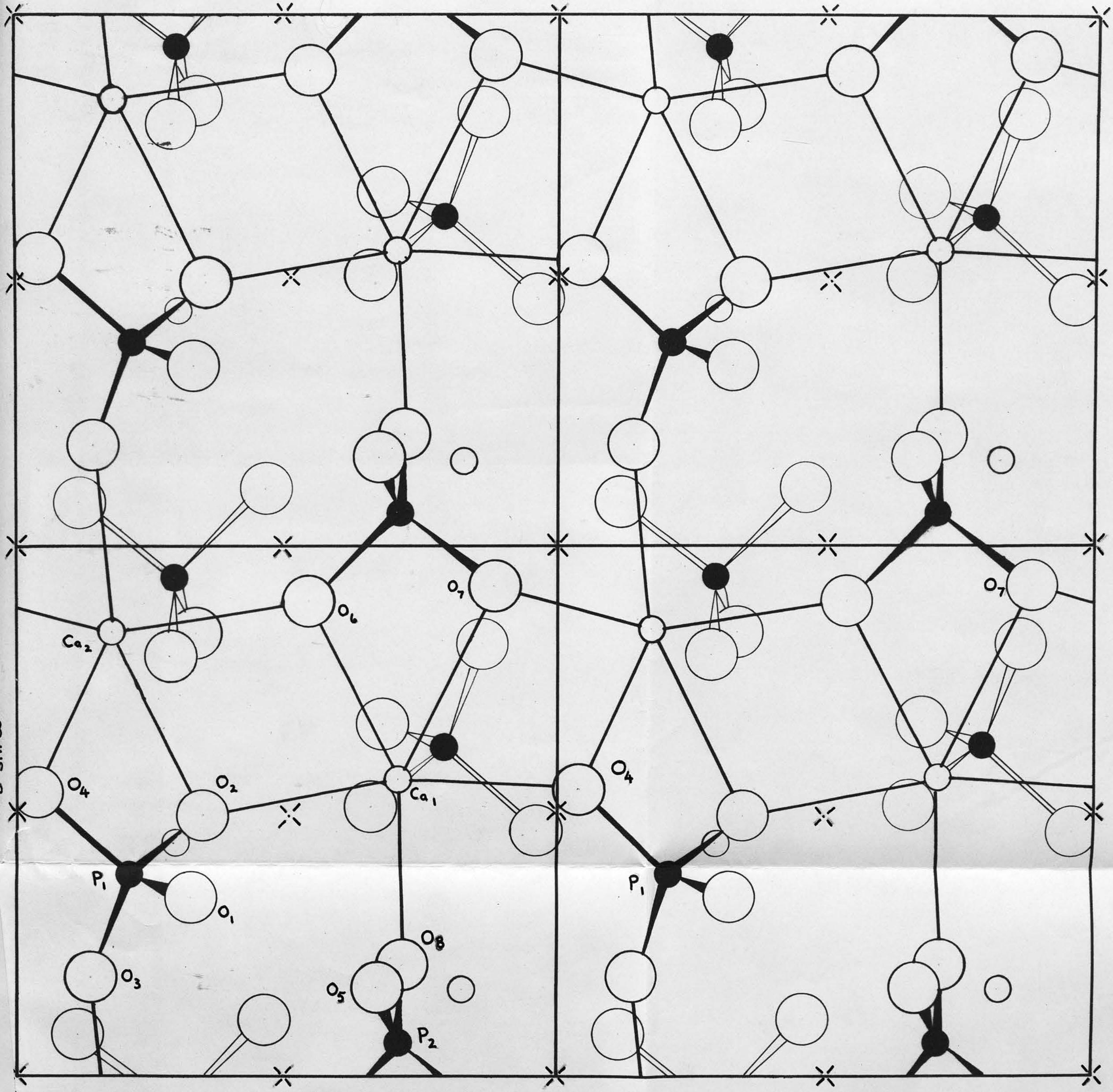

Ca2
O6
O7
O4
O2
Ca1
O7
P1
O1
O3
O8
O5
P2
O4
P1
b sin α
a sin β
0 1 2 3 4 5 A°
Ca -
P -
O -

FIGURE 8.

Part 2: The Structure of Monocalcium Phosphate Monohydrate

1. Introduction

Calcium tetrahydrogen diorthophosphate, $Ca(H_2PO_4)_2$, commonly known as monocalcium phosphate from its old formulation as a double oxide, $CaO,2H_2O,P_2O_5$, exists in the anhydrous and in a monohydrated form. The anhydrous crystals are unstable in contact with aqueous solutions at room temperature, are very hygroscopic, and do not form well-shaped crystals. The monohydrate, on the other hand, is readily preparable as well-formed, stable crystals, and is, moreover, the phase actually present in commercial superphosphate fertilizers (5).

The crystals are described by Groth (29) as triclinic pinacoidal. Their morphology was first described by Haushofer (30) and their optical properties and unit cell dimensions have recently been determined (6). The latter paper also points out some similarities in cell dimensions with those of gypsum and suggest that the structures may be analogous in some respects. This view was supported by their success in preparing orientated overgrowths of $Ca(H_2PO_4)_2H_2O$ on large crystals of gypsum suspended in the crystallizing solution.

2. Determination of Unit Cell and Space Group

Experimental:

The monocalcium phosphate used was prepared according to the equation:

$$Ca(OH)_2 + 2H_3PO_4 = Ca(H_2PO_4)_2, H_2O + H_2O$$

47.5gm. 90% A.R. phosphoric acid and 22 gm. distilled water were added to 5.2 gm. calcium hydroxide in a porcelain crucible. The mixture was heated at 100°C. in an electric oven until solution was complete, and then cooled very slowly by allowing the oven temperature to drop by about 10°C. per hour. The crystals which formed were filtered on a sintered glass funnel, washed several times with acetone and dried for a short time in a 50°C. oven.

The crystals are colourless plates, tabular on the (010) face. Their habit is shown in Figure 9. Microscopic examination, however, showed that polysynthetic twinning according to the Albite law, and contact twinning according to the Carlsbad law, are highly developed, and no single crystal suitable for X-ray examination could be found. Eventually a large crystal, about 1 mm. square, was carefully cleaved, using a razor blade, into successively smaller fragments, each of which was examined by an X-ray oscillation photograph until an untwinned

specimen was obtained. This was a lath-shaped fragment of dimensions 0.7 x 0.2 x 0.1 mm., elongated along the a axis. It was mounted on the end of a thin glass fibre by a touch of "Seccotine". Oscillation and Weissenberg photographs were taken about the three principal axes, using the same techniques as with $CaHPO_4$, but employing the faster Kodak Kodirex film which had become available. Since only one usuable crystal was available, it was remounted for rotation about each axis in turn, the old "Seccotine" being easily removed by a slightly damp artist's brush without appreciably dissolving the crystal.

Unit Cell and Space Group

The unit cell dimensions were determined by measurements of high-order (hko), (hol) and (okl) reflections in the same way as for $CaHPO_4$. The mean values obtained for the reciprocal axes are:

$a^* = 0.3113$ $\quad \alpha^* = 83^\circ 46'$

$b^* = 0.1312$ $\quad \beta^* = 62^\circ 34'$

$c^* = 0.2719$ $\quad \gamma^* = 92^\circ 57'$

The corresponding unit cell in real space is:

Since the unit cell is triclinic, the choice of space group depends only on the presence or absence of a centre of symmetry. Crystal morphology suggests that a centre is present, and the statistical test (19) was used to confirm this, as with $CaHPO_4$. When applied to the (okl) reflections of $Ca(H_2PO_4)_2H_2O$, the curve obtained, shown in Figure 10, reveals the presence of a centre of symmetry. Thus the space group is $P\bar{1}$.

3. Structure Determination

Interpretation of Patterson Syntheses

The general positions in space group $P\bar{1}$ are two-fold, and there is one molecule of $Ca(H_2PO_4)_2 H_2O$ in the unique half of the cell. All the atoms can be in general positions, so that 36 parameters are required to define the positions of all the atoms, except the hydrogens. In this crystal, however, there are only three unique heavy atoms, giving rise to nine interatomic vectors. It seemed probable, therefore, that two-dimensional Patterson syntheses would be much more informative than they had been for the $CaHPO_4$ crystal.

The projections including the long b axis were likely to provide the best resolved Patterson maps, and a start was made on the (okl) projection. The observed F^2 terms were first placed on an approximate absolute scale by an application of Wilson's method. Once again a rather ambiguous graph was obtained, and it seemed best to multiply the intensities by a constant scale factor of 15, rather than to attempt a detailed scaling against $\sin\theta$. (The structure factors were later rescaled against the calculated values when an acceptable structure had been obtained.)

The (okl) Patterson function (see Appendix) was calculated in 60ths of the cell edge in the Y direction, and in 30ths in the Z direction, where

$$Y = b \sin \gamma$$
$$Z = c \sin \beta$$
$$\angle YZ = 180^{\circ} - \alpha^{*}$$

The Patterson projection is shown in Figure 11. The outstanding feature is the appearance of four sets of two high peaks each with the same y parameter and separated by Z/2. This suggests immediately that two of the three heavy atoms are in the relative positions (0,0) and (0,30) with the third atom at one of the other high peaks. In view of the unusually symmetrical nature of the vector arrangement, it was suspected that knowledge of the (hko) projection would be valuable at this stage.

The (hko) Patterson projection was therefore computed in the same manner, after a Wilson scaling graph had again led to a scale factor of 15 being applied. The map, shown in Figure 12, indicates that each pair of heavy atom vectors in the (okl) projection have also the same x coordinate, i.e. there are four sets of vectors with the coordinates (x,y,z) and (x,y,z + 30).

The inference is that two of the heavy atoms must be superposed on the (hko) projection, in the relative positions (0,0,0) and (0,0,30). These must be the Ca and one P atom, since $Z/2 = 3.2A$ is too small a separation between two PO_4 groups, while it does correspond to the Ca - P distance of closest approach in $CaHPO_2,2H_2O$, for example.

