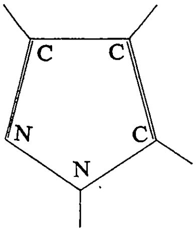
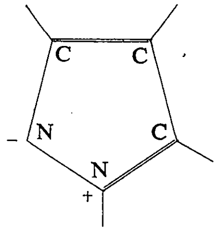
Cette dernière variation n'affecte cependant pas fondamentalement la conformation du noyau pyrazole qui dans les deux cas se rapproche beaucoup plus de la forme (I) que de la forme (II) proposée par Ehrlich (1960) pour la molécule de pyrazole.


I


II

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Crystal Structure of Ettringite

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Ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$ approximately) has a structure based on columns of empirical composition $[Ca_3[Al(OH)_6].12H_2O]^{3+}$, which run parallel to the *c* or needle axis; between them lie the sulphate ions and remaining water molecules. The structure analysis was made on crystals having the space group $P31c$; the hexagonal symmetry which has commonly been reported is attributed to disorder or twinning, in either case affecting mainly the intercolumn material. Within each column $[Al(OH)_6]^{3-}$ octahedra alternate with triplets of calcium ions disposed around a triad axis; each calcium ion is 8 coordinated, by four hydroxyl ions and four water molecules. The columns are nearly cylindrical in cross-section, and their net positive charge is probably distributed among the hydrogen atoms of the water molecules of which their surfaces are composed. In the trigonal crystals studied, there is some disorder affecting the intercolumn water molecules, but none affecting the sulphate ions or the column material.

Introduction

Ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$ approximately) occurs as a natural mineral, and is technically important because of its formation as a hydration product of Portland and super-sulphated cements, and its use, as Satin White, as a coating material for paper. The crystals are hexagonal prisms, often highly elongated. Bannister, Hey & Bernal (1936) made the first single-crystal X-ray study; they found a hexagonal unit-cell with $a=11{\cdot}26$, $c=21{\cdot}48$ Å, space-group $P6_3/mmc$, $Z=2$. From general crystal chemical reasoning and the observed behaviour on dehydration, they suggested that the structure was based on chains of Ca^{2+} and $Al(OH)_6^{3-}$ ions, between which were SO_4^{2-} ions and H_2O molecules.

Welin (1956) determined the crystal structure of a related mineral, thaumasite

$$[Ca_6H_4(SiO_4)_2(SO_4)_2(CO_3)_2\cdot 26H_2O \text{ approximately}],$$

which he found to be based on chains of Ca^{2+} and SiO_4^{4-} ions with the remaining ions and H_2O molecules in between. In contrast Bezjak & Jelenić (1966) proposed a structure for ettringite, derived from an X-ray powder study, which contained layers of linked Ca–O and Al–O polyhedra perpendicular to **c**. X-ray and other evidence indicates very close similarities between the two minerals and it appeared most unlikely that both these results could be correct. Preliminary results of X-ray structure determinations of ettringite, based on single-crystal evidence, were reported almost simultaneously and independently by Courtois, Dusausoy, Laffaille & Protas (1968) and by Moore & Taylor (1968). Both gave substantially similar results, which confirmed the general predictions of Bannister, Hey & Bernal (1936) and agreed broadly with Welin's (1956) structure for thaumasite, but not with that of Bezjak & Jelenić (1966) for ettringite. Moore & Taylor showed that the true symmetry was trigonal, with space group $P31c$ or $P\bar{3}1c$; they attributed the hexagonal symmetry normally observed to twinning. Ettringite has systematic weaknesses of $hkil$ reflexions with $l=2n+1$ and of $h0\bar{h}l$ reflexions with $l=4n+2$. If these are ignored, a pseudo-cell is obtained with $c=10{\cdot}74$ Å and space-group $P6_3/mcm$. Using this pseudo-cell a structure was proposed for ettringite which was as close to Welin's structure for thaumasite as the symmetry and composition allowed. This was refined in $hki0$ projection to give $R=0{\cdot}11$ and the $hki1$, 2 and 3 layers (referred to the pseudo-cell) were found to give $R=0{\cdot}15$, 0·13 and 0·16 respectively. It was based on columns of composition $(Ca_3[Al(OH)_6]\cdot 12H_2O)^{3+}$ running parallel to **c**, with SO_4^{2-} ions and H_2O molecules in the channels between. The pseudo-structure corresponds to a situation [Fig. 1(*a*)] in which each of the eight $\frac{1}{3}, \frac{2}{3}, nc/4$ positions in these channels in the true cell has a 0·75 probability of being occupied by an SO_4^{2-} ion, and a 0·25 probability of being occupied by a $2H_2O$ group. The SO_4^{2-} tetrahedra are randomly distributed between the 'point-up' and 'point-down' orientations. Where a position is occupied by $2H_2O$, these are assumed to be distributed randomly among six sites corresponding to those available to the basal oxygen atoms of an SO_4^{2-} tetrahedron. These groups of H_2O molecules will be referred to as 'water groups'. As sufficiently exact chemical analysis is impracticable (analyses in the literature give x ranging from 30 to 32 in the formula $3CaO.Al_2O_3.3CaSO_4.xH_2O$) the mean number of H_2O molecules per water group may in fact be somewhat lower than the value of 2 given above.

Courtois *et al.* (1968) worked with a hexagonal crystal, for which they took the space group to be $P\bar{6}2c$, referred to the cell with $c=21{\cdot}48$ Å. So far as the columns are concerned, this is compatible with the pseudo-cell and space group used by Moore & Taylor (1968), but with a different choice of origin. They refined the structure to $R=0{\cdot}142$. They showed that if this space group is assumed, there must either still be some disorder in the intercolumn material, or that alternatively the true space group must be $P31c$, the apparently hexagonal symmetry in this case arising from twinning. They mention that one crystal was found that had trigonal symmetry; this accords with the second hypothesis.

