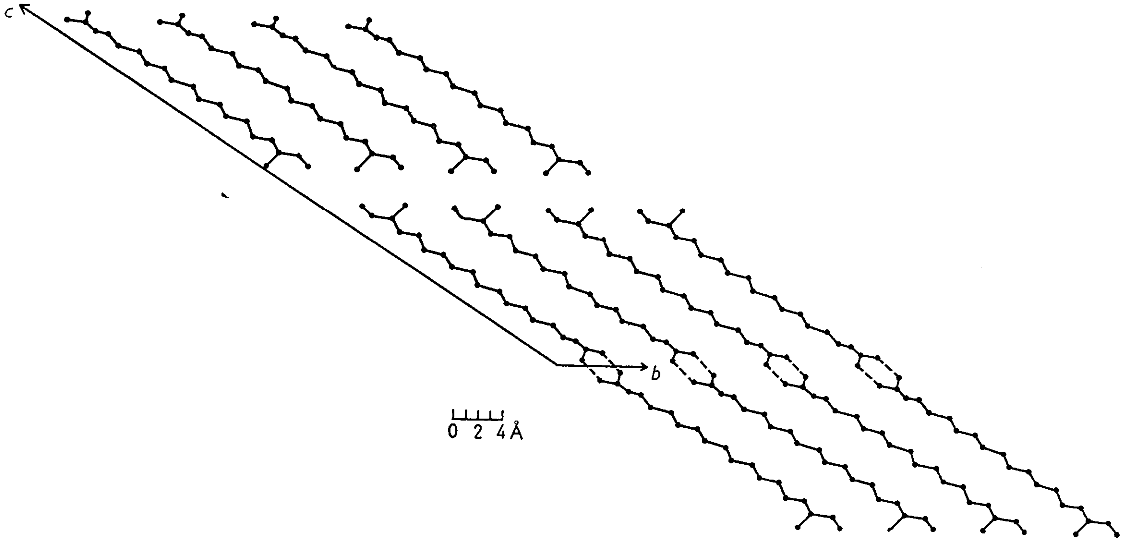

Fig. 2. Molecular arrangement of 16DL-methyloctadecanoic acid, as viewed along the shortest axis.

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The Crystal Structure of Dicalcium Phosphate Dihydrate, $CaHPO_4 . 2H_2O$

By C. A. Beevers

Department of Chemistry, University of Edinburgh, Scotland

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The structure of $CaHPO_4 . 2H_2O$ has been determined, and refined to a moderate accuracy (standard deviation of oxygen positions about 0·03 Å, R approximately 26%). The structure is similar to that of gypsum, but there is a definite change of cell dimensions and a small shift in atomic parameters. The hydrogen atoms are probably situated between pairs of water molecules. The structure contains corrugated sheets of composition $CaPO_4$, with the waters in layers between them.

Introduction

Dicalcium phosphate is of interest as a mineral (brushite) which is isomorphous with the corresponding arsenate (pharmacolite). The crystals are very similar to those of gypsum, with which, indeed, it forms a mixed series (Hill & Hendricks, 1936; O'Daniell, 1939; Smith, Lehr & Brown, 1955). It can be grown into very fine large crystals, and we are obliged to the Research Department of the Tennessee Valley Authority for specimens which were used for the cutting of crystal plates for Geiger-counter spectrometry. Smaller crystals were grown for this work by the Research Department of Scottish Agricultural Industries Limited.

Optical goniometry, unit cell and space group

The crystals were tabular on the *b* face, with edges made up from {110}, {112} and {121} faces. The smaller crystals used showed variations in their interfacial angles of up to 4′. The larger crystals, although of brilliant appearance, showed variations of up to 10′ in different parts of the same face. The small crystals showed the full symmetry 2/*m* of the monoclinic system, but the large crystals showed no mirror plane, and were evidently grown in a very unsymmetrical manner. Cell dimensions were deduced from the positions of the high-order spots, and the following cell was adopted:

$$a=5{\cdot}812\pm0{\cdot}002,\ b=15{\cdot}180\pm0{\cdot}003,\ c=6{\cdot}239\pm0{\cdot}002\ \text{Å},\quad \beta = 116^\circ\ 25'\pm2'\ .$$

This cell differs from those adopted by Miers and by Groth, but it is the smallest possible cell and corresponds to that suggested by Bragg (1937). The cell has a volume of 492·9 Å^3, and the calculated density is 2·318 g.cm.$^{-3}$, whilst the value of the measured density given by Groth is 2·317 g.cm.$^{-3}$. There are four molecules of $CaHPO_4.2\ H_2O$ per cell.