Interpretation of the (hko) projection thus resolves itself into the very simple case of two heavy atoms, $(Ca + P_1)$ and P_2. There are only 4 vectors to identify, whose heights should be proportional to the product of the scattering powers of the atoms concerned, thus:

Vector	Atoms	Proportional Height
1	$(Ca+P_1) + (Ca+P_1)$	1100
2	$(Ca+P_1) + P_2$	1000 (double weight)
3	$(Ca+P_1) - P_2$	1000 (" ")
4	$P_2 + P_2$	225

The vector heights are in the ratio 4.4 : 4 : 4 : 1. The three largest peaks on the Patterson map, in 60ths of the cell edges, are:

Peak	Position	Height
A	($28\frac{1}{2}$ $12\frac{1}{2}$)	220
B	(38 $16\frac{1}{2}$)	180
C	(5 29)	180

Unfortunately this implies that vector 4 will have a height of only 50 units (just above the first contour marked on the map) which is much too low to be noticeable in comparison with the abundant Ca - O and P - O vectors. Even so we have only 3 possibilities of fitting vectors 1, 2 and 3 to peaks A, B and C. One can be discarded immediately, since the combination A = 2, B = 3, C = 1 corresponds to P_2 at $(4\frac{3}{4}, 2)$ which is too near the centres of symmetry along the c axis.

There is little to choose between the two remaining possibilities, except that for the combination A = 3, B = 1, C = 2, vector 4 lies at $(26\frac{1}{2}\ 18\frac{1}{2})$ at a height of 70 units. This corresponds to $(Ca+P_1)$ at $(48\frac{1}{4}, 8\frac{1}{4})$ and P_2 at $(16\frac{3}{4}, 20\frac{3}{4})$. Structure factors for the (hko) zone were therefore calculated for these three atoms, a residual error R of 0.48 being obtained. This is rather a high figure even for such a rough structure, and a Fourier projection, computed using those F's whose signs were determined, was very unconvincing, and no acceptable oxygen positions were obtained. This structure was therefore abandoned, and the third possibility, namely the combination A = 1, B = 3, C = 2, was investigated. It will be seen that

only this arrangement preserves the correct peak-height relationship. It had not been favoured previously because vector 4 falls at (17 14½) at a height of only 45, but this is not really too low.

The atomic sites on this hypothesis are: (Ca+P_1) at (43½ 6¼) and P_2 at (21½ 22¾). Structure factors calculated for these atoms gave an R factor of 0.43, and 110 F's were signed for a Fourier projection, shown in Figure 13. Suitable oxygen positions, marked by crosses, were chosen. Their parameters, in 60ths of the cell edges, are:

O_1	(35 1½)	O_5	(24 15½)
O_2	(56 2)	O_6	(9 24)
O_3	(56 10)	O_7	(37 24½)
O_4	(34 11)	O_8	(15 26½)

H_2O (6 15).

Structure factors calculated for the complete trial structure gave R = 0.32 after F obs. had been multiplied by a scale factor of 1.125. This reduction of 0.11 in the residual error is strong evidence of the approximate correctness of the atomic positions. It was now decided to refine the structure by means of the (F_o - F_c) difference Fourier syntheses which had been

successful in the $CaHPO_4$ work. Two cycles of refinement reduced R to 0.28, but further improvement was not obtained. The difference map (Figure 14) indicated that the Ca and P_1 atoms should be separated slightly in the X direction, but of course it is impossible to know which way to move each atom unless another projection is studied.

Attention was accordingly given to the other projections, beginning with the (okl) which should be the best resolved. Now the coordinates of the $(Ca+P_1)$ vector on the (okl) projection must be $(12, 2z_1 + 30)$ where z_1 and $(z_1 + 30)$ are the respective z parameters of these atoms.

The peaks which fit this condition are at (12, 3) and (12, 33). Hence $z = 1\frac{1}{2}$ or $16\frac{1}{2}$. The possibility $z = 1\frac{1}{2}$ can be discounted, since it would bring the heavy atoms too close to the centres of symmetry. If $z = 16\frac{1}{2}$, then:

$$Ca = (44 \quad 6 \quad 46\tfrac{1}{2})$$
$$P_1 = (44 \quad 6 \quad 16\tfrac{1}{2}).$$

Similarly the vectors $(P_2 - Ca)$ and $(P_2 - P_1)$ must have coordinates $(16 \quad , z_2 - 46\frac{1}{2})$ and $(16 \quad , z_2 - 16\frac{1}{2})$ respectively. The two peaks available are (16 49) and (16 19). This corresponds to a choice of coordinates for P_2 between $(22 \quad 5\frac{1}{2})$ and $(22 \quad 35\frac{1}{2})$. Of these, the

latter is probably the more acceptable from packing considerations, but the former gave rather better peak-height agreements, within ± 7.5%, and it was tried out first. Structure factors calculated for the three heavy atoms alone gave R = 0.46, and possible oxygen positions were obtained from an $(F_o - F_c)$ synthesis. A new set of structure factors using these oxygen positions was quite unsatisfactory, R increasing to 0.48. A more complete $(F_o - F_c)$ error synthesis (Figure 15) was computed, and showed hollows at the chosen oxygen positions near P_1, while quite high "ghost peaks" of oxygens appeared round the Ca position. It is obvious, therefore, that the alternative position for P_2 (corresponding to an interchange of Ca and P_1) is the correct one. Structure factors calculated for the atoms:

$$\text{Ca} = (44 \quad 6 \quad 46\tfrac{1}{2})$$
$$P_1 = (44 \quad 6 \quad 16\tfrac{1}{2})$$
$$P_2 = (20 \quad 22\tfrac{1}{2} \quad 35\tfrac{1}{2})$$

gave the rather high residual error of 0.48, corresponding to the poorer peak-height agreement. However when a Fourier projection was computed using the signed F's, a quite promising set of oxygens were obtained:

$O_1 = (1\frac{1}{2}\ 20)$ $O_5 = (15\frac{1}{2}\ 36)$

$O_2 = (2\frac{1}{2}\ 11\frac{1}{2})$ $O_6 = (24\ 43)$

$O_3 = (10\ 30)$ $O_7 = (24\frac{1}{2}\ 47)$

$O_4 = (11\ 5)$ $O_8 = (26\ 19)$

$H_2O = (15\frac{1}{2}\ 59)$.

These reduced R to 0.39. Five cycles of refinement of these positions by difference syntheses were carried out, the lowest value of R obtainable being about 0.20.

The best x and z parameters obtained were then used to calculate the (hol) projection, which is unsuitable for detailed refinement because of its small area, several atoms being superposed. A residual error of 0.34 was obtained, and a difference map showed the correct directions in which to shift Ca and P_1 along the a axis, which were required to complete the (hko) refinement. When these shifts had been made, and the structure factors for all three projections had been recalculated using the best mean atomic positions, the following final residual errors were obtained:

R (okl) = 0.214

R (hko) = 0.230

R (hol) = 0.287.

For all reflections in the three principal zones, R = 0.235. This figure includes all unobserved and extinguished reflections. Moreover no attempt has been made to correct for the effects of absorption nor for a temperature factor. These two effects act in opposing senses to a large extent, making it difficult to determine temperature factors with any certainty. Moreover the solitary small crystal available was of too irregular a shape to permit a direct absorption correction to be made. However the persistence of these errors has little influence on the validity of the information which was the object of this investigation, namely the general configuration of the atoms in the crystal, with special reference to its possible similarities to related compounds. Tables of F_o and F_c for the (hko), (hol) and (okl) planes of $Ca(H_2PO_4)_2H_2O$ are given in Table 3.

The final atomic parameters, in 360ths of the cell edges, are:

Ca	262	37	278
P_1	270	35	99
P_2	127	134	222
O_1	216	9	123
O_2	324	9	63
O_3	336	63	183
O_4	204	69	33
O_5	135	90	216

Table 3. Values of F_o and F_c for the (h k 0), (h 0 l) and (0 k l) planes of $Ca(H_2PO_4)_2H_2O$

