

System (Stewart, Kundell & Baldwin, 1970), except for the Fourier retrieval programs which were written by Schilling & Nordman (1969). Support under USPHS Grant GM-10828 from the National Institutes of Health is gratefully acknowledged.

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The Crystal Structure of Twinned $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, 'Cadmium Chlorapatite'

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Twins of synthetic 'cadmium chlorapatite' were used for crystal-structure determination. The space group $P6_3/m$ is confirmed; $a = 9.633 \pm 0.004$ and $c = 6.484 \pm 0.004$ Å; $Z = 2$. The material is isostructural with fluorapatite. The volume ratio (0.35) of the crystals in the twin, and the usual structural detail have been obtained from X-ray data in which every observed reflection is the superposition of two reflections, one from each crystal in the twin. First the volume ratio and then the other parameters were adjusted in each cycle of least-squares refinement. The final R values are 5.6 and 5.5% for the two crystals in the twin.

Introduction

The members of the apatite group represented by the general formula $A_5(\text{MO}_4)_3\text{X}$ form a wide range of substitution solid solutions by partial or complete re-

placement of one kind of ion by another, with $A =$ alkaline earths, alkali metals, rare earths, Cd, Pb, Mn, etc.; $M =$ P, As, V, Si, Al, S, B, etc.; and $X =$ F, Cl, OH, O, Br, I or vacancies (Wondratschek, 1972). No complete crystal-structure investigation has been at-

tempted previously for any of the non-calcium apatites. 'Cadmium chlorapatite', $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, crystallizes in the hexagonal system with space group $P6_3/m$, as do calcium fluorapatite and hydroxylapatite. Stoichiometric calcium chlorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, crystallizes in a very closely related monoclinic structure ($b=2a$, $\gamma=120^\circ$) with space group $P2_1/b$. Since cadmium chlorapatite has a relatively short c dimension, which would imply a Cl—Cl distance less than the sum of ionic radii, it was thought possible that some structural details might be modified by the substitution of cadmium for calcium.

Experimental

The crystals used in this study were prepared by Engel (1968) from melts of cadmium chloride and cadmium phosphate. Two acicular crystals, about 0.2 mm in length and 0.05 mm in diameter, were selected; during the course of the investigation they were found to be twins (by merohedry). The cell edges were found from diffractometer measurements. Our observations have confirmed the space group reported by Engel.

Intensity data for 1840 reflections in the range $0.29 \leq \sin \theta/\lambda \leq 1.05 \text{ \AA}^{-1}$ were collected with a punched-tape-controlled single-crystal diffractometer and Zr-filtered Mo $K\alpha$ radiation. The basic experimental conditions, including assignment of standard deviations for the observations, have been described elsewhere (Sudarsanan & Young, 1969).

Absorption corrections for a cylindrical crystal (Gabe & O'Byrne, 1970) were applied. The linear absorption coefficient of this material for Mo $K\alpha$ radiation is 11.3 mm^{-1} .

Structure determination and refinement

The relative intensities of the various reflections did not show the expected correspondence with the relative intensities of the same set of reflections of the calcium fluor-, chlor- or hydroxyl- apatites, with the exceptions of $h0l$ and hhl data. Therefore a verification that the crystal structure was indeed of the apatite type was undertaken with a three-dimensional Patterson function and a difference synthesis. The only unexpected finding was that chlorine in cadmium chlorapatite has the same coordinates, $0,0,\frac{1}{4}$, as fluorine in calcium fluorapatite, in contrast to those of chlorine in calcium chlorapatite, $0,0,0.444$ (Mackie, Elliott & Young, 1972).

A three-dimensional least-squares refinement of all variable positional and temperature parameters was attempted with the chlorine held at $0,0,\frac{1}{4}$. Busing, Martin & Levy's (1962) *ORFLS* program, modified by Johnson (1966) and called *XFLS*, was used. The atomic scattering factors used for Cd^{2+} , P^{1+} and O^{1-} were those given by Cromer & Waber (1965). Relevant corrections for anomalous dispersion were made with values of $\Delta f'$ and $\Delta f''$ calculated by Cromer (1965).