Oscillation and Weissenberg photographs were taken about all three axes and also about the [101] direction, using Cu $K\alpha$ radiation. In most cases Mo $K\alpha$ radiation was also used in order to reach higher values of sin θ/λ and to reduce the absorption effects. The crystals used had cross-sections varying from 0·2 to 0·6 mm. in diameter. The linear absorption coefficients calculated from the data given in the *Internationale Tabellen* are 138 cm.$^{-1}$ for Cu $K\alpha$ radiation and 16 cm.$^{-1}$ for Mo $K\alpha$ radiation.

The absent reflexions are those of the general planes when $h+k+l$ is odd, and those of the ($h0l$) planes when h is odd. The space group is thus *Ia* or *I*2/*a*, depending upon the absence of presence of a centre of symmetry. Now natural crystals show centro-symmetry so that the crystal class has been taken as 2/*m*, and therefore the space group is *I*2/*a*. The fact that a satisfactory structure can be reached in this space group is confirmatory evidence in favour of this choice.

Table 1. *Values of calculated and observed structure factors*

(hol)

h	l	Fc	Fo	h	l	Fc	Fo	h	l	Fc	Fo	h	l	Fc	Fo	h	l	Fc	Fo	h	l	Fc	Fo
0	0	83	-	2	4	$\overline{24}$	19	6	2	$\overline{10}$	10	$\overline{2}$	4	$\overline{29}$	27	$\overline{4}$	10	20	12	$\overline{8}$	6	10	11
	2	8	6		6	$\overline{13}$	14		4	$\overline{10}$	15		6	$\overline{21}$	15	$\overline{6}$	2	$\overline{15}$	14		8	11	20
	4	21	22		8	$\overline{10}$	10		6	$\overline{15}$	10		8	$\overline{7}$	13		4	$\overline{16}$	17		10	13	5
	6	8	8	4	0	27	24	8	0	15	14		10	$\overline{11}$	8		6	$\overline{20}$	15	$\overline{10}$	2	$\overline{6}$	14
	8	12	11		2	15	15		2	11	15	$\overline{4}$	2	18	19		8	$\overline{4}$	13		4	$\overline{16}$	15
	10	14	14		4	11	11		4	6	6		4	9	12		10	$\overline{12}$	8		6	$\overline{9}$	7
2	0	$\overline{30}$	23		6	8	9	10	0	$\overline{10}$	11		6	17	13	$\overline{8}$	2	9	11		8	$\overline{7}$	14
	2	$\overline{5}$	6	6	0	$\overline{10}$	12	$\overline{2}$	2	$\overline{9}$	13		8	8	4		4	9	15				

(okl)