Experimental

The crystals were from a naturally occurring specimen from Scawt Hill, N. Ireland and labelled S. 203, which was kindly supplied by Professor C. E. Tilley, from the collection at the Department of Mineralogy and Petrology (University of Cambridge). Some of them proved on single-crystal X-ray examination to be hexagonal, but most of those examined were trigonal with space-group $P31c$ or $P\bar{3}1c$. The unit-cell parameters of all agreed substantially with those reported by Bannister, Hey & Bernal (1936).

A single crystal was selected and turned into a cylinder parallel to the c axis, about 0·5 mm in length and 0·05 mm in diameter. This was done by 'sand-blasting' the crystal with fine alumina powder while rotating it in a watchmaker's lathe. Intensity data were collected both photographically, using copper radiation, with a Nonius integrating Weissenberg camera

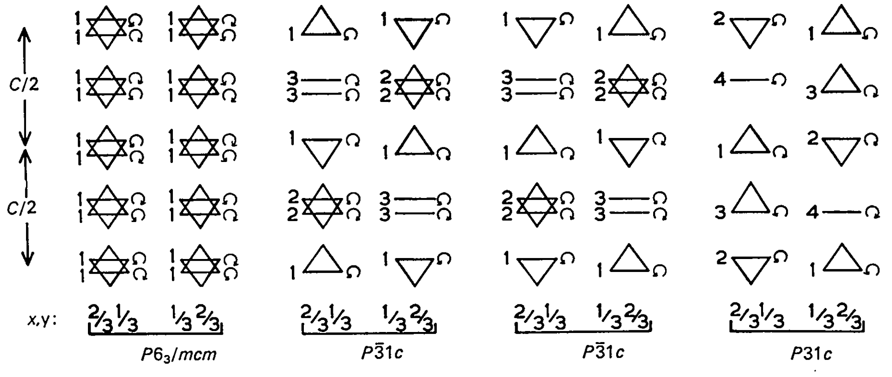


Fig. 1. Some possible arrangements of sulphate tetrahedra and water groups in accordance with space groups (*a*) $P6_3/mcm$ (for the pseudo-cell), (*b*) and (*c*) $P\bar{3}1c$, and (*d*) $P31c$, all for the true cell. Triangles denote sulphate tetrahedra, and horizontal lines water groups. Symmetry-independent tetrahedra or water groups are distinguished by numbers, and relative directions of twist, which are significant only within a given symmetry-related set, by rotation signs. Superimposed triangles and parallel pairs of horizontal lines denote respectively tetrahedra and water groups with halved occupancy. The directions of twist shown in (*c*) are those used in the trial structure for this space group, and those shown in (*d*) are the ones actually found in the final structure, in both cases as seen looking from + to − along the c axis.

with a double film technique, and also using a Hilger Automatic Linear Diffractometer, with molybdenum radiation. Results obtained with the diffractometer indicated that absorption corrections were negligible and none were applied. In general agreement was satisfactory; in the main the diffractometer data were used but in some cases, where the film data appeared more reliable, these were substituted. About 600 independent reflexions were observed and all were used; 120 non-observed reflexions not due to systematic absences were put in at an intensity half that of the weakest observed. Data were collected for 15 layers, ($l=0$-10, 12, 14, 16, 18) the inter-layer scaling being based entirely on the diffractometer measurements.

Initial computations for trial structures were performed on an Elliott 803 Computer mainly using programs kindly supplied by Daly, Stephens & Wheatley (1963). Least-squares refinements were performed by use of Pawley's tape version of Busing, Martin & Levy's (1962) *ORFLS* program, and Fourier analyses by making use of the X-ray 63 system, both on Atlas computers. The atomic scattering factors used were those for neutral atoms (*International Tables for X-ray Crystallography*, 1962).

Owing to the large number of parameters for the non-centric space groups it was possible to refine only about one-third of them in any one cycle of least-squares. Six cycles would thus be necessary to refine all parameters twice, taking care to avoid always refining the same groups of parameters together.

Refinement

It was assumed that the pseudo structure found by Moore & Taylor (1968) was essentially correct, but that the intercolumn sulphate ions and water groups were wholly or partly ordered as regards positions, and in the former case, orientation. Fig. 1(*b*)–(*d*) gives some possible arrangements of the intercolumn material for space groups $P\bar{3}1c$ and $P31c$. If the twists of the tetrahedra and water groups are reduced to zero, the arrangements for space group $P\bar{3}1c$ assume the higher symmetry $P\bar{6}2c$, and that for $P31c$ assumes the symmetry $P6_3$. Of the two possibilities shown for $P\bar{3}1c$, that at (*b*) is improbable because it brings the apices of neighbouring SO_4^{2-} tetrahedra too close together. The arrangement shown at (*c*) was therefore tested. The parameters previously reported for the column material were retained, and for the intercolumn material the coordinates assumed were those given in Table 1. These coordinates are slightly rotated from the positions in the hexagonal pseudo-structure, and were chosen on the basis of preliminary trial structure factor calculations for selected pairs of $hkil$ and $hki\bar{l}$ reflexions. This gave $R=0{\cdot}24$ for all reflexions, the agreement for the odd layers being poor. A Fourier synthesis indicated a reversion in the direction of the pseudo-structure; the space-group $P\bar{3}1c$ was therefore abandoned.

