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The Crystal Structure of β Dicalcium Silicate

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The crystal structure of β dicalcium silicate (Ca_2SiO_4) has been determined from X-ray oscillation, rotation and Weissenberg photographs. The mineral is monoclinic, space group $P2_1/n$, with cell dimensions $a = 5{\cdot}48 \pm 0{\cdot}02$, $b = 6{\cdot}76 \pm 0{\cdot}02$, $c = 9{\cdot}28 \pm 0{\cdot}02$ Å; $\beta = 94°\ 33'$. There are four molecules in the unit cell. The atomic coordinates were found by means of two-dimensional Fourier projections along two axes. The relation of this structure to the orthorhombic β potassium sulphate and trigonal glaserite structures is discussed.

Introduction

Dicalcium silicate, $2CaO.SiO_2$ or Ca_2SiO_4, is an important constituent of Portland cement, blast furnace and open hearth slags, and certain types of refractory. It occurs in four polymorphic modifications:— α (high temperature), α' (medium temperatures), β (room temperature, metastable) and γ (room temperature, stable). Inversion to the γ form is accompanied by a large expansion in volume which is undesirable in refractory products or in slags used in building. Although the β form is metastable it is the most commonly occurring modification; it has the property of setting to a hard mass when finely ground and mixed with water while the γ form has not. Three modifications α', β and γ are found in nature, the natural β Ca_2SiO_4 being called larnite.

The polymorphism of Ca_2SiO_4 has been known since the work of Le Chatelier. The true relation between the various modifications has however only recently been established, as a result of the speculations of Bredig (1950) and the powder X-ray examination made at high temperatures by Trömel (1949).

The structure of the γ form has been established by O'Daniel & Tscheischwili (1942) by analogy with Na_2BeF_4, and is of the olivine type. From powder data Bredig has suggested that the α form is trigonal (glaserite type) and that the α' form is orthorhombic (βK_2SO_4 type). No structures have previously been postulated for βCa_2SiO_4.

Material examined

Suitable crystals were prepared by Nurse (1949), an addition of 0·5 % B_2O_3 being made to prevent inversion to the γ form. After recrystallization from molten $CaCl_2$ and washing with absolute alcohol a small specimen was analysed, giving a B_2O_3 content of 0·3 % and a molecular ratio of CaO/SiO_2 of $2{\cdot}15 \pm 0{\cdot}10$. It is possible therefore that the crystals contained excess CaO in solid solution. The cell dimensions found agree very well however with measurements made by Henry (1950) on natural larnite, namely, $a = 5{\cdot}51$, $b = 6{\cdot}75$, $c = 9{\cdot}30$ kX., $\beta = 94°$.

A number of well developed prisms were selected, many of which were opaque with obvious polysynthetic twinning, but a few had faces clear enough to give good reflections on an optical goniometer, and appeared optically to be single crystals. Later X-ray examination showed even these to be twinned and all the work has been done on twinned specimens.

Optical properties

The optical properties of the specimen agree with other published data, being

$$\alpha = 1{\cdot}715,\ \gamma = 1{\cdot}740;\ 2H = 62°;\ \text{optically positive.}$$

Sundius (1933) gives $\alpha = 1{\cdot}717$, $\gamma = 1{\cdot}736$, $2V = 64$–$69°$.

The mineral crystallizes in small squat prisms showing $\{011\}$ faces and no terminal faces. By optical goniometry $b/c = 0{\cdot}728$.

Symmetry and cell dimensions

The unit-cell dimensions and symmetry elements were determined from oscillation and rotation photographs about [100], [010] and [001] using Cu $K\alpha$ radiation. We found

$$a = 5{\cdot}48 \pm 0{\cdot}02,\ b = 6{\cdot}76 \pm 0{\cdot}02,\ c = 9{\cdot}28 \pm 0{\cdot}02\ \text{Å},$$
$$\beta = 94°33';\ b/c = 0{\cdot}729\ .$$

Reflections $(h0l)$ are observed only if $(h+l)$ is even, and $(0k0)$ only if k is even, which is consistent with the monoclinic space group $P2_1/n$. There are four molecules in the unit cell giving a calculated density of 3·31 g.cm.$^{-3}$ as compared with an experimental density of 3·28 g.cm.$^{-3}$. The crystals are twinned on (100) and (001).

Intensity estimations

Weissenberg zero-layer photographs were taken about each of the three axes with Cu $K\alpha$ radiation, filtered through nickel foil, and the intensities were estimated visually using the multiple-film technique (Robertson, 1943). Owing to the very high absorption coefficient for dicalcium silicate it was necessary to reduce the absorption as much as possible by using very small crystals (*circa* 0·07 mm. cube). The remaining absorption was corrected by the method of Bradley (1935), assuming a cylindrical specimen. Lorentz and polarization corrections were made in the usual way and a set of numbers obtained proportional to $|F|$.