k	l	Fc	Fo	k	l	Fc	Fo	k	l	Fc	Fo	k	l	Fc	Fo	k	l	Fc	Fo	k	l	Fc	Fo
2	0	$\overline{22}$	17	10	2	0	3	18	4	8	8	8	8	$\overline{11}$	8	25	1	$\overline{3}$	0	7	5	$\overline{2}$	4
4		$\overline{11}$	10	12		15	15	20		$\overline{11}$	10	10		$\overline{2}$	0	27		0	0	9		$\overline{1}$	6
6		2	6	14		$\overline{16}$	16	22		1	6	12		11	9	1	3	8	4	11		$\overline{1}$	6
8		$\overline{12}$	17	16		$\overline{2}$	3	24		3	0	14		$\overline{6}$	7	3		$\overline{7}$	7	13		6	5
10		$\overline{4}$	4	18		4	9	2	6	$\overline{7}$	6	16		4	0	5		$\overline{3}$	4	15		$\overline{6}$	3
12		13	13	20		$\overline{10}$	12	4		$\overline{8}$	6	18		4	0	7		$\overline{1}$	8	17		1	0
14		$\overline{14}$	13	22		12	16	6		18	12	20		$\overline{8}$	6	9		2	7	19		$\overline{4}$	0
16		10	8	24		4	3	8		$\overline{8}$	10	3	1	1	1	11		$\overline{1}$	2	21		5	0
18		13	10	26		$\overline{10}$	7	10		4	3	5		2	8	13		$\overline{1}$	3	23		3	0
20		$\overline{18}$	11	28		5	5	12		6	10	7		5	7	15		$\overline{1}$	4	1	7	5	3
22		2	6	2	4	$\overline{2}$	3	14		$\overline{13}$	12	9		$\overline{9}$	10	17		6	3	3		$\overline{3}$	8
24		$\overline{1}$	4	4		$\overline{12}$	10	16		2	0	11		7	10	19		$\overline{1}$	0	5		$\overline{3}$	3
26		$\overline{4}$	11	6		15	17	18		5	7	13		$\overline{3}$	3	21		$\overline{2}$	4	7		$\overline{2}$	2
28		6	8	8		$\overline{19}$	15	20		$\overline{7}$	7	15		2	4	23		0	0	9		$\overline{1}$	2
2	2	$\overline{26}$	32	10		1	2	22		5	3	17		$\overline{3}$	0	25		0	0	1	9	$\overline{2}$	0
4		5	6	12		10	9	2	8	$\overline{6}$	6	19		1	0	1	5	$\overline{4}$	0	3		$\overline{2}$	0
6		26	26	14		$\overline{9}$	10	4		$\overline{1}$	3	21		$\overline{2}$	0	3		$\overline{2}$	3	5		2	0
8		$\overline{12}$	16	16		8	7	6		9	9	23		4	0	5		7	6	7		3	0

(hko)

h	k	Fc	Fo	h	k	Fc	Fo	h	k	Fc	Fo	h	k	Fc	Fo	h	k	Fc	Fo	h	k	Fc	Fo
2	2	$\overline{1}$	2	2	18	$\overline{10}$	3	6	2	7	7	1	9	8	10	3	3	$\overline{7}$	7	3	17	1	7
	4	25	17	4	2	$\overline{16}$	16		4	10	6		11	12	11		5	3	5	5	1	5	3
	6	$\overline{21}$	18		4	$\overline{5}$	8		6	$\overline{16}$	10		13	2	5		7	7	6		3	6	6
	8	17	15		6	12	14		8	6	8		15	$\overline{3}$	7		9	$\overline{2}$	3		5	3	2
	10	$\overline{4}$	2		8	$\overline{3}$	8	1	1	1	3		17	$\overline{3}$	5		11	$\overline{6}$	8		7	$\overline{5}$	4
	12	$\overline{9}$	10		10	1	5		3	0	3		19	$\overline{1}$	6		13	2	5		9	1	1
	14	15	16		12	9	8		5	$\overline{11}$	11	3	1	$\overline{1}$	4		15	3	2		11	1	2
	16	$\overline{9}$	6		14	$\overline{16}$	11		7	$\overline{13}$	13												