Table 1. *Coordinates of the intercolumn material for the* $P\bar{3}1c$ *trial structure*

	x	y	z
S(1)	$\frac{1}{3}$	$\frac{2}{3}$	0
S(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$
O(13)	$\frac{1}{3}$	$\frac{2}{3}$	0·0690
O(14)	$\frac{1}{3}$	$\frac{2}{3}$	0·8190
O(15)	0·1914	0·6047	0·2271
O(16)	0·1914	0·6047	0·5229
O(17)	0·1914	0·6047	0·7271

It was therefore decided to investigate space-group $P31c$, but to put in SO_4^{2-} ions with their apices pointing both up and down at all eight possible positions in the cell [as in Fig. 1(*a*)], and to allow the least-squares program to refine out the unwanted atoms. The sulphur atoms were initially weighted at unity, which represents an excess of $33\frac{1}{3}\%$ over the true total sulphur content, and the oxygen atoms were weighted at 0·5. The coordinates and temperature factors of the atoms in the columns were first refined, giving $R=0{\cdot}20$. The occupancies of the sulphur and oxygen atom sites in between the columns were then refined; in a total of ten cycles it was found that the arrangement was as shown in Fig. 1(*d*), with $R=0{\cdot}163$. The water groups near $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ and $\frac{2}{3},\frac{1}{3},\frac{3}{4}$ reduced to a total of six sites with z coordinates not significantly different from 0·25 and 0·75, and an occupancy of 0·57 per site. A further two cycles of refinement of the coordinates and temperature factors of the atoms in the columns reduced R to 0·134, and ten cycles of refinement covering all the atoms reduced it to 0·115, or to 0·099 if 60 high-angle unobserved reflexions were discarded. No significant improvement resulted from adoption of anisotropic temperature factors for the calcium atoms or the oxygen atoms of the hydroxyl groups.

A difference Fourier synthesis employing all the reflexions showed no peaks exceeding $\pm 1{\cdot}2$ e.Å^{-3}. Most of the positive peaks were in positions that could reasonably be assigned to hydrogen atoms, the principal exceptions being either on the triad axes or near to the calcium atom positions. In the cell there are four independent hydrogen atoms of OH groups, 16 belonging to H_2O molecules in the columns and two (with half occupancy) belonging to the intercolumn water molecules. Insertion of these atoms, at positions based partly on the difference map, and partly on consideration of O–O distances, and refinement of their positions, but not temperature factors (which were fixed at $B=3{\cdot}0$), lowered R from 0·099 to 0·091. Ten cycles of least-squares refinement of all parameters of all atoms except the hydrogen produced a further reduction to 0·088. The occupancy of the intercolumn water sites refined to $0{\cdot}56 \pm 0{\cdot}05$. A final difference synthesis showed no peaks higher than $\pm 0{\cdot}7$ e.Å^{-3} except in the region of the hydroxyl groups, where the limits were $\pm 1{\cdot}1$ e.Å^{-3}.

To see whether there might still be some disorder between SO_4^{2-} tetrahedra and water groups a refine-

Table 2. *Observed and calculated structure factors for the final structure*

Columns give k, $10\times|F_o|$, $10\times|F_c|$, and φ in millicycles.

0,K,0

1	1588	1492	0
2	370	439	0
3	1572	1571	0
4	587	520	0
5	2298	2288	0
6	2682	2558	0
7	683	660	0
8	288	356	999
9	1088	1001	0
10	487	465	0
11	384	399	0
12	589	522	0

1,K,0

1	1955	2086	987
2	389	352	992
3	837	741	957
4	853	917	956
5	776	746	9
6	348	422	10
7	791	745	995
8	95	99	934
9	382	224	960
10	684	684	3
11	69	77	160

2,K,0

2	970	875	77
3	1183	1126	988
4	189	211	894
5	438	483	964
6	185	135	857
7	485	448	6
8	380	269	53
9	155	128	988
10	283	192	41

3,K,0

3	888	814	943
4	888	917	4
5	387	337	78
6	1252	1127	3
7	345	298	940
8	275	283	991
9	230	150	956

4,K,0

4	86	109	110
5	90	91	990
6	95	103	878
7	395	360	982
8	267	248	991
9	386	268	971

5,K,0

5	947	927	34
6	383	431	28
7	86	60	137
8	189	180	36

6,K,0

6	770	773	35
7	164	111	918

0,K,1

1	379	397	14
2	287	298	54
3	282	297	45
4	130	156	27
5	182	153	41
6	71	29	222
7	182	160	951

1,K,1

2	78	69	113
3	84	127	953
4	260	208	999
5	99	135	958

1,K,-1

2	272	335	15
3	420	392	949
4	99	65	877
5	95	119	863

2,K,1

3	250	230	107
4	199	89	776
6	80	57	980
7	122	169	940

2,K,-1

3	95	87	967
4	596	458	970
6	80	86	769
7	122	95	2

3,K,1

4	72	40	205
5	265	227	54

3,K,-1

4	72	131	810
5	265	378	939

4,K,1

5	120	137	164

4,K,-1

5	120	69	214

0,K,2

0	570	521	63
1	240	234	12
2	192	257	851
3	316	296	49
4	190	219	24
5	192	137	222
6	208	219	968
7	154	97	887
8	166	183	896
9	164	128	111
10	188	64	818

1,K,2

1	437	486	33
2	1165	1135	2
3	1112	1144	984
4	399	319	0
5	479	426	968
6	116	91	41
7	737	685	12
8	519	450	979
9	178	196	966

1,K,-2

1	1127	1161	18
2	892	775	979
3	1360	1075	980
4	698	698	74
5	744	694	9
6	258	143	823
7	988	979	999
8	471	405	993
9	178	75	785

2,K,2

2	621	628	956
3	611	546	13
4	721	634	32
5	663	618	11
6	848	858	19
7	634	668	984
8	233	89	31
9	230	226	993
10	300	337	987

2,K,-2

2	295	344	830
3	842	814	25
4	825	719	12
5	345	267	930
6	695	684	5
7	468	480	16
8	175	178	857
9	310	295	21
10	414	496	988

3,K,2

3	1444	1441	981
4	678	614	982
5	100	186	775
6	399	364	986
7	287	273	1
8	230	186	8
9	415	391	970
10	356	264	11

3,K,-2

3	1069	1071	951
4	848	835	973
5	239	154	33
6	770	740	994
7	195	204	898
8	373	291	986
9	454	417	1
10	368	361	979

4,K,2

4	839	818	12
5	223	177	944
6	462	435	987
7	195	138	838
8	316	343	968
9	414	398	18

