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A preliminary examination of the structure of α-$Ca_3(PO_4)_2$.

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Introduction

β-$Ca_3(PO_4)_2$, which is identical with the mineral whitlockite, when heated above 1180° C. undergoes a polymorphic transition to the α-form and can retain this structure at room temperature if quenched. A sample of this α-form was prepared by the Building Research Station by sintering $CaHPO_4.2H_2O+\frac{1}{2}Ca(OH)_2$, together with 4% of cristobalite to promote crystallization, at about 1500° C.

Macroscopic properties

On optical examination the specimen was found to consist of a mass of fused globules, 0·05–0·1 mm. in diameter, with grain boundaries still visible. Between crossed Nicols there was a difference of the order of 5° between the extinction directions of adjoining grains; X-ray photographs confirmed this texture. Crystals were biaxial with $n \simeq 1{\cdot}585$ and small double refraction. No signs of cleavage were apparent on crushing or cutting the crystals. The density was measured as $2{\cdot}814\pm0{\cdot}01$ g.cm.$^{-3}$, but may be low because of porosity. X-ray powder photographs (see Table 1) confirmed published data (Bale, Bonner, Hodge, Adler, Wreath & Bell, 1945). A fragment which was nearly a single crystal was used for oscillation and Weissenberg photographs.

Unit cell

The unit cell is monoclinic with

$$a = 12{\cdot}86\pm0{\cdot}02,\ b = 9{\cdot}11\pm0{\cdot}01,\ c = 15{\cdot}23\pm0{\cdot}02\ \text{Å};$$
$$\beta = 125°\ 20'\pm12',$$

giving $Z_{\text{calc.}} = 7{\cdot}84$. This 2% departure from the expected value of 8 is probably due to the texture of the specimen. $h0l$ reflexions are present only when h is even, and $0k0$ reflexions only when k is even. The absences are thus characteristic for the space group $P2_1/a$, which is centrosymmetrical. The crystal lattice has the property that the plane $10\bar{2}$ is almost perpendicular to the c axis. Considerable pseudo-symmetry is visible in the $hk0$ class of reflexions, reflexions with $3h+2k = 12n$ being very strong. The $hk0$ layer shows marked pseudo-hexagonal symmetry and the corresponding Patterson projection consists almost entirely of a hexagonal array of equal, large peaks. The ratio $d_{100}:b$ is 1·137, which is near to $2/\sqrt{3}$ (= 1·154). Only the projection, and not the whole structure, is pseudo-hexagonal.

Discussion of Patterson projections

In the zones $h0l$ and $0kl$ the reflexions 400, 800, 008, $40\bar{8}$, 201, 014, 031 and $20\bar{4}$ are exceptionally strong. These reflexions dominate the Patterson projections and enable the main features of the three-dimensional Patterson function to be deduced from them with reasonable probability. The three projections are shown in Fig. 1. The Patterson density distribution could be explained in terms of the packing of all the Ca and P atoms on to 12 columns parallel to the c axis. To satisfy the centres of symmetry and the glide planes, the three independent columns must have the (x, y) parameters $(\frac{3}{8}, \frac{1}{4})$, $(\frac{1}{8}, \frac{1}{12})$ and $(\frac{1}{8}, \frac{5}{12})$. The projections combine to show that all important interatomic vectors have c components which are multiples of $\frac{1}{4}c$ (= 3·81 Å). This imples that there are only 48 possible sites in which to place 24 Ca and 16 P atoms. Almost any packing of these atoms into the 48 sites will give Patterson projections and calculated intensities close to those observed. The packing restrictions due to the size and shape of the PO_4 groups, which may be presumed to exist, limit the possibilities, but three-dimensional work will be required to make a definite decision on the particular distribution actually present.