These least-squares refinement attempts led to $R_2=23.0\%$, where $R_2=(\sum||F_o|^2-|F_c|^2|)/(\sum|F_o|^2)$, and to oxygen temperature parameters much larger than they are in fluorapatite (Young, Sudarsanan & Mackie, 1972).

A refinement was then carried out with the h and k indices of all the reflections interchanged. It yielded $R_2=26.0\%$, suggesting that some phenomenon involving interchange of x and y atomic coordinates in a substantial portion of the specimen was present (otherwise interchange of h and k would have produced a much larger increase in R_2), but that the interchange of x and y was not due to a simple interchange of \mathbf{a}_1 and \mathbf{a}_2 , such as would result from improper selection of the sense of positive z . Separate refinements with different sub-sets of the data were then undertaken to see if the difficulty could be identified from differences in the ways the same parameter would be refined. A refinement with reflections $h0l$ and hhl gave $R_2=7.2\%$ and normal values for all temperature parameters. Since, for the space group $P6_3/m$, $|F(hkl)|=|F(khl)|$ for both $h0l$ and hhl reflections, we hypothesized that the specimen used for collecting the X-ray intensities was a twin formed of two crystals, A and B , such that the coordinates x and y in the structure of crystal A were interchanged in that of crystal B (the coordinate axes of crystal A being used for crystal B). The fact that the structure refinement based on such a twin model was successful proves this twinning hypothesis. A detailed analysis of the twinning, involving directly the crystal-structure details found here, is the subject of the following paper (Donnay, Sudarsanan & Young, 1973).

Structure refinement with twin data

The type of twinning present, twinning by merohedry, cannot be detected by optical methods because the optical indicatrix is not affected by it. Neither is the twinning revealed directly in X-ray photographs, because all points of the lattice of the one structure register with the lattice points of the mirrored structure. Every observed reflection is the superposition of two reflections, hkl from crystal A in the twin and khl from the other.* The observed intensity I for the reflection indexed as hkl is given by

$$I(hkl) = I_A + I_B,$$

where I_A and I_B are the intensities contributed by crystals A and B , respectively. Noting that hkl and khl have the same Lorentz and polarization factor, and letting the absorption factor be A and the volumes of crystal A and crystal B be V_A and V_B , one may write the proportionality

$$I(hkl) \propto \text{Lp } A(V_A|F(hkl)|^2 + V_B|F(khl)|^2)$$

* In the following paper (Donnay *et al.*, 1973) it is shown that this superposition most probably arises because the coordinate axes of crystal B are symmetrical to those of crystal A by reflection in $(1\bar{1}00)$, although reflection in $(1\bar{2}10)$ would also produce the same superposition.

or the equality

$$I(hkl) = s \text{Lp} AV_A (|F(hkl)|^2 + K|F(khl)|^2),$$

where K is the crystal volume ratio V_B/V_A and s the proportionality constant. Setting

$$sV_A = \frac{1}{S},$$

one can write

$$S \frac{1}{\text{Lp} A} I(hkl) = |F(hkl)|^2 + K|F(khl)|^2 = SI_o(hkl) \quad (1)$$

where I_o is the observed intensity corrected by Lorentz, polarization and absorption factors.

The general problem of carrying out structure refinements with overlapping data is similar whether the overlapping is complete (such as it is for the twin-superimposed data here) or is only partial (as often occurs in powder diffraction patterns). Several approaches have been taken by various authors. (i) Zalkin, Forrester & Templeton (1964) have determined the structure of sodium fluosilicate from twin-produced superimposed data by finding the volume ratio of the crystals in the twin by trial of various values. (ii) Zachariasen & Plettinger (1965) employed a method of correcting the intensities for twinning. Their method was not employed here as it requires, for every intensity measured, the measured intensity of the twin-related reflection. Moreover, the unaccounted systematic and other errors in the observed intensities of the two related reflections affect the corrected intensity of every reflection. (iii) As suggested by Grainger (1969), refinement may be carried out with the twinning-insensitive sum of related-reflection intensities. As he noted, this summed-data method has the disadvantage of reducing the number of data to less than half in the final refinement. (iv) Hamilton & Ibers (1963) and Ibers & Hamilton (1966), dealing with overlapping neutron-diffraction powder data, have developed and used a least-squares refinement program that involves, directly in the normal-equations matrix, the volume fraction of each constituent. The difficulty of their method is that some special programming is needed for each specific problem.