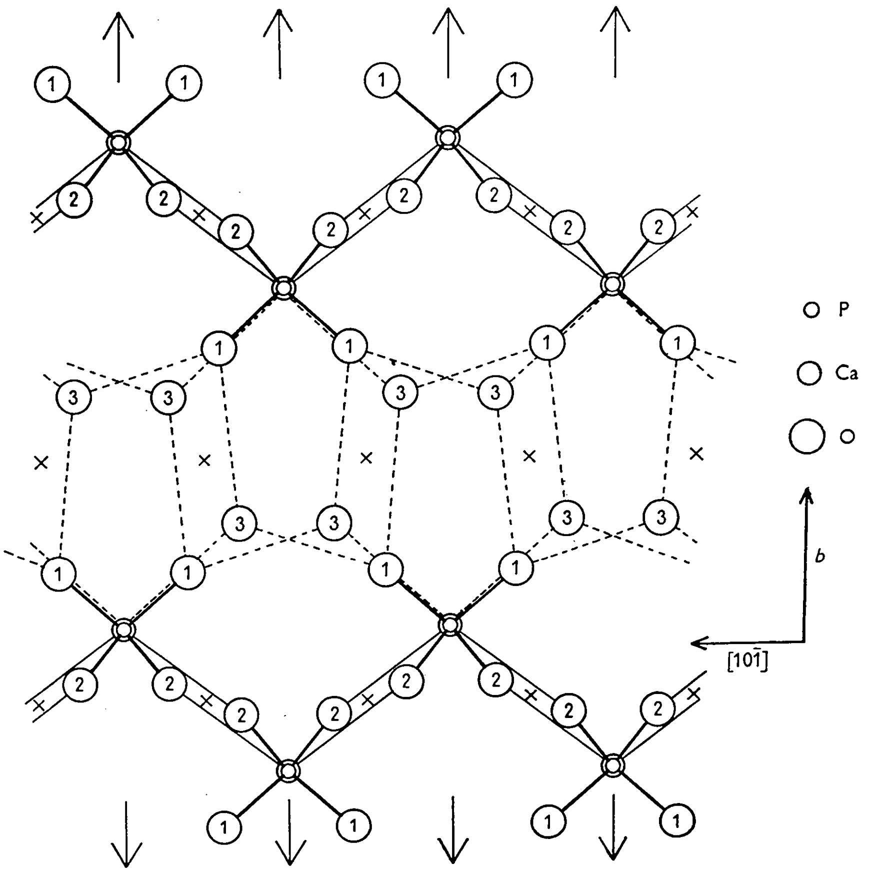


Fig. 1. Projection of the structure on to a plane perpendicular to [101].

Determination of atomic parameters

The general positions of space group *I*2/*a* are eightfold in number, whilst Ca and P atoms occur only four times in the cell. Thus Ca and P are in special positions, either on the twofold axes or the centres of symmetry (although the latter is impossible for a PO_4 group). Examination of the (*hk*0) intensities showed that the *h* even values are considerably stronger than the *h* odd ones, and this fact is readily explicable by supposing that the Ca and P atoms are both on the twofold axes with a *y* difference of almost $\frac{1}{2}$. A Patterson synthesis carried out on the (*hk*0) planes showed that values Ca at (30/120, 49/120) and P at (30/120, 39/120) for *x* and *y* were satisfactory. The *z* coordinates of these atoms are zero (if we are to put them on the twofold axes) so that the heavy-atom positions are thus known. The oxygen atoms were found by Fourier projections, using the signs of the *F*'s given by the heavy atoms in the first instance. For the *b*-axis projection the intensities were also measured by means of Geiger-counter diffractometry, using a thin slip (0·1 mm.), ground to have accurately parallel faces perpendicular to the *b* axis. Corrections for absorption were made in this part of the work, using the slip transmission formula. Refinement of the structure was carried out by difference syntheses.

Atomic parameters

The final coordinates chosen were:

Ca:	(30/120, 99/120, 0),
P:	(30/120, 39/120, 0),
O_1:	(30/120, 46/120, 24/120),
O_2:	(59/120, 32/120, 12/120),
O_3:	(20/120, 112/120, 32/120),

and it is thought that the standard deviation of these is, in the case of the oxygens, 0·03 Å. The difference maps showed negative areas of about -2 e.Å^{-2} at the oxygen positions, and also some anisotropy of the vibrations of Ca and P. Probably in order to reach a higher accuracy a more detailed study of the scattering curves of the heavy atoms would be necessary, and this should preferably be done in three dimensions.

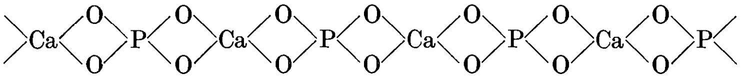
No direct evidence of the hydrogen atoms was obtained from the difference maps, no doubt owing to the inaccuracies just mentioned, but a likely position was inferred from the interatomic distances.