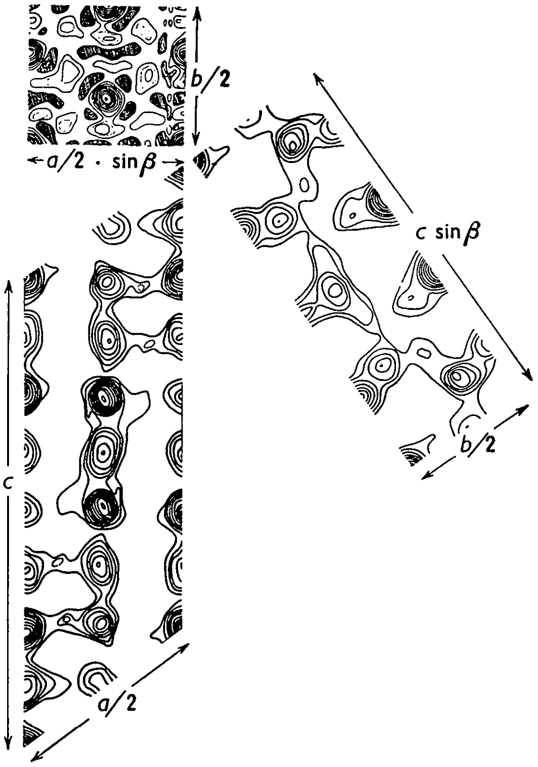

Fig. 1. The three principal Patterson projections of α-$Ca_3(PO_4)_2$. The $hk0$ projection is sharpened and in the $h0l$ and $0kl$ projections contours round the origin are at twice the usual interval.

Relationship to other $R_3(XO_4)_2$ compounds

Such a complete analysis was beyond the scope of the present investigation which had as its aim the examination of α-$Ca_3(PO_4)_2$ to see whether any explanation would emerge of the apparently anomalous structure of β-$Ca_3(PO_4)_2$, where the cell contents ($Z_{\text{obs.}} = 7$) and space

Table 1. *Powder photograph of* α-$Ca_3(PO_4)_2$

Cu $K\alpha$ radiation; 6 cm. diameter camera

		Principal planes contributing		Data given by Bale *et al.* (1945)	
I_o	d_o (Å)	*hkl*	d_c (Å)	I/I_1	*d* (Å)
vw	12·8	001	12·3	—	—
vw	9·84*	—	—	—	—
s	7·18	011	6·7	—	—
w	6·14	$20\bar{1}$, 002	6·22, 6·19	—	—
w	5·76	$11\bar{2}$	5·84	—	—
m	5·13	$21\bar{1}$, 200	5·14, 5·17	—	—
vs	3·88	201, $20\bar{4}$	4·03, 3·80	0·60	3·92
s	3·65	022	3·67	0·19	3·70
w	3·31	—	—	—	—
w	3·17	—	—	—	—
vs	2·90	014, 031	2·93, 2·95	1·00	2·90
s	2·59	400, 230	2·59, 2·62	0·67	2·61
w	2·45	—	—	—	—
w	2·36	—	—	—	—
w	2·22	—	—	—	—
s	2·150	$40\bar{7}$, 204, 025	2·147, 2·165, 2·181	0·19	2·16
w	2·061	—	—	—	—
w	2·014	—	—	—	—
s	1·926	$40\bar{8}$	1·897	0·19	1·93
w	1·915	—	—	—	—
w	1·842	—	—	—	—
m	1·803	$20\bar{8}$	1·797	—	—
w	1·746	—	—	—	—
w	1·691	—	—	—	—
w	1·656	—	—	—	—
vw	1·598	—	—	—	—
m, d	1·538	060, 630	1·519, 1·502	0·12	1·55
w	1·505	—	—	—	—
w	1·476	—	—	—	—

* Not found on single-crystal photographs; probably due to collimator or binder.

group ($R3c$) do not seem reconcilable (Frondel, 1941, 1943; Mackay, 1952).

Certain resemblances exist between the polymorphs. The β-form is trigonal with a = 10·32 Å (c = 37·0 Å) compared with d_{100} in the α-form which is 10·36 Å. Both forms seem to be built of columns, parallel to their c axes, spaced 3·0 Å apart (distortion of the columns occurs in the β-form). The spacing of atoms along these columns is regular in both forms, being 3·81 Å in the α- and 3·70 Å in the β-form. On the other hand there are considerable differences. The density decreases from 3·12 to 2·81 g.cm.$^{-3}$ (measured at room temperature) at the transformation, being a change of 11%; on heating through this transition point crystals are shattered and do not transform in any definite orientation. The space group $P2_1/a$ is not a subgroup of $R3c$, nor vice versa.

The structures of compounds with the formula $R_3(XO_4)_2$ so far examined are: $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ (Zachariasen, 1948) and $K_3MnO_4CrO_4$ (Stanley, 1952), which are all isostructural; β-$Ca_3(PO_4)_2$ (Mackay, 1952), which is related to them; $K_2Pb(SO_4)_2$ (Bellanca, 1946), which has the same size of cell as $Ba_3(PO_4)_2$ but is not isostructural; and $Pb_3(PO_4)_2$ (Rooksby, 1939; Ferrari, 1940) which has a defect apatite structure. α-$Ca_3(PO_4)_2$ thus appears to be a type of structure not yet encountered.

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