The method we have employed for carrying out structure refinement with twin data permits the use of all the measured intensities even though the separate contributions of the coinciding reflections are unknown. It is less general than the Hamilton & Ibers approach and does not involve the volume fraction in the normal equations. However, it is easily used and requires no special programming. It comprises four steps. (i) In the first step, the parameters previously obtained from the least-squares structure refinement with the $h0l$ and hhl data were used in calculations of the structure amplitudes $|F_c(hkl)|$ and $|F_c(khl)|$. (ii) The second step was an approximation of the scale factor S and the volume fraction K by least-squares minimization of the expression

$$\sum (SI_o(hkl) - |F_c(hkl)|^2 - K|F_c(khl)|^2), \quad (2)$$

the summation being carried over all measured reflections. The value of R_2 was then calculated for the specimen. The first such least-squares minimization and subsequent calculation yielded $R_2 = 10.0\%$ and $K = 0.38$. (iii) On the basis of this value for the volume fraction, the corrected observed intensities were separated into the two parts due, presumably, to the two crystals in the twin:

$$|F_{oA}(hkl)|^2 = SI_o(hkl) \frac{|F_c(hkl)|^2}{|F_c(hkl)|^2 + K|F_c(khl)|^2}$$

and

$$K|F_{oB}(khl)|^2 = SI_o(hkl) - |F_{oA}(hkl)|^2$$

where $|F_{oA}|$ and $|F_{oB}|$ are the values individually allocated for the observed structure amplitudes for the two crystals in the twin.* (iv) The final step of the procedure was the least-squares refinement of positional and thermal parameters, carried out in the usual manner with one (or both) of the sets of separated data. The four-step cycle of operations was then repeated, the latest parametral values being used each time in step one. Four such iterations gave $K = 0.35$, the final R values reported in Table 1 and structure-factor data as listed in Table 2.

Table 1. Final R values (%) with $K = 0.35$

	R_1	R_2	WR_2
For the specimen	—	8.9	10.5
For crystal A	5.2	8.4	10.3
For crystal B	6.3	10.2	9.6
$R_1 = \frac{\sum F_o - F_c }{\sum F_o }$		$R_2 = \frac{\sum F_o ^2 - F_c ^2 }{\sum F_o ^2}$	
$WR_2 = \left[\frac{\sum W(F_o ^2 - F_c ^2)^2}{\sum W F_o ^4} \right]^{1/2}$			

As a verification, a least-squares structure refinement was then carried out with the data allocated to crystal B . Finally, a least-squares refinement was carried out with the data sets for both crystal A and crystal B used simultaneously. The weights were based on standard deviations separately calculated for the two crystals from the conditions

$$\frac{\sigma_A(hkl)}{\sigma_B(khl)} = \frac{|F_A(hkl)|^2}{|F_B(khl)|^2}$$

and

$$\sigma_A(hkl) + \sigma_B(khl) = S\sigma_o(hkl)$$

where $\sigma_A(hkl)$ is the standard deviation in the determination of $|F_A(hkl)|^2$, $\sigma_B(khl)$ is that in $|F_B(khl)|^2$ and $\sigma_o(hkl)$ is the standard deviation assigned to the composite reflection intensity according to the proce-

* $|F_{oA}(hkl)|$ and $|F_{oB}(khl)|$ should approximate the $|F(hkl)|$ and $|F(khl)|$, introduced in equation (1), which cannot actually be 'observed'.