4,K,-2

4	455	393	983
5	137	78	246
6	362	277	23
7	207	135	17
8	425	440	996
9	390	408	12

5,K,2

5	100	163	33
7	154	114	896
8	250	274	990

5,K,-2

5	468	468	48
7	154	160	935
8	250	157	948

6,K,2

6	115	54	238
7	358	398	36

6,K,-2

6	115	236	52
7	285	288	13

0,K,3

1	415	481	961
2	682	613	992
3	84	101	38
4	284	406	124
5	389	360	8
6	132	130	813
7	147	112	49
8	505	369	21

1,K,3

2	580	569	49
3	556	596	972
4	155	169	891
5	487	484	104
6	315	250	972
7	172	105	161
8	115	183	132

1,K,-3

2	483	493	991
3	480	433	3
4	155	107	860
5	355	291	926
6	315	295	948
7	172	186	969
8	115	112	51

2,K,3

3	772	758	16
4	209	243	977
6	212	216	7
7	160	161	30

2,K,-3

3	380	273	944
4	210	261	991
6	212	320	8
7	160	124	943

3,K,3

4	329	456	983
5	147	136	954

3,K,-3

4	328	272	88
5	147	103	860

4,K,3

5	273	222	928

4,K,-3

5	273	392	78

0,K,4

0	100	77	171
1	1250	1216	992
2	922	972	973
3	2179	2103	3
4	980	721	987
5	912	930	18
6	337	359	43
7	162	125	964
8	283	288	14
9	710	609	988
10	511	410	76
11	239	286	4

1,K,4

1	1840	1773	987
2	70	75	221
3	842	844	965
4	599	531	6
5	792	815	962
6	184	256	892
7	872	831	997
8	551	486	13
9	260	278	982
10	135	141	100
11	118	120	97

1,K,-4

1	1860	1898	991
2	70	58	775
3	827	837	42
4	615	644	113
5	775	795	9
6	200	227	911
7	980	887	972
8	494	527	68
9	253	288	968
10	135	117	127
11	118	108	87

2,K,4

2	712	728	8
3	719	718	48
4	58	51	934
5	763	769	15
6	440	451	9
7	382	412	980
9	604	593	19
10	73	66	11

2,K,-4

2	690	749	954
3	730	774	57
4	58	105	187
5	667	699	989
6	460	475	998
7	477	442	968
9	600	599	21
10	73	67	103

3,K,4

3	1255	1294	977
4	284	348	24
5	333	325	978
6	792	718	997
7	197	194	13
8	240	253	989
9	655	625	997
10	117	136	7

3,K,-4

3	1173	1236	970
4	403	347	998
5	259	300	971
6	792	751	27
7	197	209	34
8	240	273	13
9	659	607	15
10	117	116	970

4,K,4

4	1120	1030	967
5	265	234	18
6	515	502	983
7	264	282	41
8	239	228	23
9	205	205	957

4,K,-4

4	1172	1072	986
5	265	240	37
6	515	508	998
7	264	302	50
8	239	210	8
9	285	199	965

5,K,4

5	123	120	8
6	450	424	993
7	84	79	884
8	390	434	24

5,K,-4

5	123	149	879
6	450	432	18
7	84	78	17
8	390	382	984

6,K,4

6	310	295	973
7	299	214	21

6,K,-4

6	310	293	963
7	299	298	939

0,K,5

1	227	270	997
4	390	389	958
6	104	193	49
7	185	43	57
8	194	129	18

1,K,-5

2	248	220	140
3	149	171	874
4	389	399	990
5	99	109	192

1,K,5

2	194	181	956
3	74	129	890
4	87	83	230
5	199	256	1

2,K,-5

3	237	267	847

2,K,5

3	475	429	934

3,K,-5

4	105	183	961

3,K,5

4	185	90	767

4,K,-5

5	193	124	826

4,K,5

5	193	212	50

0,K,6

0	290	286	59
1	147	154	34
4	55	103	210
7	80	84	198
8	85	64	959
10	79	25	141

1,K,6

1	781	742	916
2	1895	1746	4
3	1686	1551	10
4	282	214	913
5	153	159	74
7	289	323	96
8	566	541	9
9	144	152	99
10	182	69	868
11	288	218	990

1,K,-6

1	943	975	992
2	1980	1817	4
3	1570	1452	3
4	262	386	859
5	152	70	790
7	288	262	111
8	594	522	12
9	142	201	1
10	73	108	945
11	280	241	962

2,K,6

2	2785	2778	7
3	340	304	18
4	230	256	959
5	980	536	982
6	385	345	16
7	869	728	21
8	380	402	18
9	77	74	817
10	289	98	66

2,K,-6

2	2685	2719	1
3	369	361	973
4	230	222	962
5	414	437	6
6	475	415	62
7	990	887	3
8	269	364	35
9	77	35	8
10	127	94	965

3,K,6

3	122	86	77
4	800	698	0
5	253	322	30
6	240	222	919
8	80	97	893
9	195	186	25
10	98	43	868

3,K,-6

3	122	156	266
4	611	649	970
5	253	249	19
6	190	89	982
8	80	38	119
9	200	237	14
10	98	39	783

4,K,6

4	1350	1304	998
5	359	374	38
6	160	164	15
7	412	343	979
8	225	182	998
9	253	270	43

4,K,-6

4	1485	1448	11
5	254	281	987
6	167	94	26
7	487	448	995
8	160	151	976
9	368	294	74