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
010	-	38	$1\bar{6}0$	33	32	$2,\bar{13},0$	24	18	470	6	$\bar{9}$	600	21	$\bar{28}$	$20\bar{1}$	35	14	$50\bar{3}$	27	31	$08\bar{1}$	3	$\bar{4}$	$0,\bar{15},2$	2	7	094	33	31	$0,\bar{11},5$	0	$\bar{5}$
020	19	17	$1\bar{7}0$	20	12	$2,\bar{14},0$	7	$\bar{7}$	480	0	$\bar{2}$	610	24	$\bar{48}$	$20\bar{2}$	22	17	$50\bar{4}$	43	$\bar{39}$	$09\bar{1}$	10	15	013	16	$\bar{20}$	0,10,4	30	24	$0,\bar{12},5$	9	$\bar{9}$
030	9	1	$1\bar{8}0$	28	24	300	30	29	490	10	6	620	12	$\bar{9}$	$20\bar{3}$	58	49	$50\bar{5}$	0	$\bar{15}$	$0,\bar{10},1$	11	8	023	14	$\bar{11}$	0,11,4	7	1	016	22	19
040	38	$\bar{43}$	$1\bar{9}0$	30	24	310	25	$\bar{17}$	4,10,0	42	40	630	2	4	$20\bar{4}$	16	$\bar{7}$	$50\bar{6}$	24	24	$0,\bar{11},1$	11	$\bar{4}$	033	6	2	$01\bar{4}$	48	52	026	11	12
050	22	24	$1,\bar{10},0$	16	$\bar{16}$	320	35	$\bar{31}$	4,11,0	16	13	640	0	$\bar{4}$	$20\bar{5}$	35	$\bar{29}$	$50\bar{7}$	17	$\bar{12}$	$0,\bar{12},1$	10	6	043	20	20	$02\bar{4}$	27	22	036	28	29
060	48	$\bar{51}$	$1,\bar{11},0$	36	$\bar{30}$	330	0	$\bar{6}$	4,12,0	15	13	650	16	16	$20\bar{6}$	50	37	$60\bar{1}$	13	$\bar{18}$	$0,\bar{13},1$	7	$\bar{1}$	053	3	0	$03\bar{4}$	10	$\bar{14}$	046	35	37
070	5	$\bar{2}$	$1,\bar{12},0$	30	$\bar{21}$	340	46	$\bar{52}$	$41\bar{0}$	31	29	660	11	12	$20\bar{7}$	8	$\bar{12}$	$60\bar{2}$	23	26	$0,\bar{14},1$	9	4	063	0	$\bar{6}$	$04\bar{4}$	17	$\bar{12}$	056	9	8
080	24	26	$1,\bar{13},0$	39	$\bar{29}$	350	4	$\bar{5}$	$42\bar{0}$	4	$\bar{3}$	$61\bar{0}$	16	$\bar{12}$	$20\bar{8}$	14	$\bar{10}$	$60\bar{3}$	4	5	$0,\bar{15},1$	15	20	073	13	$\bar{10}$	$05\bar{4}$	33	$\bar{41}$	066	13	14
090	11	11	$1,\bar{14},0$	10	$\bar{15}$	360	20	26	$43\bar{0}$	30	$\bar{44}$	$62\bar{0}$	0	$\bar{3}$	301	7	10	$60\bar{4}$	12	$\bar{19}$	012	35	$\bar{47}$	083	9	8	$06\bar{4}$	30	$\bar{34}$	076	19	$\bar{15}$
0,10,0	33	33	200	40	$\bar{40}$	370	36	46	$44\bar{0}$	19	$\bar{19}$	$63\bar{0}$	17	17	302	0	0	$60\bar{5}$	5	6	022	37	$\bar{36}$	093	22	21	$07\bar{4}$	13	$\bar{9}$	$01\bar{6}$	23	$\bar{23}$
0,11,0	34	29	210	0	$\bar{8}$	380	52	69	$45\bar{0}$	32	$\bar{45}$	$64\bar{0}$	5	10	303	13	16	$60\bar{6}$	14	$\bar{13}$	032	21	16	0,10,3	27	$\bar{25}$	$08\bar{4}$	22	$\bar{25}$	$02\bar{6}$	14	$\bar{10}$
0,12,0	16	15	220	38	$\bar{36}$	390	4	$\bar{1}$	$46\bar{0}$	0	$\bar{6}$	001	25	$\bar{28}$	304	16	$\bar{18}$	$60\bar{7}$	9	15	042	41	50	0,11,3	0	$\bar{5}$	$09\bar{4}$	19	14	$03\bar{6}$	17	$\bar{13}$
0,13,0	22	$\bar{19}$	230	15	$\bar{15}$	3,10,0	5	7	$47\bar{0}$	0	$\bar{2}$	002	39	$\bar{47}$	305	5	10	$70\bar{2}$	11	$\bar{21}$	052	40	40	0,12,3	9	$\bar{4}$	$0,\bar{10},4$	22	18	$04\bar{6}$	14	10
0,14,0	34	$\bar{31}$	240	56	70	3,11,0	0	13	$48\bar{0}$	0	$\bar{9}$	003	16	14	$30\bar{1}$	47	$\bar{45}$	$70\bar{3}$	17	$\bar{10}$	062	15	12	0,13,3	4	$\bar{4}$	$0,\bar{11},4$	21	15	$05\bar{6}$	20	24
0,15,0	24	$\bar{35}$	250	17	18	3,12,0	36	$\bar{20}$	$49\bar{0}$	39	39	004	22	15	$30\bar{2}$	0	4	$70\bar{4}$	16	23	072	3	$\bar{7}$	$01\bar{3}$	14	$\bar{14}$	$0,\bar{12},4$	25	41	$06\bar{6}$	24	24
100	20	$\bar{16}$	260	52	63	3,13,0	13	$\bar{7}$	$4,\bar{10},0$	15	18	005	23	20	$30\bar{3}$	16	$\bar{19}$	011	31	43	082	8	$\bar{8}$	$02\bar{3}$	4	2	$0,\bar{13},4$	2	0	$07\bar{6}$	34	38
110	20	17	270	7	8	$31\bar{0}$	22	17	$4,\bar{11},0$	14	12	006	22	$\bar{17}$	$30\bar{4}$	17	11	021	33	$\bar{39}$	092	52	$\bar{51}$	$03\bar{3}$	41	41	015	10	$\bar{12}$	$08\bar{6}$	18	22
120	59	97	280	20	$\bar{21}$	$32\bar{0}$	22	15	500	0	$\bar{1}$	007	11	$\bar{12}$	$30\bar{5}$	36	42	031	8	6	$0,10,2$	17	$\bar{19}$	$04\bar{3}$	16	$\bar{19}$	025	4	3	$09\bar{6}$	11	$\bar{12}$
130	35	28	290	4	5	$33\bar{0}$	22	22	510	15	13	101	29	29	$30\bar{6}$	48	$\bar{38}$	041	4	7	$0,11,2$	12	$\bar{8}$	$05\bar{3}$	16	10	035	30	30	$0,\bar{10},6$	3	$\bar{8}$
140	40	48	$2,10,0$	60	$\bar{58}$	$34\bar{0}$	21	25	520	20	19	102	3	$\bar{12}$	$30\bar{7}$	4	$\bar{5}$	051	29	$\bar{30}$	$0,12,2$	3	$\bar{6}$	$06\bar{3}$	30	$\bar{29}$	045	5	$\bar{4}$	017	9	$\bar{10}$
150	10	$\bar{6}$	$2,11,0$	24	$\bar{11}$	$35\bar{0}$	4	$\bar{1}$	530	30	34	103	0	3	$30\bar{8}$	44	32	061	14	$\bar{13}$	$0,13,2$	28	28	$07\bar{3}$	0	$\bar{7}$	055	18	14	027	5	1
160	31	$\bar{27}$	$2,12,0$	18	$\bar{8}$	$36\bar{0}$	28	$\bar{36}$	540	21	15	104	51	43	401	0	$\bar{2}$	071	32	$\bar{34}$	$0,14,2$	4	6	$08\bar{3}$	29	31	065	17	$\bar{17}$	037	4	$\bar{5}$
170	12	12	$2,13,0$	11	$\bar{8}$	$37\bar{0}$	46	$\bar{67}$	550	0	3	105	15	$\bar{16}$	402	24	$\bar{29}$	081	21	$\bar{15}$	$01\bar{2}$	0	$\bar{5}$	$09\bar{3}$	31	$\bar{34}$	075	0	$\bar{1}$	$01\bar{7}$	11	10
180	42	$\bar{39}$	$2,14,0$	32	29	$38\bar{0}$	21	$\bar{24}$	560	11	0	106	0	$\bar{2}$	403	0	9	091	12	14	$02\bar{2}$	59	$\bar{74}$	$0,\bar{10},3$	19	15	085	30	38	$02\bar{7}$	11	$\bar{11}$
190	34	$\bar{27}$	$21\bar{0}$	7	$\bar{8}$	$39\bar{0}$	6	$\bar{2}$	570	14	$\bar{15}$	$10\bar{1}$	10	$\bar{6}$	$40\bar{1}$	22	22	$0,10,1$	4	$\bar{5}$	$03\bar{2}$	35	$\bar{35}$	$0,\bar{11},3$	0	7	095	0	$\bar{1}$	$03\bar{7}$	13	10
1,10,0	6	6	$22\bar{0}$	35	$\bar{24}$	$3,\bar{10},0$	12	$\bar{13}$	580	21	$\bar{30}$	$10\bar{2}$	46	47	$40\bar{2}$	24	$\bar{9}$	$0,11,1$	0	$\bar{10}$	$04\bar{2}$	36	37	$0,\bar{12},3$	11	1	$0,10,5$	2	9	$04\bar{7}$	13	22
1,11,0	18	15	$23\bar{0}$	27	17	$3,\bar{11},0$	30	20	590	9	$\bar{16}$	$10\bar{3}$	42	$\bar{33}$	$40\bar{3}$	22	$\bar{20}$	$0,12,1$	8	1	$05\bar{2}$	19	19	$0,\bar{13},3$	19	20	$01\bar{5}$	20	$\bar{17}$	$05\bar{7}$	6	$\bar{8}$
1,12,0	50	46	$24\bar{0}$	47	42	$3,\bar{12},0$	10	6	$5,10,0$	14	$\bar{20}$	$10\bar{4}$	10	5	$40\bar{4}$	43	43	$0,13,1$	16	$\bar{13}$	$06\bar{2}$	47	65	$0,\bar{14},3$	18	$\bar{21}$	$02\bar{5}$	4	$\bar{4}$	$06\bar{7}$	3	2
1,13,0	40	31	$25\bar{0}$	50	58	$3,\bar{13},0$	12	14	$51\bar{0}$	35	$\bar{44}$	$10\bar{5}$	8	1	$40\bar{5}$	0	2	$0,14,1$	0	$\bar{3}$	$07\bar{2}$	4	$\bar{1}$	014	3	3	$03\bar{5}$	0	6			
1,14,0	10	9	$26\bar{0}$	23	29	400	6	$\bar{3}$	$52\bar{0}$	18	$\bar{19}$	$10\bar{6}$	48	39	$40\bar{6}$	18	$\bar{23}$	$0\bar{1}1$	8	$\bar{9}$	$08\bar{2}$	0	$\bar{8}$	024	17	$\bar{16}$	$04\bar{5}$	0	$\bar{2}$			
1,15,0	8	8	$27\bar{0}$	6	4	410	31	27	$53\bar{0}$	22	$\bar{22}$	$10\bar{7}$	15	17	$40\bar{7}$	4	5	$0\bar{2}1$	30	26	$09\bar{2}$	10	$\bar{8}$	034	33	$\bar{42}$	$05\bar{5}$	8	$\bar{8}$			
$1\bar{1}0$	5	$\bar{2}$	$28\bar{0}$	9	$\bar{9}$	420	23	16	$54\bar{0}$	0	$\bar{5}$	201	13	17	$40\bar{8}$	24	$\bar{11}$	$0\bar{3}1$	25	$\bar{30}$	$0,\bar{10},2$	52	$\bar{61}$	044	19	$\bar{18}$	$06\bar{5}$	19	$\bar{13}$			
$1\bar{2}0$	82	$\bar{98}$	$29\bar{0}$	50	$\bar{52}$	430	4	$\bar{5}$	$55\bar{0}$	17	30	202	54	85	501	0	$\bar{17}$	$0\bar{4}1$	33	42	$0,\bar{11},2$	8	$\bar{6}$	054	29	$\bar{36}$	$07\bar{5}$	6	$\bar{2}$			
$1\bar{3}0$	46	$\bar{47}$	$2,\bar{10},0$	20	$\bar{10}$	440	25	$\bar{26}$	$56\bar{0}$	0	$\bar{2}$	203	33	$\bar{46}$	502	11	19	$0\bar{5}1$	6	$\bar{3}$	$0,\bar{12},2$	14	$\bar{5}$	064	19	$\bar{20}$	$08\bar{5}$	13	14			
$1\bar{4}0$	25	$\bar{21}$	$2,\bar{11},0$	27	$\bar{18}$	450	35	$\bar{44}$	$57\bar{0}$	24	23	204	26	$\bar{24}$	$50\bar{1}$	4	0	$0\bar{6}1$	14	9	$0,\bar{13},2$	3	$\bar{4}$	074	21	23	$09\bar{5}$	9	3			
$1\bar{5}0$	9	$\bar{7}$	$2,\bar{12},0$	5	$\bar{4}$	460	30	$\bar{35}$	$58\bar{0}$	14	18	205	12	6	$50\bar{2}$	4	$\bar{17}$	$0\bar{7}1$	40	41	$0,\bar{14},2$	26	19	084	13	10	$0,\bar{10},5$	29	$\bar{29}$			