Table 2 (cont.)

k				h				k				h				k				h				
k	h	l	intensity	k	h	l	intensity	k	h	l	intensity	k	h	l	intensity	k	h	l	intensity	k	h	l	intensity	
2	6077	2433	2382	1	745	938	435	1	811	761	751	1	122	928	9	1	238	200	333	1	102	200	333	
3	11	5	2	2	1702	333	306	14	11	11	11	14	11	11	11	14	11	11	11	14	11	11	11	14
5	591	987	500	5	630	518	523	15	173	1005	491	15	173	1005	491	15	173	1005	491	15	173	1005	491	
7	685	173	172	7	540	210	338	17	173	1005	491	17	173	1005	491	17	173	1005	491	17	173	1005	491	
8	688	11	11	8	2611	1410	1571	18	173	1005	491	18	173	1005	491	18	173	1005	491	18	173	1005	491	
10	341	47	17	10	210	480	1515	19	173	1005	491	19	173	1005	491	19	173	1005	491	19	173	1005	491	
11	11	11	11	11	9513	3571	3210	20	173	1005	491	20	173	1005	491	20	173	1005	491	20	173	1005	491	
12	1027	447	47	12	133	1210	1063	21	173	1005	491	21	173	1005	491	21	173	1005	491	21	173	1005	491	
13	131	271	8	13	1811	1230	1671	22	173	1005	491	22	173	1005	491	22	173	1005	491	22	173	1005	491	
14	131	271	8	14	3111	2310	2711	23	173	1005	491	23	173	1005	491	23	173	1005	491	23	173	1005	491	
15	131	271	8	15	15103	16210	17251	24	173	1005	491	24	173	1005	491	24	173	1005	491	24	173	1005	491	
16	131	271	8	16	15103	16210	17251	25	173	1005	491	25	173	1005	491	25	173	1005	491	25	173	1005	491	
17	131	271	8	17	15103	16210	17251	26	173	1005	491	26	173	1005	491	26	173	1005	491	26	173	1005	491	
18	131	271	8	18	15103	16210	17251	27	173	1005	491	27	173	1005	491	27	173	1005	491	27	173	1005	491	
19	131	271	8	19	15103	16210	17251	28	173	1005	491	28	173	1005	491	28	173	1005	491	28	173	1005	491	
20	131	271	8	20	15103	16210	17251	29	173	1005	491	29	173	1005	491	29	173	1005	491	29	173	1005	491	
21	131	271	8	21	15103	16210	17251	30	173	1005	491	30	173	1005	491	30	173	1005	491	30	173	1005	491	
22	131	271	8	22	15103	16210	17251	31	173	1005	491	31	173	1005	491	31	173	1005	491	31	173	1005	491	
23	131	271	8	23	15103	16210	17251	32	173	1005	491	32	173	1005	491	32	173	1005	491	32	173	1005	491	
24	131	271	8	24	15103	16210	17251	33	173	1005	491	33	173	1005	491	33	173	1005	491	33	173	1005	491	
25	131	271	8	25	15103	16210	17251	34	173	1005	491	34	173	1005	491	34	173	1005	491	34	173	1005	491	
26	131	271	8	26	15103	16210	17251	35	173	1005	491	35	173	1005	491	35	173	1005	491	35	173	1005	491	
27	131	271	8	27	15103	16210	17251	36	173	1005	491	36	173	1005	491	36	173	1005	491	36	173	1005	491	
28	131	271	8	28	15103	16210	17251	37	173	1005	491	37	173	1005	491	37	173	1005	491	37	173	1005	491	
29	131	271	8	29	15103	16210	17251	38	173	1005	491	38	173	1005	491	38	173	1005	491	38	173	1005	491	
30	131	271	8	30	15103	16210	17251	39	173	1005	491	39	173	1005	491	39	173	1005	491	39	173	1005	491	
31	131	271	8	31	15103	16210	17251	40	173	1005	491	40	173	1005	491	40	173	1005	491	40	173	1005	491	
32	131	271	8	32	15103	16210	17251	41	173	1005	491	41	173	1005	491	41	173	1005	491	41	173	1005	491	
33	131	271	8	33	15103	16210	17251	42	173	1005	491	42	173	1005	491	42	173	1005	491	42	173	1005	491	
34	131	271	8	34	15103	16210	17251	43	173	1005	491	43	173	1005	491	43	173	1005	491	43	173	1005	491	