In order to increase the number of terms for two-dimensional Fourier syntheses silver radiation filtered with rhodium was used for a further series of zero-layer Weissenberg photographs about [100] and [010]. With this radiation the absorption effects were negligible and it was possible to use a larger crystal, but exposure times were greatly increased because of the shorter wave length and low intensity of the radiation used. The intensity estimation on these photographs was difficult because the low-angle reflections were superimposed on streaks due to 'white' radiation, and the high-angle reflections were weak. For this series of data the intensities were estimated with the aid of a Hilger photometer, calibrated with a scale produced on one film by a stepped set of exposures of a chosen reflection. The intensities were corrected for Lorentz and polarization factors and the $|F|$ values obtained were correlated with those obtained from the films taken with copper radiation, using the clearest reflections common to both films.

In the Fourier analyses the copper radiation values were used where possible, and the silver radiation values for reflections which did not appear on the copper photograph. There was still a high proportion of accidental absences but it was not thought practicable to increase exposures which were already as long as four weeks (500 hours).

Intensity estimations in the ($h0l$) projection were complicated by twinning across the face (001). Reciprocal nets of the two components of the twin

Table 1 (*a*). *Comparison of observed and calculated $F(h0l)$'s*

hkl	$\|F_o\|$	F_c
101	18	+34
103	115	−134
105	62	−69
107	53	+26
109	20	+17
1,0,11	49	+56
1,0,13	< 20	− 4
$10\bar{1}$	14	+13
$10\bar{3}$	115	+124
$10\bar{5}$	49	+41
$10\bar{7}$	33	−16
$10\bar{9}$	< 20	−13
$1,0,\overline{11}$	62	−69
$1,0,\overline{13}$	< 20	+ 4
200	160	−129
202	62	−59
204	62	−59
206	78	+88
208	66	+77
2,0,10	< 20	− 9
2,0,12	< 20	− 3
2,0,14	45	−46
$20\bar{2}$	41	−26
$20\bar{4}$	50	+57
$20\bar{6}$	66	+62
$20\bar{8}$	70	+75
$2,0,\overline{10}$	37	−32
$2,0,\overline{12}$	26	−26
$2,0,\overline{14}$	29	−28
301	25	−15
303	123	+129
305	29	+28
307	< 20	+14
309	< 20	−13
3,0,11	58	−66
3,0,13	25	+10
3,0,15	< 20	+ 1
$30\bar{1}$	< 20	− 8
$30\bar{3}$	94	−93
$30\bar{5}$	94	−77
$30\bar{7}$	54	+65
$30\bar{9}$	< 20	+19
$3,0,\overline{11}$	53	+44
$3,0,\overline{13}$	< 20	+ 2
$3,0,\overline{15}$	25	−28
400	124	+100
402	< 20	+21
404	41	+34
406	33	−41
408	41	−49
4,0,10	< 20	− 4
4,0,12	< 20	− 4
4,0,14	29	+46
$40\bar{2}$	< 20	− 6
$40\bar{4}$	66	−65
$40\bar{6}$	33	−28
$40\bar{8}$	53	−46
$4,0,\overline{10}$	29	+32
$4,0,\overline{12}$	< 20	+24
$4,0,\overline{14}$	< 20	+17
501	33	+ 8
503	74	−81
505	29	−18
507	< 20	−17
509	25	+25
5,0,11	25	+42
5,0,13	< 20	− 2
5,0,15	< 20	+ 8
$50\bar{1}$	45	+46
$50\bar{3}$	49	+39
$50\bar{5}$	53	+37
$50\bar{7}$	33	−37
$50\bar{9}$	25	−20
$5,0,\overline{11}$	45	−30
$5,0,\overline{13}$	< 20	− 3
$5,0,\overline{15}$	25	+30
600	53	−37
602	< 20	−18
604	45	−43
606	50	+52
608	< 20	+28
6,0,10	< 20	+ 8
6,0,12	29	+ 4
6,0,14	< 20	−39
$60\bar{2}$	29	−13
$60\bar{4}$	33	+49
$60\bar{6}$	< 20	+ 8
$60\bar{8}$	45	+39
$6,0,\overline{10}$	< 20	−19
$6,0,\overline{12}$	37	−35
$6,0,\overline{14}$	< 20	− 2
701	33	−12
*703	41	+50
*705	< 20	+15
*707	< 20	+24
*709	< 20	−20
*$70\bar{1}$	< 20	−30
*$70\bar{3}$	21	−22
*$70\bar{5}$	41	−38
*$70\bar{7}$	54	+37
$70\bar{9}$	33	+21
800	29	+24
802	< 20	+17
804	< 20	+21
$80\bar{2}$	< 20	+18
$80\bar{4}$	25	−38
907	25	−27
$90\bar{1}$	25	+38

* Unreliable owing to the overlapping of the reflections from the two individuals of the twin.