O_6	60	147	261
O_7	228	150	282
O_8	81	147	135
H_2O	24	90	0

A fourier projection on (okl) using all the terms signable by the final set of structure factors, but with F_o modified by a temperature factor to reduce the diffraction rings of the heavy atoms, is shown in Figure 16. Contours are at 5 e/A^2 intervals. The positions and heights of the atomic peaks are generally satisfactory, and only traces of the diffraction rings remain.

Standard Deviations.

The accuracy of the determination was estimated using Cruikshank's equations (24). The standard deviation in electron density, $\sigma(\rho)$ = 1.2 e/A^2 on the (okl) projection. The standard deviation in atomic coordinates in the c direction is $\sigma(z)$ = 0.008A for Ca, 0.010A for P, and 0.036A for O. The corresponding values for other directions in the crystal will not be significantly different. The standard deviations in bond length are:

Ca - O = 0.037A

P - O = 0.039A

O - O = 0.050A

O - O = 0.072A (if related by a centre).

These values are very similar to those obtained for $CaHPO_4$.

4. Description of Structure.

As in all orthophosphates, the structure of $Ca(H_2PO_4)_2H_2O$ consists essentially of discrete PO_4''' tetrahedra and Ca^{++} ions, the latter coordinated by a shell of oxygen atoms and, in this case, water molecules. Figure 17 shows a projection of the structure down the a axis, the contents of four unit cells being included. The outstanding feature is the presence of sheets of composition $CaPO_4$ in the (010) plane. These sheets are virtually identical with those found in $CaHPO_4,2H_2O$ (2) and hence analagous to the sheets of $CaSO_4$ in gypsum (12).

The sheets contain parallel chains of composition $= Ca = PO_4 = Ca = PO_4 =$, along the c axis. Adjoining chains differ in height along the b axis by 2.3A to give a corrugation effect, the higher set of chains being related to the lower by centres of symmetry. The distance between sheets is equal to the (010) spacing, and the sheets are separated by the water molecules coordinated to the calcium ion, and by the remaining PO_4 tetrahedra, which face each other across a centre of symmetry in a similar orientation to that found in the structure of H_3PO_4 (10).

Apart from a change of symmetry from monoclinic to triclinic, the main difference between the structures of $Ca(H_2PO_4)_2H_2O$ and $CaHPO_4, 2H_2O$ is that the place of the second water molecule in the calcium coordination shell of the latter crystal has been taken in the former compound by one of the oxygens of the extra PO_4 group. The sheets are thereby moved further apart, the axial spacing $b/2 = 7.59A$ in $CaHPO_4, 2H_2O$ being lengthened to $b = 11.89A$ in the monocalcium salt. Otherwise the cell dimensions are very similar.

Along the chains, Ca is coordinated to O_1 and O_3 on the one side and O_2 and O_4 on the other, and to O_1' and O_2' of the neighbouring chain. Its total coordination of eight is made up by bonds to the water molecule and to O_5, belonging to the second phosphate group.

The observed bond lengths and angles are:

$P_1 - O_1 = 1.50A$	$Ca - O_1 = 2.57A$
$P_1 - O_2 = 1.43$	$Ca - O_2 = 2.59$
$P_1 - O_3 = 1.59$	$Ca - O_3 = 2.74$
$P_1 - O_4 = 1.64$	$Ca - O_4 = 2.65$
$P_2 - O_5 = 1.44$	$Ca - O_5 = 2.44$
$P_2 - O_6 = 1.50$	$Ca - O_1' = 2.30$
$P_2 - O_7 = 1.54$	$Ca - O_2' = 2.36$
$P2 - O8 = 1.49$	$Ca - H20 = 2.49$

$O_1P_1O_2$= 109.0°	$O_5P_2O_6$= 105.5°
$O_1P_1O_3$= 106.5°	$O_5P_2O_7$= 108.0°
$O_1P_1O_4$= 116.5°	$O_5P_2O_8$= 109.0°
$O_2P_1O_3$= 113.5°	$O_6P_2O_7$= 109.0°
$O_2P_1O_4$= 108.5°	$O_6P_2O_8$= 109.0°
$O_3P_1O_4$= 102.5°	$O_7P_2O_8$= 115.5°

The average P - O bond length is 1.52A, the average Ca - O bond length is 2.52A, and the average distance O - O within the Po_4 groups is 2.48A.

It has not been feasible to identify the six hydrogen atomic positions in a direct manner. It is very probable that these atoms lie between oxygens of neighbouring phosphate tetrahedra and round the oxygen of the water molecule, forming hydrogen bonds. It is customary in such cases to attempt to locate these hydrogen bonds by the resultant shortening of the normal O - O interatomic distance, generally over 3.0A (the Vander Waal's distance). The somewhat large standard deviation (0.05A) in O - O distances in this crystal makes this procedure not altogether unequivocal, but some hydrogen bonds present can reasonably be assumed from the general spatial configuration. These are listed below:

$O_3 - O_5 = 2.50A$

$O_7 - O_8' = 2.79A$

$H_2O - O_4 = 2.61A$

$H_2O - O_3 = 2.68A$

$H_2O - O_6 = 3.00A$

This tentative list would account for five of the six hydrogens, leaving O_1 and O_2 without any hydrogen bonds so far. These atoms do not lie close enough to any others to suggest hydrogen bonding, with the exception in each case of their symmetry-related atom, where the distances are:

$O_1 - O_1' = 2.91A$

$O_2 - O_2' = 2.92A.$

These together would account for the sixth hydrogen, the centres of symmetry having a multiplicity of only one. Instances of a hydrogen bond across a centre of symmetry (the hydrogen not being at the centre but on one side or the other in a random distribution) are well known (31, 32). The distances in these crystals were much smaller, however (2.55 and 2.61A respectively). Thus there is insufficient evidence for assuming hydrogens in these positions, though there seems to be no other likely alternative, all other O - O distances being over 3.0A.

To summarize, the structure of $Ca(H_2PO_4)_2H_2O$ consists of corrugated sheets of $CaPO_4$ parallel to the (010) plane, separated by water molecules and PO_4 tetrahedra, linking the sheets together by ionic and hydrogen bonding. The hydrogens cannot be located with certainty. The calcium coordination is eight.

The crystal habit, tabular on the (010) face with elongation parallel to the c axis, agrees with this structure though there does not seem to be a good cleavage parallel to the (010) plane, as one might expect from the plane of weakness in the structure. The almost invariable presence of multiple twinning according to the Albite law, i.e. with (010) as the twinning and composition plane, is also accounted for, since there are no great packing difficulties to be overcome if one sheet happens to grow in an orientation rotated through 180° around an axis perpendicular to (010). Indeed in $CaHPO_4,2H_2O$, and $CaSO_4,2H_2O$, there are screw axes already in this position so that alternate sheets are always disposed in this manner. The substitution of random Albite twinning for this regular alternation corresponds to the loss of monoclinic symmetry.

Appendix: Formulae and Methods of Calculation.

Collected structure factor and electron density formulae for the space group $P\bar{1}$.

All such formulae used in the two structure determinations are listed below. The expression F(hkl) means the structure factor associated with the set of crystal planes of indices (hkl); $(x_r y_r z_r)$ are the coordinates of a scattering unit, expressed as fractions of the cell axes multiplied by 2π; and (X,Y,Z) is the electron density at a point of indices (X,Y,Z) again expressed as fractions of the cell axes multiplied by 2π.

Structure factor calculations

The general formula for the structure factor can be written:

$$|F(hkl)|^2 = A^2 + B^2$$

where $A = \Sigma\Sigma f_r \cos(hx_r + ky_r + lz_r)$

$B = \Sigma\Sigma f_r \sin(hx_r + ky_r + lz_r)$

$f_r =$ atomic scattering factor for atom r and plane (hkl).

In $P\bar{1}$, the origin is taken at the centre of symmetry, so $B \neq 0$, and the positions (x,y,z) and $(\bar{x},\bar{y},\bar{z})$ are equivalent. Hence we have

$$F(hkl) = 2\sum f_r \cos(hx_r + hy_r + lz_r)$$

where the summation is over half the unit cell.

For two-dimensional calculations, e.g. in the zone (hko), this is expanded to

$$F(hko) = 2\sum f_r(\cos hx_r \cos ky_r - \sin hx_r \sin ky_r).$$

Electron density calculations.

The electron density formula for $P\bar{1}$ is:

$$\rho(X,Y,Z) = \frac{1}{V}\left[F(0,0,0)+2\sum_{h=0}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} F(hkl)\cos(hX+kY+lZ)\right].$$

For two-dimensional syntheses, this reduces to:

$$\rho(X,Y) = \frac{1}{A}\Big[F(000)+2\sum_{h=1}^{\infty} F(hoo)\cos hX+2\sum_{k=1}^{\infty} F(oko)\cos kY$$
$$+ 2\sum_{h=1}^{\infty}\left\{\sum_{k=1}^{\infty}\left[F(hko)+F(\bar{h}ko)\right]\cos hX\right\}\cos kY$$
$$- 2\sum_{h=1}^{\infty}\left\{\sum_{k=1}^{\infty}\left[F(hko)-F(\bar{h}ko)\right]\sin hX\right\}\sin kY\Big]$$

Difference Fourier syntheses were similarly computed, substituting $\Delta(hko) = [F\text{ obs.}(hko) - F\text{ calc.}(hko)]$ for F(hko), and omitting F(000).

