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### Refinement of the structure of $11\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot \text{CaF}_2$ . By P. P. WILLIAMS, *Chemistry Division, DSIR, Petone, New Zealand*

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A refinement is reported ( $R=6.7\%$ ) of the structure of the fluoride analogue of cubic hydrated  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ . It has been confirmed that the fluoride ion sites are only partially occupied and that calcium atoms adjacent to filled fluoride positions are displaced. No evidence has been found to indicate an ordered structure in a lower-symmetry space group.

Reports on the crystal structure of the cementitious compound  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  have appeared previously (Büsem & Eitel, 1936; Jeevaratnam, Dent Glasser & Glasser, 1962; Bartl, 1969) and the structure of the fluoride analogue of the monohydrate has also been reported (Williams, 1968, 1969). This communication details the results of further refinement of the latter structure.

The material used for the study, the data collection procedures, and an approximate structure have been previously described (Williams, 1968, 1969). The crystals are cubic,

$I\bar{4}3d$  (No. 220) with  $a=11.970\text{ \AA}$ ,  $Z=2$ . Full-matrix least-squares refinement of the structure, including site-occupancy parameters for calcium and fluorine atoms led to the parameters in Table 1. The conventional  $R$  at this stage for 213 'observed' [ $F > 3\sigma(F)$ ] reflections was 0.067. The scattering factors used were those given for  $\text{Ca}^+$ ,  $\text{Al}^+$ ,  $\text{O}^-$ ,  $\text{F}^-$  in *International Tables for X-ray Crystallography* (1962). The structure factors are listed in Table 2, and Table 3 gives interatomic distances and bond angles.

The structure is disordered in that there are two sites,

Table 1. *Atom parameters*

	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>B</i>
Ca(1)	0.1103 (6)	0	0.25	0.74 (3)	0.57 (11)
Ca(2)	0.0682 (15)	0	0.25	0.28 (3)	0.35 (25)
Al(1)	0.375	0	0.25		0.19 (9)
Al(2)	0.2306 (2)	0.2306 (2)	0.2306 (2)		0.27 (9)
O(1)	0.1919 (6)	0.2857 (6)	0.0991 (6)		0.80 (11)
O(2)	0.3139 (6)	0.3139 (6)	0.3139 (6)		0.80 (19)
F	0.875	0	0.25	0.33 (7)	2.2 (13)

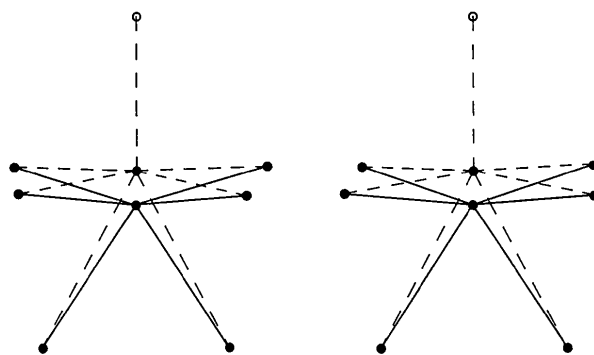


Fig. 1. Stereoscopic representation of the possible coordination shells for the calcium atoms. The central atom is calcium; bold lines denote six coordination contacts from the Ca(1) site, fine lines are the seven contacts in the Ca(2) site.