Table 1 (*b*). *Comparison of observed and calculated $F(0kl)$'s*

hkl	$\lvert F_o \rvert$	F_c
002	24	+24
004	33	−40
006	76	−73
008	95	−91
0,0,10	33	+28
0,0,12	< 10	+10
0,0,14	38	+43
0,0,16	15	+19
0,0,18	25	−21
011	< 10	+ 1
013	42	+33
015	60	−60
017	27	+29
019	16	−16
0,1,11	< 10	− 6
0,1,13	22	+22
012	17	−15
014	52	+54
016	19	+12
018	< 10	0
0,1,10	< 10	−10
0,1,12	16	−17
0,1,14	< 10	− 5
020	32	−26
022	53	−58
024	48	+40
026	43	+43
028	< 10	+ 5
0,2,10	17	+19
0,2,12	37	−40
021	22	+20
023	67	+62
025	59	+56
027	< 10	+ 2
029	35	−38
0,2,11	22	−29
0,2,13	8	− 5
031	89	−96
033	30	+32
035	14	− 5
037	57	+59
039	21	+11
0,3,11	< 10	− 3
0,3,13	< 10	+ 2
0,3,15	38	−34
032	49	+31
034	14	+14
036	23	+20
038	18	−19
0,3,10	19	−22
0,3,12	< 10	− 1
0,3,14	< 10	+ 4
040	54	+64
042	48	−35
044	14	+22
046	11	+ 2
048	27	−37
0,4,10	35	+36
0,4,12	19	−12
041	31	−29
043	58	−59
045	46	−43
047	< 10	+ 5
049	43	+36
0,4,11	27	+27
0,4,13	< 10	+ 5
051	22	−26
053	19	+30
055	25	−24
057	35	+28
059	11	−10
0,5,11	< 10	− 8
052	40	−44
054	38	−46
056	24	−24
058	19	+27
0,5,10	36	+40
0,5,12	< 10	+14
060	70	+65
062	< 10	+ 1
064	< 10	+ 3
066	21	−18
068	33	−36
0,6,10	< 10	+ 9
0,6,12	< 10	− 8
0,6,14	14	+22
061	< 10	+10
063	12	+20
065	< 10	+ 3
067	12	− 9
069	< 10	− 5
071	27	+26
073	24	+23
075	49	−52
077	< 10	0
079	13	−17
0,7,11	< 10	+ 4
0,7,13	27	+28
072	26	+35
074	18	+26
076	23	+15
078	13	−17
0,7,10	22	−24
0,7,12	< 10	−10
0,7,14	< 10	0
080	37	+32
082	19	−26
084	11	+ 6
086	< 10	+11
088	21	−16
0,8,10	14	+20
0,8,12	14	−17
081	< 10	0
083	< 10	+ 9
085	13	+11
087	< 10	+ 4
089	< 10	− 4
0,8,11	< 10	−11
091	52	−46
093	13	+10
095	< 10	+ 5
097	43	+52
099	< 10	+10
0,9,11	< 10	−15
0,9,13	< 10	−13
0,9,15	18	−29
092	13	− 2
094	21	+ 5
096	< 10	+ 4
098	< 10	− 2
0,9,10	< 10	− 3
0,9,12	< 10	− 2
0,9,14	< 10	+ 1
0,10,0	< 10	+ 4
0,10,2	10	−23
0,10,4	< 10	+12
0,10,6	< 10	+12
0,10,8	< 10	− 4
0,10,10	16	+22
0,10,1	< 10	− 4
0,10,3	< 10	− 2
0,10,5	< 10	− 4
0,10,7	< 10	− 4
0,10,9	< 10	+ 1
0,11,1	< 10	+ 6
0,11,3	< 10	+17
0,11,5	19	−26
0,11,7	< 10	0
0,11,2	< 10	−15
0,11,4	24	−24
0,11,6	< 10	− 5
0,12,0	31	+32
0,12,2	< 10	− 4
0,12,4	< 10	+ 3
0,12,6	< 10	− 9
0,12,8	18	−24
0,12,1	< 10	− 6
0,12,3	16	−10
0,12,5	< 10	− 8
0,12,7	< 10	+ 1
0,14,0	18	+15
0,16,6	18	+12

showed that there would be partial overlapping of the $(70l)$ reflections of one individual and $(7,0,\overline{l-2})$ reflections of the other individual. No satisfactory method of correcting for this partial overlapping was discovered. These reflections are marked by an asterisk in Table 1, and were not included in the Fourier analyses. In the table the observed $|F|$ value is derived from the total intensity although it has been assigned to the dominant individual of the twinned crystal.