Table 1 gives the values of calculated and observed *F* values for the (*h*0*l*), (0*kl*) and (*hk*0) planes.

Description of the structure

A brief account of the structure has already been given

(Beevers & Raistrick, 1954). There are discrete PO_4 groups, the oxygens of which are shared by Ca atoms on each side, to give continuous chains of Ca and P atoms linked by the oxygens, thus:



These chains run perpendicularly to the twofold axes which pass through the Ca and P atoms, in a direction parallel to the short diagonal of the (010) face of the cell. The P–O distances are: P–O_1 = 1·53 Å, P–O_2 = 1·54 Å. The O–O distances within the phosphate tetrahedra are 2·50–2·52 Å, so that the tetrahedron is a regular one to within the limits of error. The Ca–O distances in these chains are Ca–O_1 = 2·82 Å and Ca–O_2 = 2·44 Å, the former distance thus being considerably longer than the usual Ca–O bond. Fig. 1 of Beevers & Raistrick (1954) gives a projection of these chains on to (010). In Fig. 1 of the present paper is shown a projection down the length of the chains, and it therefore shows Ca and P atoms behind one another, with thick continuous lines joining them to the shared oxygens. In addition to these four Ca bonds to O's within the chains, each Ca makes a contact to two oxygens (O_2's) in neighbouring chains, the Ca–O_2 distances being 2·35 Å, and these bonds result in the formation of a zigzag or corrugated sheet of composition $CaPO_4$ arranged about one of the sets of centres of symmetry. The bonds linking the chains together to form the sheets are shown in thin continuous lines in Fig. 1. Fig. 2 shows a sketch of the bonding within a sheet.

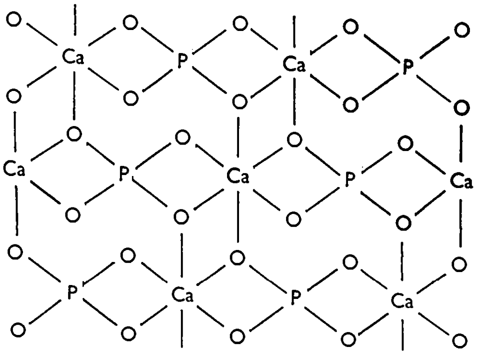


Fig. 2. Diagram of the bonding between the atoms in one of the corrugated sheets of composition $CaPO_4$.

These corrugated sheets are joined together by the water molecules (O_3), two of which form direct bonds to each Ca, with a Ca–O_3 distance of 2·54 Å. Each water molecule also bonds to an O_1 of the same sheet (O_3–O_1 = 2·62 Å), and to an O_1 of a neighbouring sheet (O_3–O_1 = 2·82 Å). The water molecules lie at a distance of only 1·31$_5$ Å from the rotation axes, so that there is a water-to-water distance of 2·63 Å. The hydrogen atoms of the structure might be expected to lie on a short O–O distance, and there are two of these available, namely, O_3–O_1 = 2·62 Å and O_3–O_3' = 2·63 Å. The position at the centre of the latter bond has the correct number of equivalent positions and can therefore be taken to be the probable situation of the hydrogen atom, as far as can be presumed from the present work. Thus the probable hydrogen coordinates are:

$$H: (30/120, 112/120, 60/120) .$$

The bond strengths can be given values as in Fig. 3,

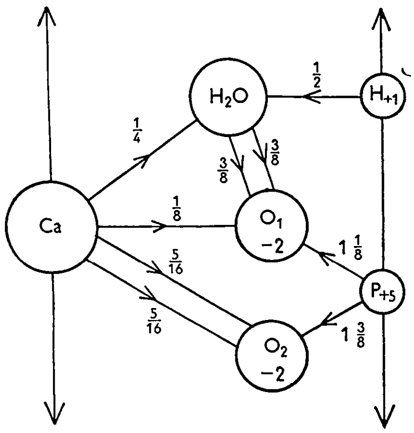


Fig. 3. Possible bond strengths in the crystal structure of $CaPO_4.2\,H_2O$.

making the Ca–O_1 bond a weaker one than the other Ca–O bonds in view of its greater interatomic distance.