35	131	271	8	35	15103	16210	17251	44	173	1005	491	44	173	1005	491	44	173	1005	491	44	173	1005	491	
36	131	271	8	36	15103	16210	17251	45	173	1005	491	45	173	1005	491	45	173	1005	491	45	173	1005	491	
37	131	271	8	37	15103	16210	17251	46	173	1005	491	46	173	1005	491	46	173	1005	491	46	173	1005	491	
38	131	271	8	38	15103	16210	17251	47	173	1005	491	47	173	1005	491	47	173	1005	491	47	173	1005	491	
39	131	271	8	39	15103	16210	17251	48	173	1005	491	48	173	1005	491	48	173	1005	491	48	173	1005	491	
40	131	271	8	40	15103	16210	17251	49	173	1005	491	49	173	1005	491	49	173	1005	491	49	173	1005	491	
41	131	271	8	41	15103	16210	17251	50	173	1005	491	50	173	1005	491	50	173	1005	491	50	173	1005	491	
42	131	271	8	42	15103	16210	17251	51	173	1005	491	51	173	1005	491	51	173	1005	491	51	173	1005	491	
43	131	271	8	43	15103	16210	17251	52	173	1005	491	52	173	1005	491	52	173	1005	491	52	173	1005	491	
44	131	271	8	44	15103	16210	17251	53	173	1005	491	53	173	1005	491	53	173	1005	491	53	173	1005	491	
45	131	271	8	45	15103	16210	17251	54	173	1005	491	54	173	1005	491	54	173	1005	491	54	173	1005	491	
46	131	271	8	46	15103	16210	17251	55	173	1005	491	55	173	1005	491	55	173	1005	491	55	173	1005	491	
47	131	271	8	47	15103	16210	17251	56	173	1005	491	56	173	1005	491	56	173	1005	491	56	173	1005	491	
48	131	271	8	48	15103	16210	17251	57	173	1005	491	57	173	1005	491	57	173	1005	491	57	173	1005	491	
49	131	271	8	49	15103	16210	17251	58	173	1005	491	58	173	1005	491	58	173	1005	491	58	173	1005	491	
50	131	271	8	50	15103	16210	17251	59	173	1005	491	59	173	1005	491	59	173	1005	491	59	173	1005	491	
51	131	271	8	51	15103	16210	17251	60	173	1005	491	60	173	1005	491	60	173	1005	491	60	173	1005	491	
52	131	271	8	52	15103	16210	17251	61	173	1005	491	61	173	1005	491	61	173	1005	491	61	173	1005	491	
53	131	271	8	53	15103	16210	17251	62	173	1005	491	62	173	1005	491	62	173	1005	491	62	173	1005	491	
54	131	271	8	54	15103	16210	17251	63	173	1005	491	63	173	1005	491	63	173	1005	491	63	173	1005	491	
55	131	271	8	55	15103	16210	17251	64	173	1005	491	64	173	1005	491	64	173	1005	491	64	173	1005	491	
56	131	271	8	56	15103	16210	17251	65	173	1005	491	65	173	1005	491	65	173	1005	491	65	173	1005	491	
57	131	271	8	57	15103	16210	17251	66	173	1005	491	66	173	1005	491	66	173	1005	491	66	173	1005	491	
58	131	271	8	58	15103	16210	17251	67	173	1005	491	67	173	1005	491	67	173	1005	491	67	173	1005	491	
59	131	271	8	59	15103	16210	17251	68	173	1005	491	68	173	1005	491	68	173	1005	491	68	173	1005	491	
60	131	271	8	60	15103	16210	17251	69	173	1005	491	69	173	1005	491	69	173	1005	491	69	173	1005	491	
61	131	271	8	61	15103	16210	17251	70	173	1005	491	70	173	1005	491	70	173	1005	491	70	173	1005	491	
62	131	271	8	62	15103	16210	17251	71	173	1005	491	71	173	1005	491	71	173	1005	491	71	173	1005	491	
63	131	271	8	63	15103	16210	17251	72	173	1005	491	72	173	1005	491	72	173	1005	491	72	173	1005	491	
64	131	271	8	64	15103	16210	17251	73	173	1005	491	73	173	1005	491	73	173	1005	491	73	173	1005	491	
65	131	271	8	65	15103	16210	17251	74	173	1005	491	74												