5,K,6

5	195	149	946
6	385	359	17
7	172	96	47

5,K,-6

5	193	84	853
6	240	304	7
7	199	91	97

0,K,7

4	487	489	24
5	187	197	11

1,K,7

2	290	356	51

1,K,-7

2	220	276	20

2,K,7

3	270	360	71
4	497	419	25
5	198	165	167
6	118	112	985

2,K,-7

3	421	325	962
4	195	187	157
5	138	85	778
6	118	104	15

3,K,7

4	107	67	188
5	234	315	909

3,K,-7

4	107	123	19
5	234	314	64

4,K,7

5	122	87	831

4,K,-7

5	122	85	179

0,K,8

0	2120	2087	959
2	870	853	987
3	450	449	943
4	840	713	30
5	1557	1534	974
6	490	465	93
7	240	182	72
8	660	558	8
10	575	558	976

1,K,8

1	575	686	874
2	50	84	864
3	425	375	951
4	1495	1493	2
5	649	600	47
6	184	154	19
7	50	37	903
8	530	494	68
9	300	275	940
10	780	742	16

1,K,-8

1	530	520	984
2	50	108	755
3	472	473	68
4	1520	1523	978
5	655	587	10
6	230	219	903
7	50	14	896
8	448	380	993
9	322	287	953
10	827	753	8

2,K,8

2	760	759	8
4	632	557	999
5	482	472	39
6	518	460	973
7	494	454	993
8	299	258	996
9	265	223	929

2,K,-8

2	552	580	961
4	632	648	55
5	449	457	11
6	506	447	972
7	425	502	1
8	264	224	968
9	333	220	19

3,K,8

3	50	81	198
4	184	172	796
5	322	195	956
6	402	372	966
8	50	138	58

3,K,-8

3	50	78	888
4	50	89	831
5	264	160	17
6	425	386	28
8	50	162	67

4,K,8

4	495	413	18
5	397	443	44
6	633	595	971
7	643	578	967

4,K,-8

4	437	466	47
5	345	395	4
6	599	597	954
7	661	629	965

5,K,8

5	1271	1259	997
6	562	566	994

5,K,-8

5	1271	1219	8
6	587	554	969

6,K,8

6	438	409	18

6,K,-8

6	390	351	9

0,K,10

0	170	121	3
2	100	107	142
3	100	163	846
4	100	108	934
5	100	64	240
6	100	120	829

1,K,10

1	343	355	879
2	1248	1214	5
3	1069	1056	977
4	433	413	911
5	100	94	850
7	533	545	968
8	465	420	16

1,K,-10

1	777	840	945
2	973	971	17
3	1098	1271	996
4	518	543	986
5	100	205	37
7	731	692	996
8	257	409	30

2,K,10

2	474	469	3
3	304	301	24
5	463	364	29
6	691	652	25
7	260	497	14

2,K,-10

2	645	684	979
3	192	194	910
5	239	206	146
6	442	528	31
7	367	344	38

3,K,10

3	670	736	938
4	334	361	978
5	253	189	983
6	260	243	27

3,K,-10

3	609	625	953
4	578	526	2
5	253	291	25
6	260	393	18

4,K,10

4	722	784	4

4,K,-10

4	488	564	42

0,K,12

0	2600	2402	7
1	1040	1083	986
2	207	228	0
3	583	637	14
5	1056	1073	16
6	274	445	991
7	100	249	31

1,K,12

1	1207	1167	970
2	333	266	103
3	560	524	968
4	235	466	38
5	606	634	989
7	896	607	8
8	100	142	968

1,K,-12

1	1207	1119	56
2	243	350	896
3	528	543	23
4	235	482	20
5	646	581	12
7	716	614	9
8	100	149	130

2,K,12

2	1880	1594	994
3	562	596	28
5	925	816	980
6	188	141	9
7	188	333	999
8	616	582	986

2,K,-12

2	1465	1475	986
3	983	982	4
5	647	769	11
6	100	163	967
7	100	302	979
8	459	493	978

3,K,12

3	720	869	27
4	533	511	33
5	100	252	65
6	100	250	18

3,K,-12

3	621	620	988
4	553	549	987
5	100	176	990
6	100	256	997

4,K,12

4	1135	1044	986
6	100	158	907
7	245	437	16

4,K,-12

4	1132	1092	28
6	100	203	33
7	245	409	39

5,K,12

5	100	190	834
5	250	349	3

5,K,-12

6	250	354	35

0,K,14

0	170	155	933
1	180	64	117

1,K,14

1	653	634	8
2	487	543	954
3	440	307	943
4	259	320	955
5	448	449	972
7	668	623	7

1,K,-14

1	290	308	32
2	550	449	21
3	394	380	52
4	170	190	106
5	170	306	987
7	578	420	17

2,K,14

3	617	580	2
4	680	626	6
5	170	180	990
6	390	414	1
7	556	510	997

2,K,-14

3	398	432	990
4	643	520	975
5	170	345	977
6	310	437	14
7	667	536	993

3,K,14

3	673	631	17
4	655	620	982
6	462	446	972

3,K,-14

3	673	751	994
4	568	599	960
6	100	373	954

4,K,14

4	100	213	997
6	272	353	19

4,K,-1

4	100	[illegible]	58
6	272	[illegible]	9

5,K,14

5	275	337	997

5,K,-14

5	100	166	986

0,K,16

0	2100	2118	985
1	292	983	21
5	976	818	969
6	971	915	18

1,K,16

1	750	718	38
2	175	146	44
4	1027	920	14
5	735	578	997

1,K,-16

1	568	594	52
2	175	138	5
4	892	788	25
5	735	686	981

2,K,16

3	273	363	3
5	485	372	938

2,K,-16

3	273	386	46
5	485	487	987

ment was attempted with the groups at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ and $\frac{1}{3},\frac{2}{3},\frac{3}{4}$ rearranged. A sulphur atom at 0·1 occupancy was added at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ and the oxygen atoms around this site were duplicated to give a sixfold group with halved occupancy; this would permit two water molecules to occupy sites 180° apart, which would be more satisfactory than occupying two out of three sites 120° apart. In addition the tetrahedron at $\frac{1}{3},\frac{2}{3},\frac{3}{4}$ was reduced to 0·9 occupancy with the oxygen atoms disordered (*i.e.* the tetrahedron pointing both up and down). These alterations increased R to 0·114, and when occupancies and positions were refined the changes were all such as to restore the ordered arrangement, which was therefore retained.