Patterson syntheses.

The general Patterson formula for $P\bar{1}$ is similar to the electron density formula, substituting $F^2(hkl)$ for F(hkl). For ease of computation of the three-dimensional series, $F^2(000)$ was omitted and the expression expanded thus:

$$P(X,Y,Z) = {}^{2}/_{V}\sum_{h=0}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\Big\{\left[F^2(hkl)+F^2(\bar{h}kl)+F^2(h\bar{k}l)\right.$$
$$\left.+ F^2(hk\bar{l})\right] \cdot \cos hX \cos kY \cos lZ$$
$$+\left[F^2(\bar{h}kl)+F^2(h\bar{k}l)-F^2(hkl)-F^2(hk\bar{l})\right]\sin hX \sin kY \cos lZ$$
$$+\left[F^2(\bar{h}kl)+F^2(hk\bar{l})-F^2(hkl)-F^2(h\bar{k}l)\right]\sin hX \cos kY \sin lZ$$
$$+\left[F^2(h\bar{k}l)+F^2(hk\bar{l})-F^2(hkl)-F^2(\bar{h}kl)\right]\cos hX \sin kY \sin lZ\Big\}$$

Using this general formula, $F^2(hko)$, $F^2(hol)$ and $F^2(okl)$ must be divided by 2 and $F^2(hoo)$, $F^2(oko)$ and $F^2(ool)$ divided by 4.

For two-dimensional Patterson summations, an expression analogous to that for the Fourier projection was used.

Methods of calculation.

For structure factor calculations, two-figure tables of cos hx and sin hx in intervals of thousandths of the cell edge were used for Ca and P atoms, and Beevers-Lipson strips at 3^o intervals for the O atoms. Atomic scattering factors were obtained from graphs, using the values for Ca^{++} given by Hartree (33) and for neutral P and O those given by James and Brindley (34).

Patterson, Fourier and difference syntheses were computed with the aid of an electrical analogue computer of the Hägg-Laurent type (35). This machine provides one-dimensional summations, with wave-numbers up to 15, at intervals of 60ths of the cell edges. Two-dimensional summations are performed in one-fifth of the time required when using Beevers-Lipson strips, with an accuracy sufficient for most purposes when visual estimation of intensities are utilized.

ACKNOWLEDGEMENTS

The author wishes to record his sincere gratitude for the enthusiastic encouragement and advice given to him by Dr C.A. Beevers throughout this work. He is also indebted to the Department of Scientific and Industrial Research for a Maintenance Allowance.

BIBLIOGRAPHY

(1) C.A. Beevers and D.B. MacIntyre, Min. Mag., 1946, 27, 254.

(2) C.A. Beevers and B. Raistrick, Nature, 1954, 173, 542.

(3) S. Eisenberger, A. Lehrman and W.D. Turner, Chem. Rev., 1940, 26, 257.

(4) P.W. Arnold, Trans. Far. Soc., 1950, 46, 1061.

(5) S.B. Hendricks and W.L. Hill, Ind. Eng. Chem., 1936, 28, 440.

(6) J.R.Lehr, J.P. Smith and W.E. Brown, S.E. Regional meeting, Amer. Chem. Soc., October 1952.

(7) J. West, Z. Krist., 1930, 74, 306.

(8) G.E.R. Schulze, Z. physikal. Chem., 1934, B24, 215.

(9) L. Helmholz, J. Chem. Phys., 1936, 4, 316.

(10) J.P. Smith, W.E. Brown and J.R. Lehr, J.A.C.S., 1955, 77, 2728.

(11) S. Naray-Szabo, Z. Krist., 1930, 75, 387.

(12) W.A. Wooster, Z. Krist., 1936, 94, 375.

(13) W.F. Bale, et al., Ind. Eng. Chem. (anal.), 1945, 17, 491.

(14) A. de Schulten, Bull. Soc. Franc. Min., 1901, 24, 323; 1903, 26, 11; 1904, 27, 120.

(15) J.W. Mellor, "Inorganic and Theoretical Chemistry", London, Longmans Green, 1923.

(16) H. Bassett, Z. anorg. Chem., 1908, 59, 1.

(17) W. Cochran, J. Sci. Inst., 1948, 25, 253.

(18) A.J.C. Wilson, Nature, 1942, 150, 152.

(19) E.R.Howells, D.C. Phillips and D. Rogers, Acta Cryst., 1950, 3, 210.

(20) H. Lipson and W. Cochran, "Determination of Crystal Structures", p.163. London, Bell, 1953.

(21) C.A. Beevers and J.H. Robertson, Acta Cryst., 1950, 3, 164.

(22) M.J. Buerger, Proc. Nat. Acad. Sci., 1950, 36, 376; 36, 738.

(23) W. Cochran, Acta Cryst., 1951, 4, 408.

(24) D.W.J. Cruikshank, Acta Cryst., 1949, 2, 65.

(25) A.F. Wells, "Structural Inorganic Chemistry", Oxford, Clarendon Press, 1950.

(26) J.V. Smith, Acta Cryst., 1953, 6, 9.

(27) E.C.S. Dickson and W. Binks, Phil. Mag., 1926, 2, 114.

(28) G. MacLennan and C.A. Beevers, Acta Cryst., 1955, in the press.

(29) P. Groth, "Chemische Krystallographie", Leipzig, Engelmann, 1908.

(30) K. Haushofer, Z. Krist., 1883, 7, 265.

(31) J.C. Speakman, J. Chem. Soc. 1949, 3357.

(32) J.M. Skinner and J.C. Speakman, J.Chem. Soc., 1951, 185.

(33) D.R. Hartree and W. Hartree, Proc. Roy. Soc., 1938, A164, 167.

(34) R.W. James and G.W. Brindley, Z. Krist., 1931, 78, 470.

(35) F. Stern, Thesis, Univ. of Edinburgh, 1950.

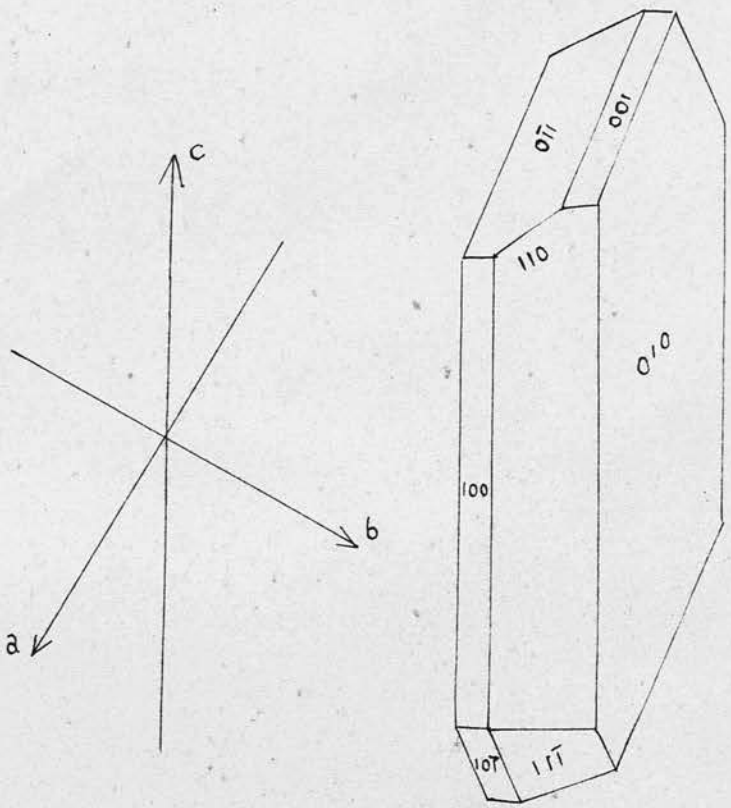


Fig. 9. Crystal habit of $Ca(H_2PO_4)_2H_2O$, after Lehr et al.