Table 1 (*c*). *Comparison of observed and calculated* $F(hk0)$*'s*

hkl	$\lvert F_o\rvert$	F_c	hkl	$\lvert F_o\rvert$	F_c	hkl	$\lvert F_o\rvert$	F_c
110	< 18	−12	270	< 18	+ 5	450	18	+24
120	39	+42	280	18	−14	460	30	+34
130	30	−29				470	< 18	−12
140	39	−42	310	32	+60			
150	< 18	−21	320	46	−49	510	21	−29
160	< 18	+13	330	23	+19	520	35	+34
170	< 18	+ 1	340	39	+42	530	42	−38
180	< 18	+ 2	350	25	+31	540	30	−34
			360	< 18	− 9	550	15	−28
210	39	+24	370	21	+17	560	< 18	+11
220	39	−18						
230	15	− 6	410	27	− 7	610	24	+ 1
240	36	−40	420	20	−29	620	18	−25
250	< 18	− 5	430	< 18	−13	630	< 18	−21
260	53	+61	440	24	+18			

Structure determination

The β and α' forms of dicalcium silicate differ only slightly in optical properties and density. From thermal data it was known that the energy change involved in the $\beta-\alpha'$ inversion is small. It seemed reasonable to suppose therefore that the β structure involves only a slight distortion of the α' structure, which Bredig postulates to be of the β K_2SO_4 type. The cell dimensions and symmetry elements of β dicalcium silicate showed a marked resemblance to those of β K_2SO_4.

The structure of the latter, as obtained from *Strukturbericht* (1928–32, p. 86), was therefore used as a starting point, distorting the cell to make $\beta = 94°33'$ and substituting Ca for K and Si for S.

Structure factors were calculated for (h00), (0k0) and (00l) planes, using the atomic scattering factors given by Bragg & West (1928), and these showed fair agreement with the observed $|F|$ values. It appeared that the best resolution of the atoms would be obtained in a Fourier projection in the b direction, and this was prepared. For the determination of the signs of the observed $|F|$ values, provisional structure factors were calculated for (h0l) reflections, using the coordinates suggested by analogy with β potassium sulphate. Though agreement between observed and calculated (h0l) structure factors was not very good, the signs of the stronger reflections were thought to be reliable, and were used with the observed $|F|$ values for a Fourier synthesis. Beevers–Lipson strips were used for the synthesis giving divisions of 6° in all cell directions. Successive Fourier projections, including more terms as the signs became more certain, gave increased agreement and the calcium and silicon positions became well resolved, but the oxygen positions remained uncertain. Successive (0kl) projections, calculated in the same way, gave good resolution of the calcium and silicon but little indication of the oxygen positions.

A wire model was then constructed with fixed calcium and silicon positions and free rotation of the oxygen tetrahedra about the silicons. From packing considerations it became obvious that there was one orientation of the tetrahedron preferable to all the others, and when the appropriate oxygen coordinates were used in calculating structure factors the agreement between observed and calculated $|F|$ values was improved. Repeated Fourier projections in the two directions, until all the observed terms were included and no sign changes were obtained, refined the coordinates and gave resolution of some oxygens.

The (h0l) and (0kl) final projections are reproduced in Fig. 1. The resolution of overlapping oxygens is still poor in the (0kl) projection. The x and y coordinates of $\mathrm{O_{II}}$, $\mathrm{O_{III}}$ and $\mathrm{O_{IV}}$ (Table 2) can be obtained from the (h0l) projection but those of $\mathrm{O_I}$ remain uncertain. Similarly the (0kl) projection gives the y and z coordinates of $\mathrm{O_I}$ and only rough positions of $\mathrm{O_{II}}$ and $\mathrm{O_{III}}$. $\mathrm{O_{IV}}$ lies on top of $\mathrm{Ca_I}$ in this projection. These known coordinates were used to calculate the other coordinates so as to give a nearly regular tetrahedron. Slight modifications were made by trial and error to improve structure-factor agreement and obtain normal bond lengths, but the changes were too small to produce a change of sign for any of the observed reflections. A comparison of observed and calculated structure factors for the final structure is given in Table 1. The reliability factor $R = \Sigma\{|F_o|-|F_c|\}\div\Sigma|F_o|$ is 0·17 for (0kl) reflections and 0·20 for (h0l) reflections, absent reflections being included when the calculated intensity exceeded the minimum observable level.