Comparison with other structures

It is of interest to compare the present structure with that of gypsum, the unit cell of which was measured by Onorato (1929). Mr A. Nicholson in this laboratory has used high-order spot positions to get more accurate cell constants (which agree well with those of Onorato). Converting to the cell used in this paper we obtain:

Gypsum: a=5·700, b=15·17, c=6·502 Å, β=118° 23′.

These values are thought to be within 0·01 Å and 10′ respectively of the true lengths and angle. It will thus be seen that the dicalcium phosphate structure shows a small expansion in the a direction, and a considerably greater contraction in the c direction, the b axes remaining practically identical in the two compounds. Comparison of the atomic coordinates with those determined by Wooster (1936) for gypsum shows that the structural changes amount to a small rotation of the oxygen tetrahedra, the shift of the oxygens amounting to $\frac{1}{4}$ Å, and a change in the water positions so as to cause the water–water separation across the twofold axis to be only 2·63 Å in calcium phosphate, whilst it is 3·2 Å in gypsum. The latter change lends support to the idea that the hydrogen is between the water molecules in the dihydrogen phosphate and that the resulting bond contraction is responsible for the slight general rearrangement.

As has been previously reported (MacLennan & Beevers, 1956), the structure of monocalcium phosphate monohydrate shows the same corrugated sheets of $CaPO_4$ as in the structure now being described. It therefore seems possible that these sheets are a common feature of calcium phosphate structures. They may occur, for example, in $Ca_3(PO_4)_2$ (Mackay, 1953), a structure which shows vectors of 3·8 Å, which is approximately equal to the shortest Ca–Ca distance in the corrugated sheets. However, the sheets do not seem to be present in the structure of $Sr_3(PO_4)_2$ (Zachariasen, 1948).

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An Equation between Structure Factors for Structures Containing Unequal or Overlapped Atoms. I. The Equation and its Properties

By M. M. Woolfson

Physics Department, College of Science and Technology, Manchester 1, England

(*Received 2 September* 1957)

An equation between structure factors has been developed which holds precisely for centrosymmetric resolved structures containing not more than two types of atom. The form of the equation is

$$F_{\mathbf{h}} = A_{\mathbf{s}}\cdot\frac{1}{V}\sum_{\mathbf{h}'} F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'} + B_{s}\cdot\frac{1}{V^2}\sum_{\mathbf{h}'}\sum_{\mathbf{h}''} F_{\mathbf{h}'}F_{\mathbf{h}''}F_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''},$$

where $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ are functions of $\mathbf{s}$, the position vector of $\mathbf{h}$ in reciprocal space, and V is the volume of the unit cell. The equation may also be applied to resolved projections if V is replaced by A, the area, or l, the length, of the projection.

It is shown that the same equation will approximately hold in some cases of projections containing partially or completely overlapped equal atoms and also for resolved structures containing more than two types of atom.

The theory of the equation is fully developed and its applicability to various types of structure is illustrated by numerical examples.

1. Introduction

Sayre (1952) was the first to show that, for a structure containing equal resolved atoms, the structure factors are quantitatively related to each other. This relationship is in the form of the equation

$$F_{\mathbf{h}} = A_{\mathbf{s}}\frac{1}{V}\sum_{\mathbf{h}'} F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'}\,, \qquad (1)$$

the $\mathbf{h}'$ under the summation sign indicating that the summation is taken over all values of $\mathbf{h}'$. The equation may also be applied to two-dimensional or one-dimensional data if V, the volume of the unit cell, is replaced by either A, the area, or l, the length of the projection.

The equation was derived by Sayre in the following way. For a structure containing equal resolved atoms the operation of squaring the electron density, $\varrho_{\mathbf{r}}$, retains the condition of equal resolved atoms but changes the shape of each atom. It may be shown in the case of a centrosymmetrical structure that

$$\frac{1}{V}\sum_{\mathbf{h}'} F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'}$$

equals the hth Fourier coefficient of $\varrho_{\mathbf{r}}^2$. The factor $A_{\mathbf{s}}$,