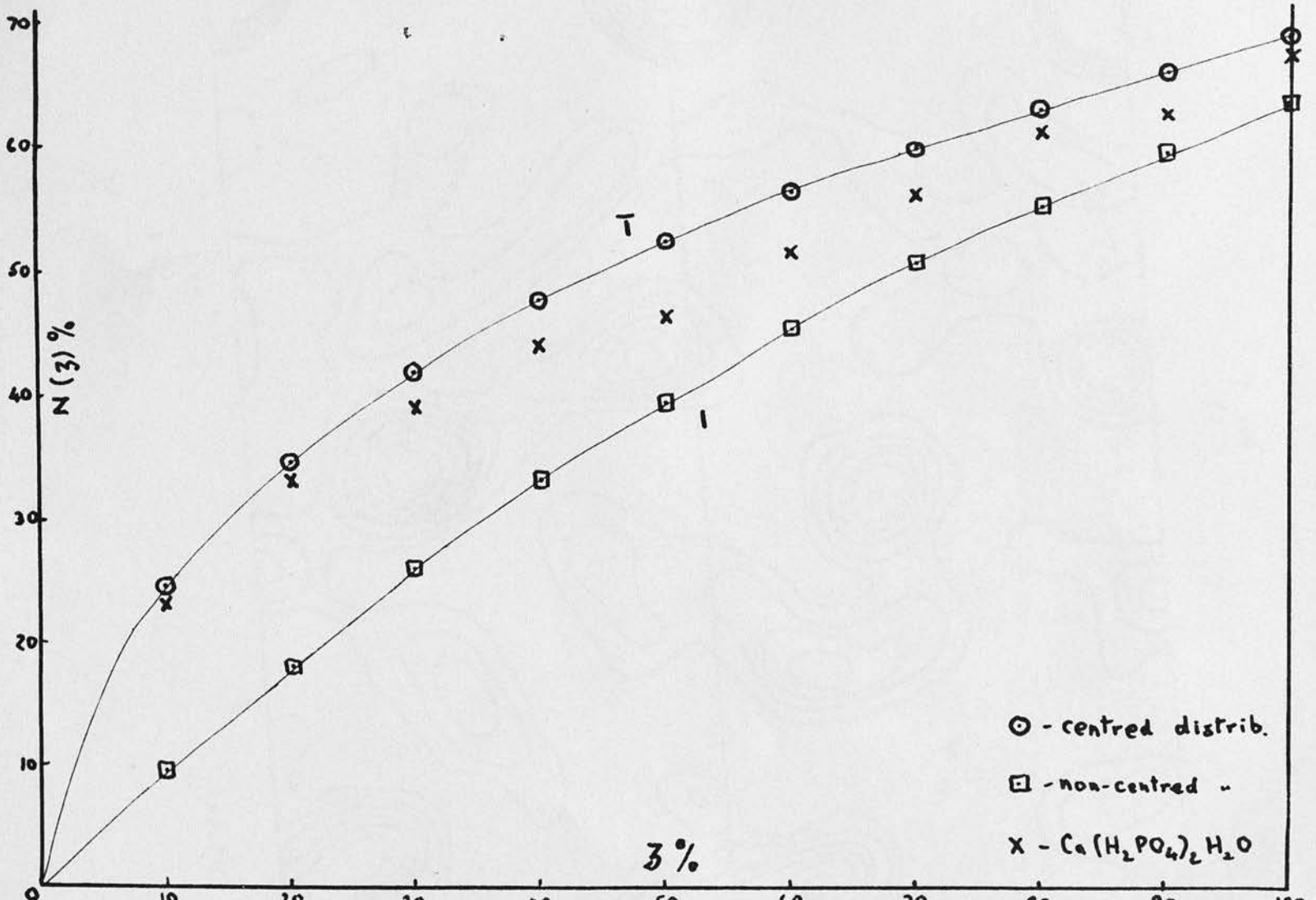

N (3) %
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
T
I
3 %
⊙ - centred distrib.
⊡ - non-centred "
X - $Ca(H_2PO_4)_2 H_2O$

FIGURE 10.

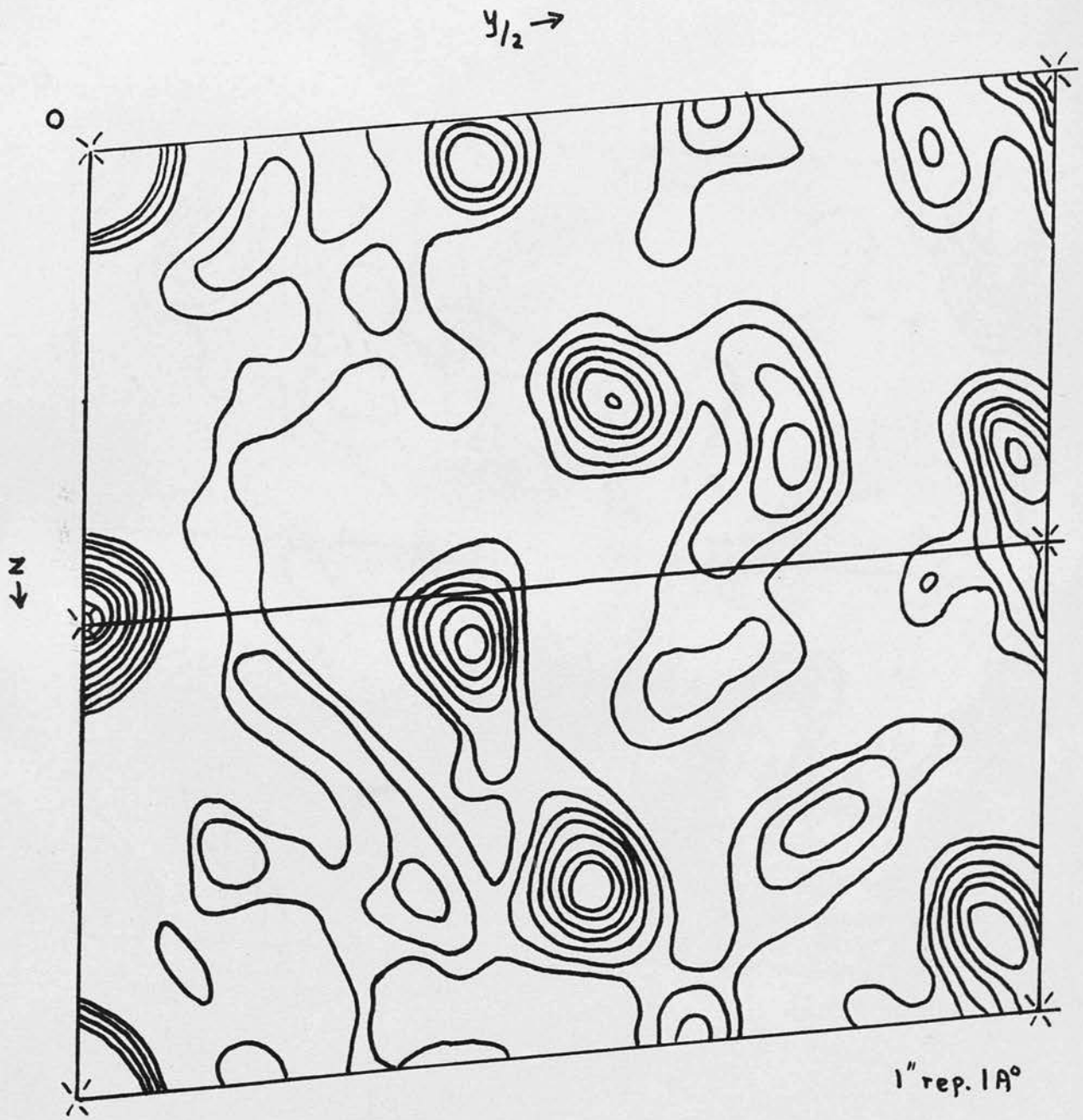


Fig. 11. (okl) Patterson projection of $Ca(H_2PO_4)_2H_2O$.

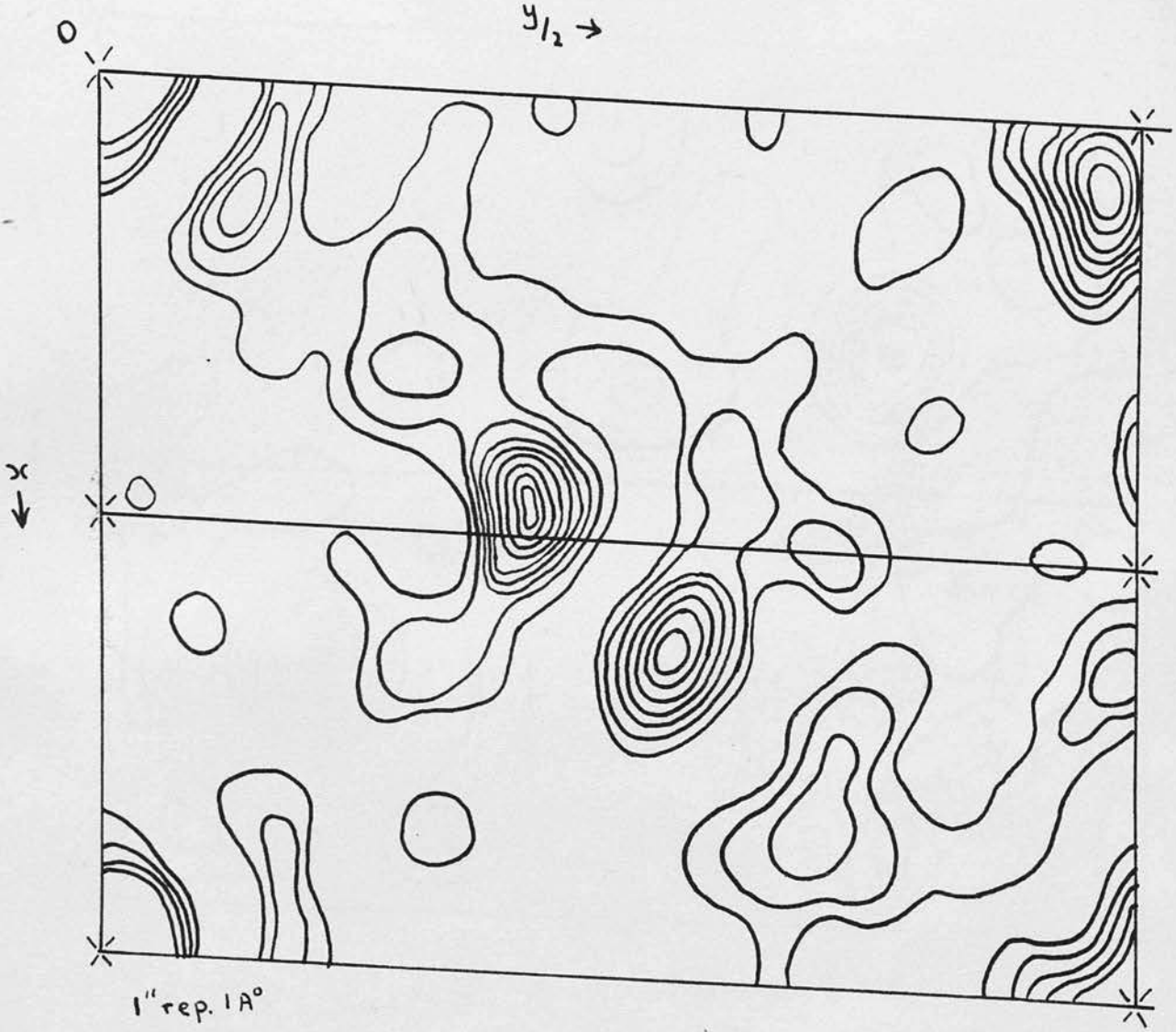


Fig. 12. (hko) Patterson projection of $Ca(H_2PO_4)_2H_2O$.