Table 2. Observed and calculated structure factors

$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$				
11	0	1	13	5	9	15	15	2	39	41	13	10	22	35	15	7	36	40	10	9	24	23	10	9	24	23		
0	0	12	132	15	5	24	31	4	3	9	2	12	11	64	36	10	8	17	14	12	9	40	36	11	10	83	77	
0	0	237	236	6	6	41	43	6	3	71	20	12	8	46	41	11	10	83	77	6	3	77	76	10	7	113	110	
12	0	110	112	6	6	38	35	8	3	51	49	11	12	26	22	14	8	30	36	12	11	26	22	6	5	77	76	
3	1	107	100	10	6	37	40	10	5	50	51	11	8	35	33	9	9	76	66	9	6	40	38	11	8	58	58	
7	1	110	111	12	6	32	34	12	3	43	40	4	2	202	211	11	8	33	33	4	2	237	240	8	7	127	124	
9	1	146	148	14	6	29	29	14	3	31	9	8	2	45	42	13	9	27	32	12	10	36	32	10	7	34	31	
11	1	20	21	11	7	20	24	7	4	119	115	12	2	61	60	12	10	36	32	11	11	29	27	8	4	55	50	
13	1	45	48	15	7	31	34	9	4	62	78	5	3	139	138	11	8	33	33	12	4	169	169	9	8	55	50	
15	1	41	47	8	8	28	30	11	4	52	57	7	3	78	76	11	11	29	27	7	5	83	79	11	8	51	48	
4	2	259	277	10	8	42	36	15	4	31	34	9	3	65	61	9	5	67	63	10	9	18	18	8	4	107	105	
6	2	63	64	12	8	30	25	8	5	63	67	13	1	39	42	10	3	119	115	11	5	33	32	12	9	17	16	
8	2	37	35	14	8	31	24	8	5	85	87	13	1	39	42	10	3	119	115	11	5	33	32	11	10	80	76	
10	2	123	129	11	9	14	9	10	5	59	58	6	4	271	226	5	4	39	33	6	4	146	140	12	11	35	33	
12	2	116	125	13	9	15	14	12	5	13	11	8	4	127	127	7	4	158	150	8	6	108	106	12	10	85	86	
14	2	46	34	10	10	15	4	14	5	34	36	10	4	119	115	9	4	37	33	10	6	89	80	12	10	38	36	
5	3	97	83	12	10	39	68	7	6	43	43	12	4	38	37	11	4	59	55	12	6	21	22	8	6	40	43	
7	3	41	41	18	10	37	67	9	6	20	17	14	4	34	35	13	4	25	28	11	7	48	48	12	6	65	64	
9	3	43	41	12	12	9	9	11	6	43	42	5	5	111	107	6	5	44	39	11	7	48	48	7	7	36	37	
11	3	43	41	13	8	36	38	7	5	77	77	8	5	73	73	6	8	33	24	9	7	48	41	10	9	19	16	
13	3	112	113	8	7	44	34	8	7	67	64	9	5	65	60	10	5	73	73	10	8	100	109	11	7	45	40	
15	3	46	40	6	1	30	33	12	7	42	40	11	5	39	38	12	5	36	27	10	8	100	109	11	10	25	22	
8	4	270	273	10	1	34	30	9	8	14	15	9	6	16	15	9	6	46	36	11	9	29	26	12	8	68	68	
8	4	150	151	14	1	16	17	11	8	37	35	10	6	21	28	11	6	42	30	10	9	26	24	9	9	71	63	
10	4	150	150	3	2	27	24	13	8	19	24	12	6	42	47	8	7	107	105	10	10	89	84	11	9	36	37	
12	4	15	4	5	2	154	152	10	9	33	34	14	6	19	10	7	34	35	12	10	27	25	12	10	37	36		
14	4	67	110	7	2	33	34	12	9	51	57	7	7	61	58	12	7	79	73	11	9	37	37	11	11	31	27	
7	5	168	164	9	2	21	27	14	9	27	25	9	7	36	32	9	8	42	37	9	8	42	37	9	8	42	37	
9	5	20	23	11	2	7	8	11	10	65	62	11	7	22	23	11	8	33	33	11	8	33	33	11	8	33	33	
11	5	10	4																									

The good agreement between the refined occupancy factor for fluorine and the predicted factor, and between the site occupancy for the Ca(2) position and the fluorine position suggests very strongly that the Ca(2) position is occupied only when the fluorine position is also occupied. There are thus two distinct coordination shells possible for the calcium atoms, as shown in Fig. 1. Two-thirds of the calcium atoms show a very distorted 6-fold coordination environment, which in the remaining one-third is modified and made more symmetric by inclusion of fluorine into the coordination shell.

It would be expected that the existence of two alternative calcium sites would be accompanied by distinct alternative sites for neighbouring oxygen atoms. However, no evidence could be found in difference Fourier syntheses to support this, indicating that any such effect, if it exists, is too small to be revealed by the data used in this study.

The structure described here conforms closely with that suggested by Bartl (1969) for  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot (0-1.0)\text{H}_2\text{O}$ , but is described in terms of a disordered cubic structure rather than the ordered tetragonal form suggested by Bartl. No evidence was found in this study to suggest that the structure should more properly be described in terms of a lower space group, although the postulated existence of such, giving regions of short range order within a crystal which is effectively disordered on a macroscopic scale cannot be refuted by the results presented here. No anomalous bond lengths or angles, such as those found by Bartl in his disordered structure of the hydrate, occur in the structure of the fluoride to indicate that the disorder is anything but simple.

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Table 3. Interatomic distances and bond angles

Al(1)-O(1)	1.742 (7)	O-O Distances	
Al(2)-O(1)	1.768 (10)	O(1)-Al(1)-O(1)	112.1 (5)°
Al(2)-O(2)	1.727 (10)		104.3 (5)
Ca(1)-O(1)	2.340 (7)	O(1)-Al(2)-O(1)	101.3 (7)
Ca(1)-O(1)	2.510 (12)	O(1)-Al(2)-O(2)	116.7 (7)
Ca(1)-O(2)	2.420 (7)	Al(1)-O(1)-Al(2)	136.9 (5)
Ca(2)-O(1)	2.366 (7)		
Ca(2)-O(1)	2.944 (19)		
Ca(2)-O(2)	2.356 (7)		
Ca(2)-F	2.313 (18)		

0.50 Å apart, which may be occupied by calcium atoms, and the 12-fold sites used by fluorine atoms are only partially occupied. The degree of correlation between various parameters in the full matrix refinement was, predictably, high, amounting to 0.86 between the single variable positional coordinate for each of the two calcium sites, and this correlation is reflected in the relatively large standard deviations of all the parameters.

The presumed unit-cell contents  $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\text{F}_4$ , derived from the stoichiometric formula, require that one-third of the 12-fold sites used by fluorine atoms should be occupied.