Table 3. *Coordinates (expressed as fractions of the cell edges) and isotropic temperature factors* ($B=8\pi^2u$ in Å^2) *for the final structure*

E.s.d.'s on the last significant figures are in parentheses.

		x	y	z	B
Al(1)		0	0	0·000 (1)	1·2 (1)
Al(2)		0	0	0·250 (1)	1·2 (1)
Ca(1)		0·009 (1)	0·816 (1)	0·875 (1)	1·7 (1)
Ca(2)		0·994 (1)	0·189 (1)	0·125 (1)	1·8 (1)
O(1)		0·994 (3)	0·134 (3)	0·948 (1)	2·2 (5)
O(2)		0·996 (3)	0·865 (2)	0·057 (1)	1·0 (4)
O(3)	OH	0·004 (3)	0·146 (2)	0·805 (1)	1·6 (4)
O(4)		0·004 (3)	0·876 (2)	0·198 (1)	1·0 (4)
O(5)		0·000 (4)	0·348 (3)	0·047 (2)	3·9 (6)
O(6)		0·010 (2)	0·663 (2)	0·958 (1)	1·8 (4)
O(7)		0·997 (3)	0·345 (3)	0·199 (1)	3·6 (6)
O(8)	H_2O	0·996 (3)	0·655 (3)	0·788 (1)	3·1 (5)
O(9)		0·263 (3)	0·405 (3)	0·618 (2)	2·9 (6)
O(10)		0·744 (4)	0·593 (4)	0·374 (2)	4·8 (9)
O(11)		0·259 (3)	0·406 (3)	0·126 (2)	4·8 (9)
O(12)		0·768 (2)	0·598 (2)	0·870 (2)	1·7 (5)
O(13)		$\frac{1}{3}$	$\frac{2}{3}$	0·420 (3)	1·9 (9)
O(14)		$\frac{1}{3}$	$\frac{2}{3}$	0·814 (3)	7·8 (16)
O(15)	SO_4^{2-}	$\frac{1}{3}$	$\frac{2}{3}$	0·070 (3)	4·2 (13)
O(16)		0·195 (3)	0·642 (3)	0·518 (2)	4·7 (8)
O(17)		0·195 (3)	0·620 (3)	0·723 (1)	4·3 (7)
O(18)		0·192 (2)	0·585 (2)	0·982 (1)	2·1 (4)
O(19)	H_2O	0·197 (5)	0·637 (5)	0·243 (3)	5·4 (15)
S(1)		$\frac{1}{3}$	$\frac{2}{3}$	0·491 (1)	2·2 (5)
S(2)		$\frac{1}{3}$	$\frac{2}{3}$	0·750 (2)	1·6 (2)
S(3)		$\frac{1}{3}$	$\frac{2}{3}$	0·009 (1)	1·4 (4)

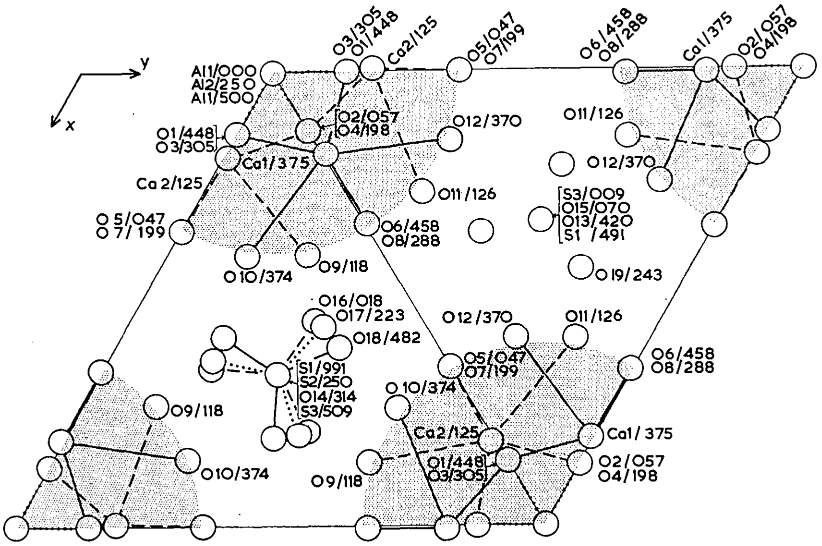


Fig. 2. Projection of the structure on (0001). In general, only atoms in the lower half of the cell are shown; z coordinates are expressed as 1000 z/c. The columns are shaded.

Table 2 gives observed and calculated structure factors, Table 3 gives the corresponding parameters, Fig. 2 shows the structure projected along **c**, and Fig. 3 shows the partial structure of one column projected on to (11$\bar{2}$0). Hydrogen atoms are omitted from Table 3 and Figs. 2 and 3, because their parameters cannot be considered as more than plausible; a general indication of their proposed positions is given in the next section.

Description of the structure

The results obtained for the occupancy of the sites in the water groups show that the formula of the ettringite crystal studied may be written as

$$Ca_6[Al(OH)_6]_2(SO_4)_3 . 25{\cdot}7H_2O\ ,$$

or

$$3CaO . Al_2O_3 . 3CaSO_4 . 31{\cdot}7H_2O\ .$$

This water content need not apply to other specimens, or even to all crystals of the present specimen; as indicated earlier, the occupancy of the sites in the water groups may well be variable.