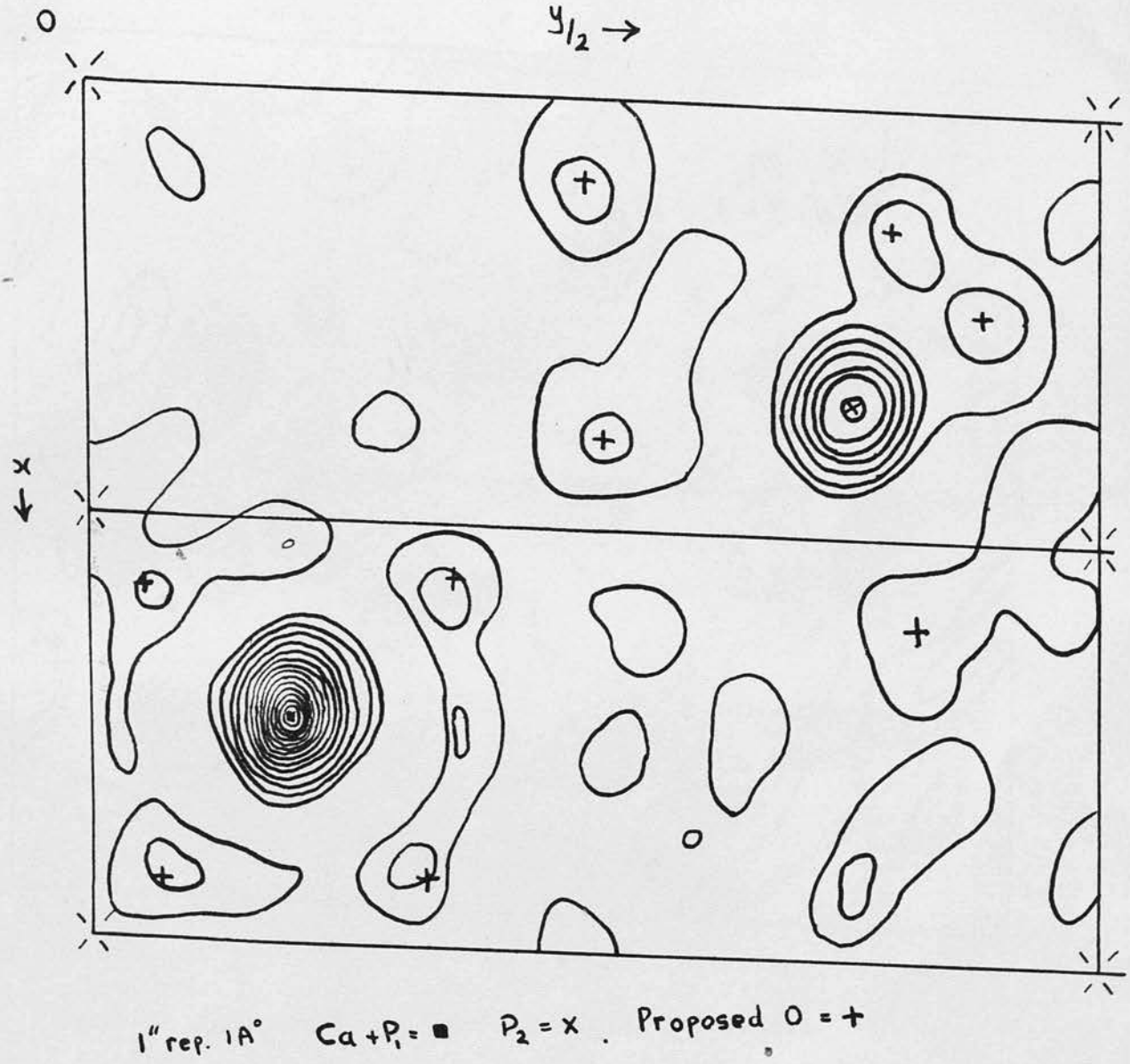


Fig. 13. (hko) Fourier projection using 110 terms signed by the heavy atoms alone, to discover the oxygen positions. Contours at 5, 10, 15 . . . . 70 e/A^2.

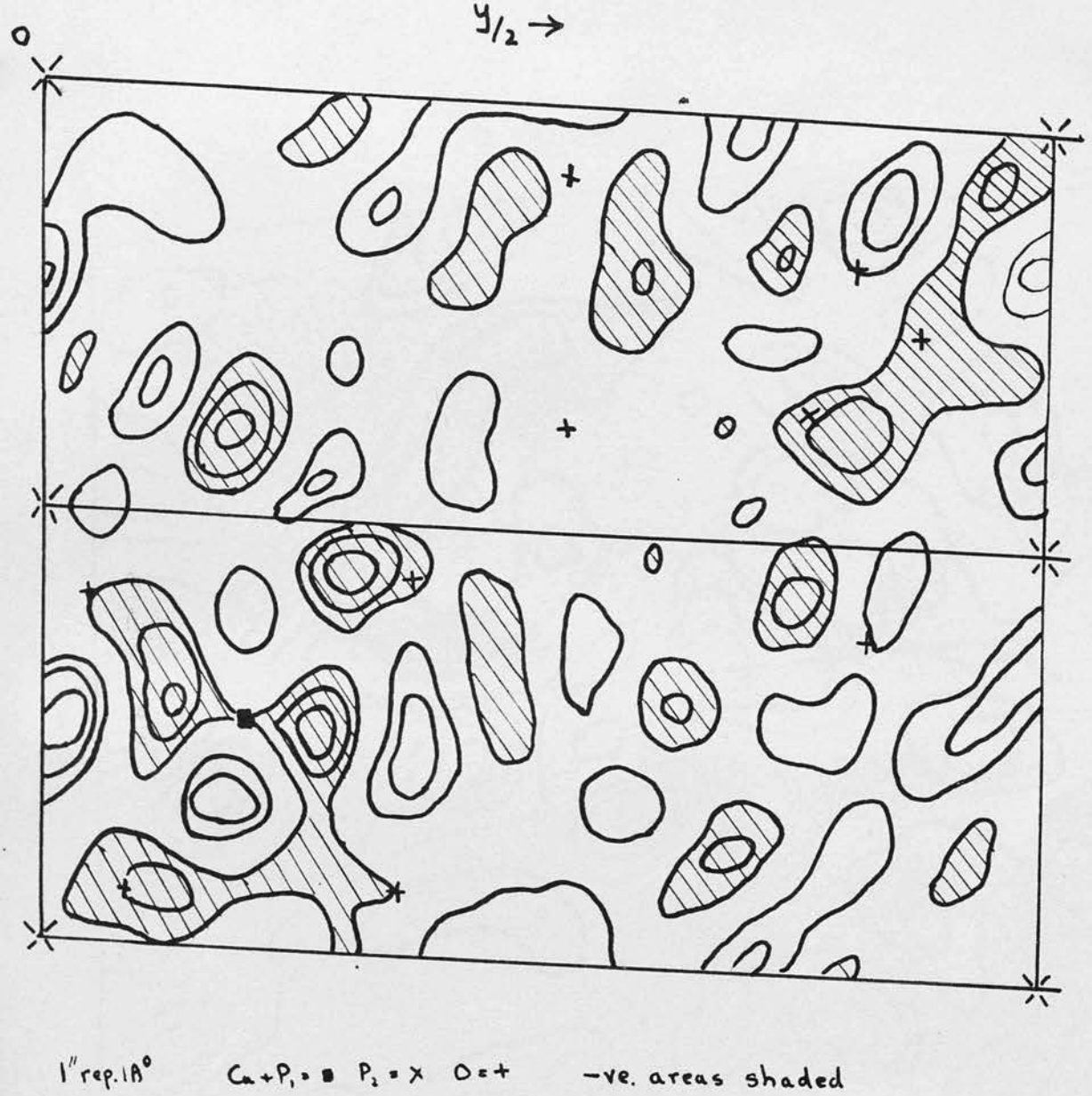


Fig. 14. (hko) (F_o - F_c) difference synthesis, indicating need to separate Ca and P_1 in the X direction. Contours at 2 e/A^2 intervals, with zero contour omitted.