Table 3. *Positional and thermal parameters of 'cadmium chlorapatite'*

All values, except fractions, are multiplied by 10^4 ; standard deviations are given within parentheses for the parameters varied. The refinements were carried out with data from crystal *A* and crystal *B* together.

	Multiplier	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O _I	4938 (63)	3512 (1)	5021 (1)	$\frac{1}{4}$	53 (1)	28 (1)	28 (1)	36 (1)	0	0
O _{II}	5190 (60)	5909 (1)	4598 (1)	$\frac{1}{4}$	19 (1)	37 (1)	51 (2)	13 (1)	0	0
O _{III}	9509 (83)	3442 (1)	2667 (1)	598 (1)	58 (1)	28 (1)	10 (2)	16 (1)	-18 (1)	-7 (1)
P	5148 (24)	4047 (1)	3773 (1)	$\frac{1}{4}$	23 (1)	22 (1)	10 (1)	11 (1)	0	0
Cd _I	3315 (7)	$\frac{1}{2}$	$\frac{3}{4}$	54 (1)	39 (1)	39	4 (1)	19 (1)	0	0
Cd _{II}	5005 (10)	-188 (1)	2534 (1)	$\frac{1}{4}$	36 (1)	35 (1)	12 (1)	19 (1)	0	0
Cl	1389 (14)	0	0	$\frac{1}{4}$	24 (1)	24	218 (3)	12	0	0

ture previously used (Sudarsanan & Young, 1969) which includes counting statistics and a lower limit for detectable intensity. The results for all three refinements agreed within 2 standard deviations in the parameters; Table 3 shows those for the composite refinement. In the final cycle, all shifts were smaller than the standard deviations in the parameters.

Structure

Cadmium chlorapatite (Fig. 1) is isostructural with (calcium) fluorapatite. Bond angles and interatomic distances (Table 4) were determined from the refinement results shown in Table 3. The side length of the Cd_{II} triangle is 4.41 Å whereas that of the Ca_{II} triangle is 3.97 Å in calcium fluorapatite and 4.21 Å in calcium chlorapatite. In contrast to the calcium triangle in

calcium chlorapatite, the cadmium triangle in cadmium chlorapatite is large enough to accommodate the chlorine atom at its center. The Cd-Cl interatomic distance is 2.545 Å, well within the normal range for Cd-Cl.

The parameters from the least-squares refinement are normal, in comparison with those known for several closely related calcium apatites (fluorapatite, hydroxylapatite and chlorapatite), with the exceptions of some site-occupancy factors and the apparent temperature factor β_{33} for chlorine along the *c* direction. The site-occupancy factor which appears most to require physical justification is that for Cl; a 15% to 18% deficiency of Cl appears to be indicated. Deficiency in the occupancy of this, the 'halogen', site has often been noted in apatites (Sudarsanan & Young, unpublished) and has been particularly studied in synthetic chlorapatite, Ca₅(PO₄)₃Cl (Prener, 1967; Prener, 1971; Mackie *et al.*, 1972).

The β_{33} value for chlorine is more than double that of fluorine in synthetic calcium fluorapatite ($\beta_{33} = 0.0128$; P. Mackie, unpublished) or in the mineral ($\beta_{33} = 0.0144$; Young *et al.*, 1972), an intriguing fact for which we have as yet no firm explanation. This large apparent temperature factor may in some way be related to the short Cl-Cl distance (3.24 Å *vs.* ~3.62 Å for the sum of ionic radii). The markedly low Cl site-occupancy factor suggests that a significant number of Cl vacancies occur, the charge balance presumably being maintained by loss of one half as many Cd ions in the manner reported by Prener (1971) for calcium chlorapatite. It is thus conceivable that the large value of β_{33} reflects differences, in individual Cl positions, associated with scattered Cl vacancies: by permitting the adjacent Cl ions on either side to relax toward it, a vacancy enables the actual distances between consecutive Cl ions in the neighborhood to be larger than the distance *c*/2 between their crystallographic sites.