The parameters of the atoms in the columns show only small changes from those reported by Moore & Taylor (1968) for the pseudo-structure, and also agree closely with those found by Courtois *et al.* (1968). The columns are based on lines of $[Al(OH)_6]^{3-}$ octahedra running along $(0,0,z)$, which are linked to each of their neighbours through groups of three Ca^{2+} ions, the coordination polyhedra of which are completed by water molecules. Each Ca^{2+} ion is eight-coordinated, by four H_2O molecules and four OH^- ions; its polyhedron may be described as a trigonal prism with its axis parallel to **c** and having two additional apices at approximately the same z coordinate as the Ca^{2+} ion. Each shares two edges with adjacent $[Al(OH)_6]^{3-}$ octahedra. The arrangement of the intercolumn SO_4^{2-} ions and H_2O molecules has already been described, and is shown in Fig. 1(*d*).

Tables 4 and 5 give the more important interatomic distances and bond angles respectively. Within the $[Al(OH)_6]^{3-}$ octahedra, the Al–O distances are 1·82–2·00 Å, the O–O distances 2·46–2·84 Å, and O–Al–O angles 84·7–95·6°. With one exception, the horizontal O–O edges are shorter than the others, and the hydrogen atoms of the OH groups possibly form hydrogen bonds along them. However, the final difference synthesis did not support this conclusion, and the extreme shortness (2·46 Å) of one of the O–O distances casts some doubt on the accuracy of the coordinates involved.

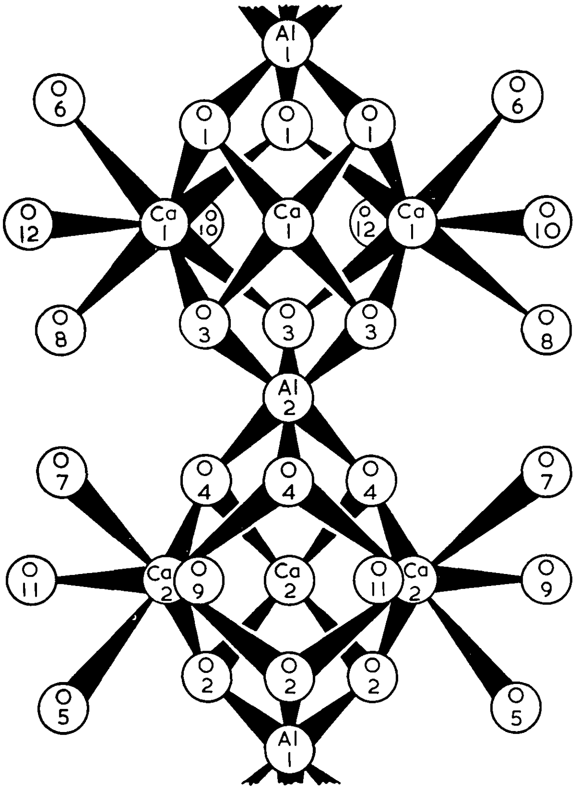


Fig. 3. Part of a single column projected on (11$\bar{2}$0). For clarity, the water molecules coordinated to calcium ions lying in the central vertical line of the Figure are omitted, as are all hydrogen atoms.

Table 4. *Interatomic distances* (Å)

O–O distances above 2·9 Å are not given.

(*a*) Within AlO_6 octahedra (*h* = horizontal)	
Al(1)–O(1)	1·92
Al(1)–O(2)	1·92
Al(2)–O(3)	2·00
Al(2)–O(4)	1·82
O(1) –O(1) (*h*)	2·67
O(1) –O(2)	2·84
O(1) –O(2)	2·74
O(1) –O(2) (*h*)	2·59
O(3) –O(3) (*h*)	2·80
O(3) –O(4)	2·77
O(3) –O(4)	2·77
O(4) –O(4) (*h*)	2·46
(*b*) Within CaO_8 polyhedra	
Ca(1)–O(1)	2·46
Ca(1)–O(1)	2·46
Ca(1)–O(3)	2·52
Ca(1)–O(3)	2·36
Ca(1)–O(6)	2·48
Ca(1)–O(8)	2·56
Ca(1)–O(10)	2·62
Ca(1)–O(12)	2·60
Ca(2)–O(2)	2·48
Ca(2)–O(2)	2·35
Ca(2)–O(4)	2·46
Ca(2)–O(4)	2·46
Ca(2)–O(5)	2·43
Ca(2)–O(7)	2·36
Ca(2)–O(9)	2·67
Ca(2)–O(11)	2·75
(*c*) Within SO_4 tetrahedra or water groups	
S(1)—O(13)	1·51
S(1)—O(16)	1·56
S(2)—O(14)	1·36

Table 4 (*cont.*)

S(2)—O(17)	1·49
S(3)—O(15)	1·31
S(3)—O(18)	1·48
O(13)–O(16)	2·55
O(14)–O(17)	2·38
O(15)–O(18)	2·33
O(16)–O(16)	2·50
O(17)–O(17)	2·37
O(18)–O(18)	2·39
O(19)–O(19)	2·41
(*d*) Between different polyhedra	
O(5)–O(18)	2·82
O(6)–O(16)	2·70
O(6)–O(18)	2·66
O(7)–O(17)	2·77
O(8)–O(17)	2·82
O(8)–O(19)	2·50
O(9)–O(11)	2·81
O(9)–O(16)	2·59
O(9)–O(17)	2·82

Within the CaO polyhedra, the Ca–O distances are 2·35–2·75 Å. The smallest O–Ca–O angle is 64·7°, and the shortest O–O edge, apart from those shared with the $[Al(OH)_6]^{3-}$ octahedra, is 2·91 Å. These values are in the normal range. Those water molecules which are at approximately the same *z* coordinates as the calcium ions to which they are attached [O(9)–O(12)] probably have their hydrogen atoms in a vertical plane, while those which are at the vertices of the trigonal prisms [O(5)–O(8)] probably have them in a horizontal plane. This arrangement, which was well supported by the difference syntheses, permits some hydrogen bonding on to the sulphate ions and intercolumn water molecules. The shortest distance between the oxygen atoms of the column water molecules and those of the sulphate groups or intercolumn water molecules is 2·50 Å.