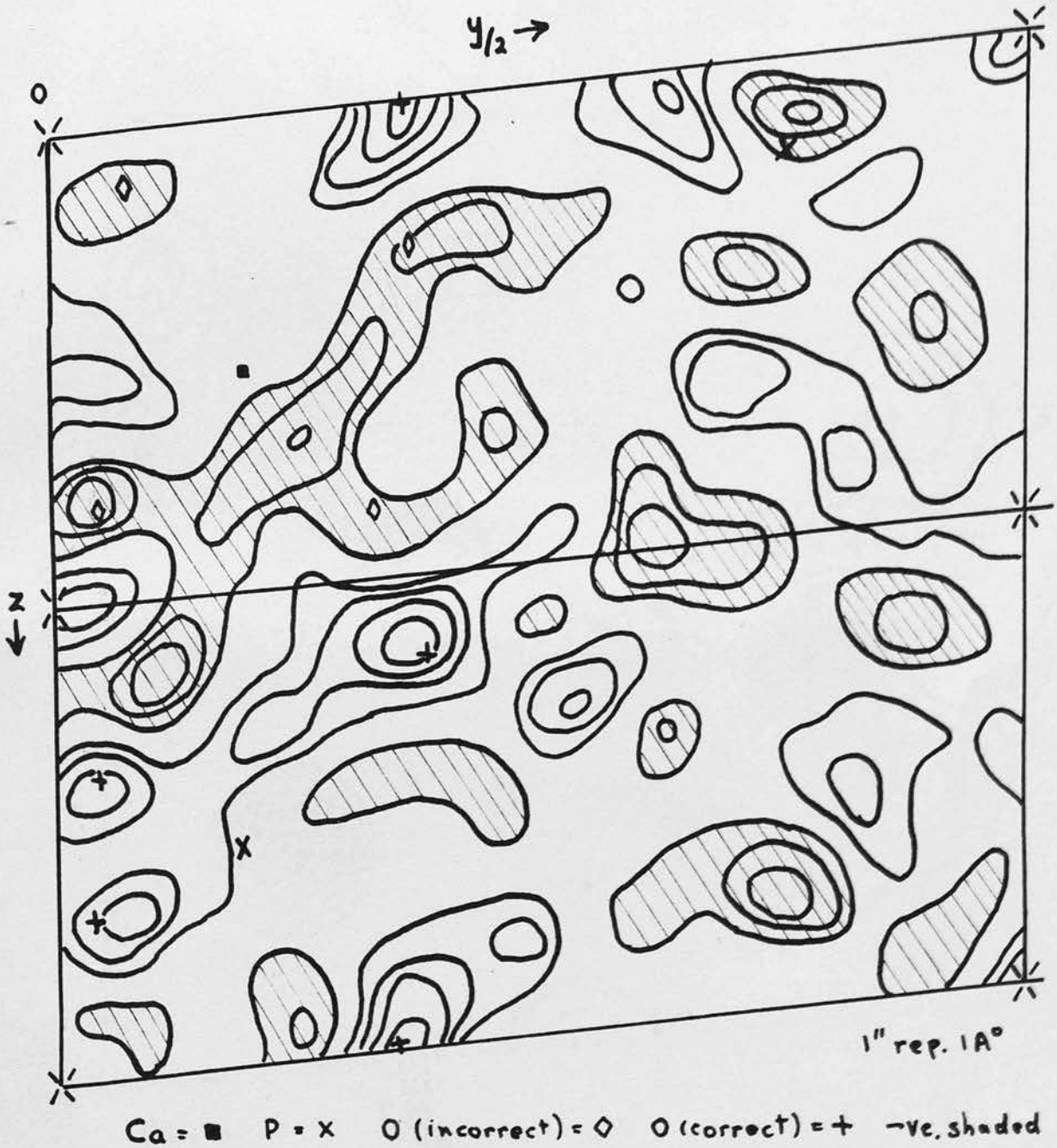


Fig. 15. (okl)error synthesis, showing wrongly chosen oxygens in hollows and "ghost peaks" at the correct oxygen positions instead. Contours at 2 e/A^2 intervals, with zero contour omitted.

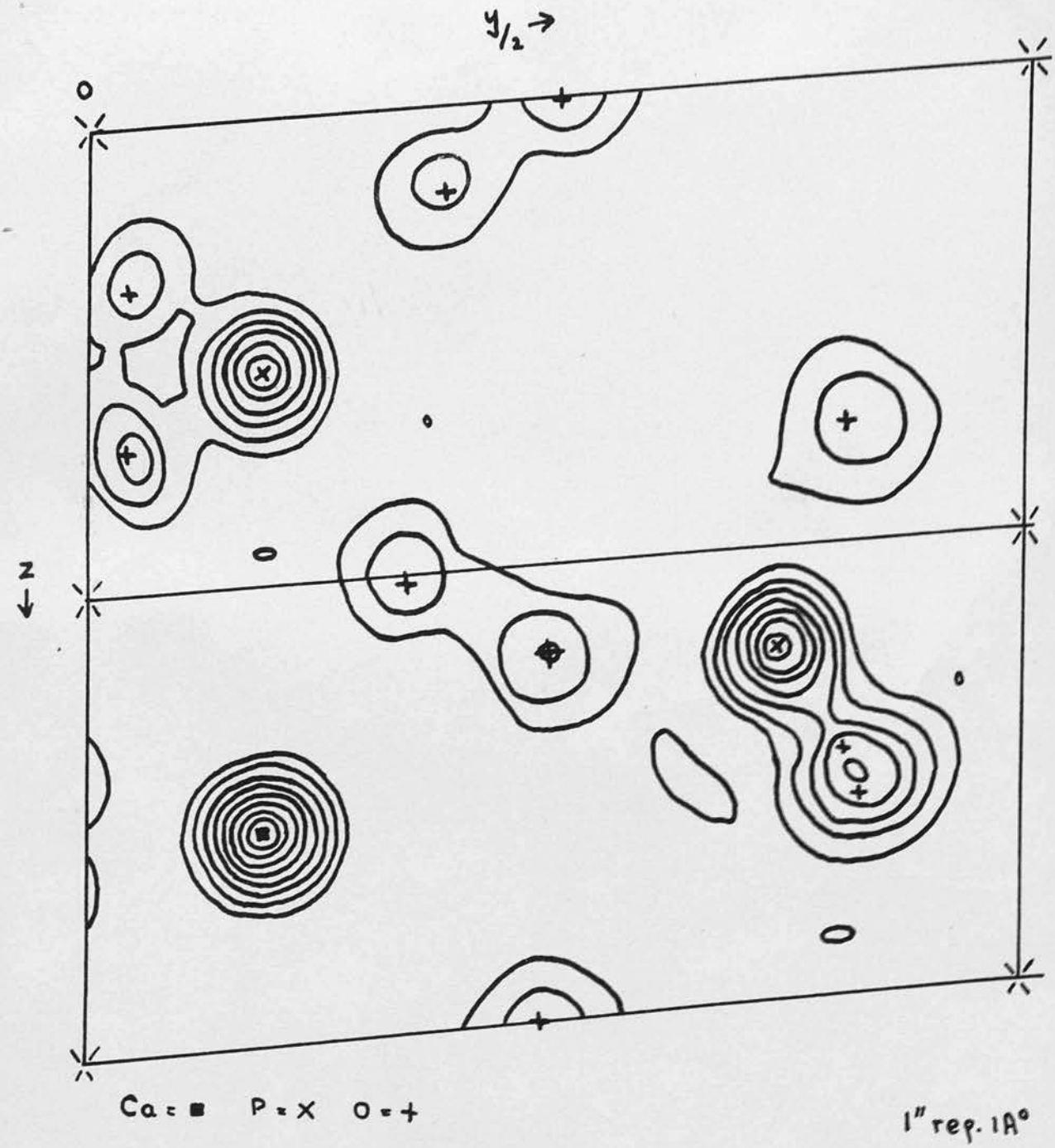
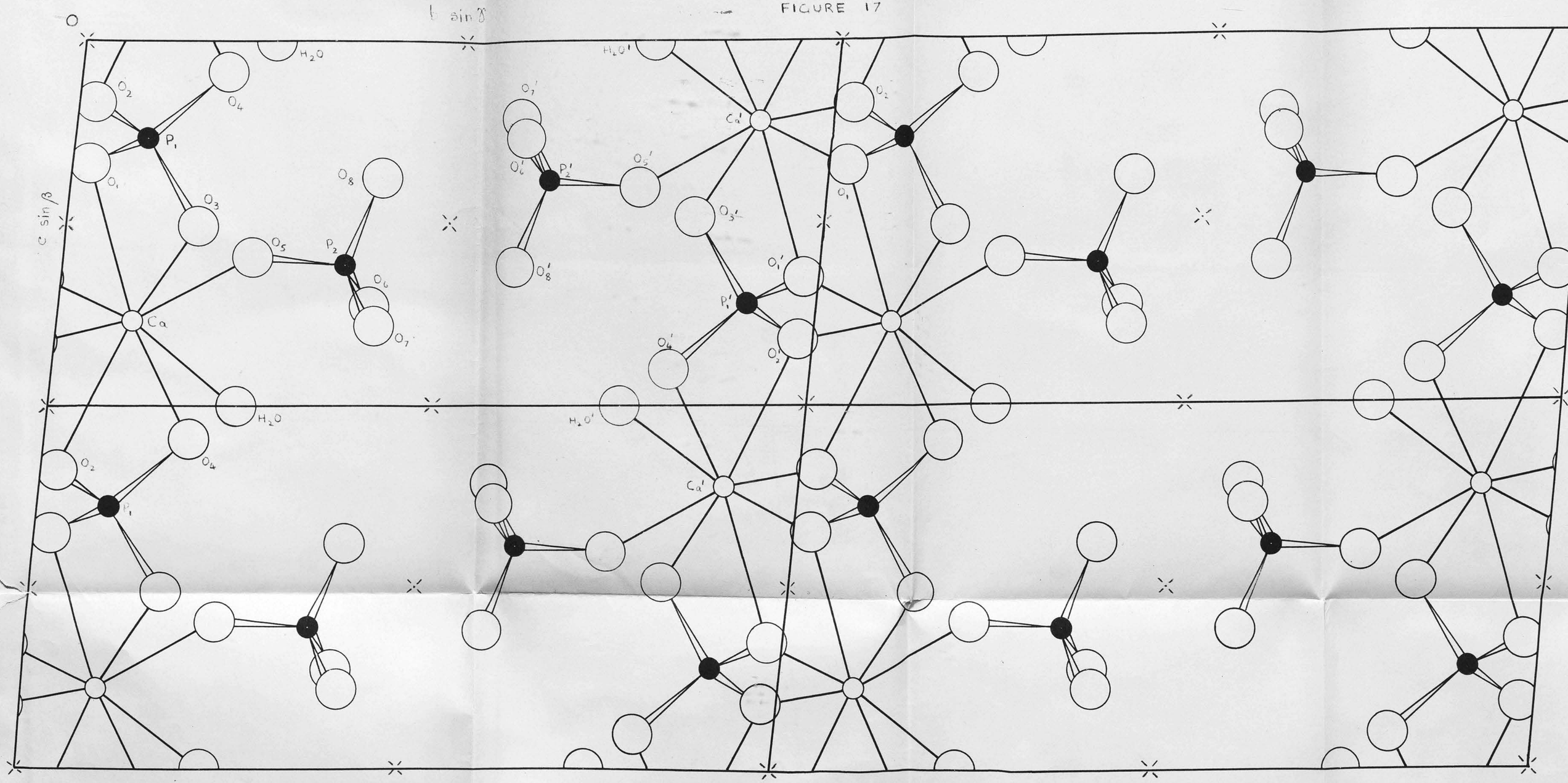


Fig. 16. (okl) Fourier projection of $Ca(H_2PO_4)_2H_2O$, for final structure. Contours at 5, 10, 15 . . . . 45 e/Å.

FIGURE 17


O
b sin γ
c sin β
H_2O
O_2
O_4
P_1
O_1
O_3
O_8
O_5
P_2
O_6
Ca
O_7
H_2O'
O_7'
O_6'
P_2'
O_5'
Ca'
O_2'
O_1'
O_3'
O_8'
P_1'
O_4'
0 1 2 3 4 5 A
Ca-○ P-● O-○