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Table 4. *Bond angles and interatomic distances*

(a) Bond angles and their standard deviations†

O _I -P-O _{III}	112.7 (0.1)°
O _I -P-O _{II}	110.7 (0.1)
O _{II} -P-O _{III}	107.1 (0.1)
O _{III} -P-O _{III}	106.2 (0.1)

(b) Interatomic distances and their standard deviations†

O _I -P	1.531 (1) Å
O _{II} -P	1.562 (1)
O _{III} -P	1.542 (1)*
O _I -O _{II}	2.545 (2)
O _{II} -O _{III}	2.497 (2)*
O _I -O _{III}	2.558 (2)*
O _{III} -O _{III}	2.466 (2)*
Cd _I -O _I	2.313 (1)**
Cd _I -O _{II}	2.380 (1)**
Cd _I -O _{III}	2.881 (2)**
Cd _{II} -O _I	3.157 (2)
Cd _{II} -O _{III}	2.203 (1)*
Cd _{II} -O _{III}	2.465 (1)*
Cd _{II} -O _{II}	2.253 (2)
Cd _{II} -Cl	2.545 (1)

†(i) Standard deviations, referred to the last significant digit, are given in parentheses.

(ii) O_{III} is related to O_{III} by reflection in *m* at *z* = $\frac{1}{4}$. A doubly primed symbol (O_{III}) designates an atom with coordinates *y*, *y* - *x*, *z*, where *x*, *y*, *z* are those of the atom designated by the unprimed symbol (O_{III}).

(iii) The Function and Error Program (ORFFE) of Busing, Martin & Levy (1964) was used for the calculations.

* The number of asterisks indicates the number of times the distance is repeated for symmetry-related sites of the second atom.

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Twinning in Relation to Structural Detail in $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, 'Cadmium Chlorapatite'

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Synthetic $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ ('cadmium chlorapatite') was found to be twinned by merohedry. Of the two possible forms of twin mirrors, $.m' = \{1\bar{2}10\}$ and $.m' = \{1\bar{1}00\}$, $.m'$ can be ruled out structurally because it requires too short interatomic distances across the expected composition surface, which is made up of planar segments parallel with the faces of $\{1\bar{2}10\}$. The space-group symmetry of the twin is therefore $P6_3/mc'm'$ rather than $P6_3/mm'c'$. Chemically the cadmium analogue of calcium chlorapatite, cadmium chlorapatite is isostructural with calcium fluorapatite, in which the authors observed no such twinning. With the acceptable twin law $.c'm'$ the distance between nearest oxygen atoms across the composition surface would be shorter in calcium fluorapatite (1.8 Å) than it is in cadmium chlorapatite (2.0 Å). Re-positioning displacements of the phosphate groups would also be larger in calcium fluorapatite than in cadmium chlorapatite in the process of twin formation.

Introduction

In a structure investigation of 'cadmium chlorapatite', $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, with X-ray data (Sudarsanan, Young & Donnay, 1973), it was found that the specimens are twinned by merohedry. The structural detail reported in the previous paper has led us to examine the *atomic arrangement* to try to answer the following questions. Firstly, can one twin law be selected over another possible one, which would be equivalent if only the *lattice* were considered? Secondly, why is this twinning by merohedry less fre-

quently observed in the isostructural calcium fluorapatite?

Nature of the twinning

It is known (see, for instance, Friedel, 1904 or 1926) that twinning by merohedry, found here in cadmium chlorapatite, can occur whenever the point symmetry of the crystal is lower than that of the lattice. For point group $6/m$ the hexagonal lattice, with point symmetry $6/m\ 2/m\ 2/m$, possesses twelve additional symmetry operations, *viz.* two sets of three rotations and three reflections each, expressed by the $2/m$ sym-