Within the columns, Pauling's second rule is obeyed. It is perhaps reasonable to think of the entire net positive charge of the columns as being distributed, approximately uniformly, among the hydrogen atoms of which their surfaces are composed.

Within the SO_4^{2-} groups, the S–O distances are 1·31–1·56 Å, the O–O distances 2·33–2·55 Å, and the O–S–O angles 105·6–113·2°. The wide range of the S–O distances casts doubt on the accuracy of the coordinates, the normal value being about 1·49 Å (Wells, 1962). However, it is possibly significant that Courtois *et al.* (1968) reported the even shorter distance of 1·23 Å for one of the S–O bonds lying along the threefold axis.

The distances between the oxygen sites in the intercolumn water groups are also abnormally low (2·41 Å). However, the mean occupancy is approximately 1·7 atoms per group of three sites, so that most or all of the groups presumably contain either one or two water molecules. Where two are present, thermal movements could possibly cause these to move cooperatively among all three of the sites in such a way that the mean separation between the atoms is greater than the 2·41 Å separation between the sites.

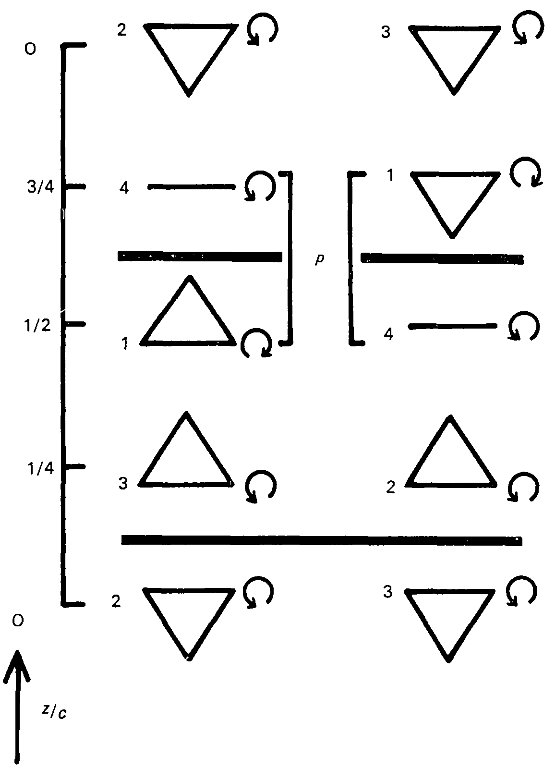
Crystal with hexagonal symmetry

As was shown by Courtois *et al.* (1968), the hexagonal symmetry of some crystals might be explained by either twinning or disorder. The latter is perhaps the more probable. Its effect is almost wholly on some of

Table 5. *Bond angles*

O–Ca–O angles above 115° not given.

Al(1)	O(1)–O(1)	88·4°	S(1)	O(13)–O(16)	112·5°
	O(1)–O(2)	95·6		O(16)–O(16)	106·3
	O(1)–O(2)	91·4			
	O(2)–O(2)	84·7	S(2)	O(14)–O(17)	113·2
				O(17)–O(17)	105·6
Al(2)	O(3)–O(3)	92·9			
	O(3)–O(4)	92·9	S(3)	O(15)–O(18)	112·3
	O(3)–O(4)	92·9		O(18)–O(18)	106·5
	O(4)–O(4)	85·3			
Ca(1)	O(1)–O(1)	65·8°	Ca(2)	O(2)–O(2)	64·7°
	O(1)–O(3)	75·9		O(2)–O(4)	77·9
	O(1)–O(6)	85·0		O(2)–O(5)	90·3
	O(1)–O(6)	86·6		O(2)–O(5)	90·1
	O(1)–O(10)	75·4		O(2)–O(9)	71·4
	O(1)–O(12)	74·9		O(2)–O(11)	71·9
	O(3)–O(3)	70·0		O(4)–O(4)	60·0
	O(3)–O(8)	84·4		O(4)–O(7)	74·2
	O(3)–O(8)	86·0		O(4)–O(7)	91·3
	O(3)–O(10)	72·4		O(4)–O(9)	77·7
	O(3)–O(12)	70·0		O(4)–O(11)	73·1
	O(6)–O(8)	93·0		O(5)–O(7)	86·2
	O(6)–O(10)	74·7		O(5)–O(9)	74·7
	O(6)–O(12)	75·1		O(5)–O(11)	74·9
	O(8)–O(10)	76·8		O(7)–O(9)	78·3
	O(8)–O(12)	68·7		O(7)–O(11)	74·3



(a) (b)

Fig. 4. Sequences of SO_4 tetrahedra and water groups along $\frac{2}{3},\frac{1}{3},z$ for twinned orientations (*a* and *b*) in the space group $P31c$ related by the operation of mirror planes at $z=\frac{1}{8}$ and $\frac{5}{8}$, which are shown by heavy, horizontal lines. *p*: see text; in other respects the notation is as in Fig. 1.

the SO_4^{2-} tetrahedra and the intercolumn water groups. The space group $P\bar{6}2c$ assigned by Courtois *et al.* is derived from $P31c$ by the addition of mirror planes perpendicular to the *c* axis; for the choice of origin used in the present work, these must be placed at $z=\frac{1}{8}$ and $\frac{5}{8}$. Operation by such mirror planes has only a minor effect on the columns, because these already possess pseudo mirror planes at these heights. Its effect on the intercolumn material is shown in Fig. 4; it is to invert groupings of an SO_4^{2-} tetrahedron and a water group (marked '*p*' in the Figure), leaving the positions and orientations of the remaining tetrahedra unaffected apart from small changes in the angles of twist around the threefold axis. It is not established whether the effect operates so as to produce irregularities in the sequence of SO_4^{2-} tetrahedra and intercolumn water groups along individual channels, or whether it operates on channels as a whole.

The space group $P6_3/mmc$, which has usually been assigned to the hexagonal crystals, is incompatible with the symmetry of the columns and is thus most unlikely to be correct.

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