Table 2. *Atomic coordinates*

	x	y	z
$\mathrm{Ca_I}$	0·260	0·338	0·429
$\mathrm{Ca_{II}}$	0·284	−0·002	−0·299
Si	0·260	−0·224	0·421
$\mathrm{O_I}$	0·320	0·002	0·434
$\mathrm{O_{II}}$	0·033	−0·253	0·308
$\mathrm{O_{III}}$	0·483	−0·360	0·366
$\mathrm{O_{IV}}$	0·178	−0·325	−0·421

A Fourier projection for the (hk0) reflections was now attempted but no additional information was obtained. R for the (hk0) reflections observed (Cu $K\alpha$ radiation only) was 0·30. The higher value of R in this direction is probably due to many of the structure factors depending almost entirely on oxygen atoms, the positions of which are slightly uncertain, though believed to be essentially correct.

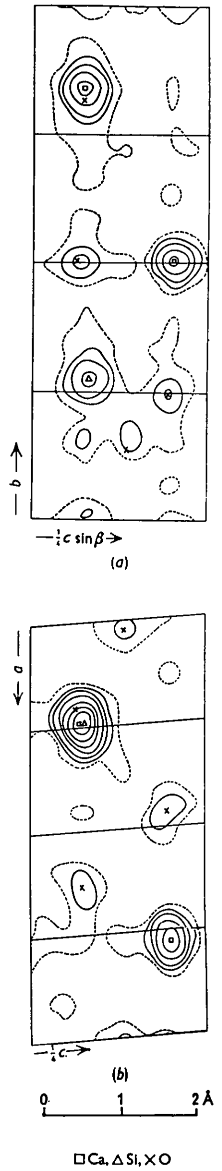

Fig. 1. Electron density projection along (*a*) *a* axis, (*b*) *b* axis. Contours are plotted at 50, 100, 200, 300, 400, 500 arbitrary units. Zero contour is broken.

The overall *R* value for the three projections is 0·19. The final atomic coordinates are given in Table 2.

Discussion of structure

The structure is built up of isolated $\mathrm{SiO_4}$ tetrahedra and Ca ions. Four of the eight Ca ions ($\mathrm{Ca_{I}}$) are positioned alternately above and below $\mathrm{SiO_4}$ tetrahedra in the *y* direction so that the structure may be regarded as strings of alternating Ca ions and tetrahedra, the strings being linked by the remaining four Ca ions ($\mathrm{Ca_{II}}$) which are accommodated in the holes left between the tetrahedra. The pseudo trigonal arrangement of tetrahedra about these latter calcium ions is illustrated in Fig. 2. The coordination of the $\mathrm{Ca_{II}}$ type of calcium is irregular but there are eight nearest neighbours contributed by the surrounding six tetrahedra at distances ranging between 2·36 and 2·80 Å. Each oxygen therefore contributes 2/8.

The first type of calcium ion, $\mathrm{Ca_{I}}$, has a tetrahedron immediately above and below in the *y* direction, and is surrounded by three more tetrahedra approximately on the same level, again in a pseudo trigonal arrangement. Even allowing for the uncertainty as to the exact position of the oxygens the lattice must be considered to be compressed slightly in the *y* direction and some of the Ca–O and O–O distances are rather short.

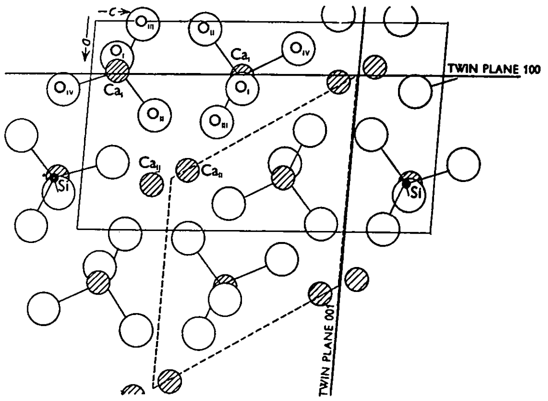

Fig. 2. Diagrammatic projection along *b* axis. Twin planes are shown by heavy lines. The pseudo hexagonal cell is shown by broken lines.

The coordination of $\mathrm{Ca_{I}}$ is again irregular with six nearest neighbours at distances 2·30–2·75 Å, and another six which are not shielded by the first six and probably also contribute to the coordination, at distances 2·98–3·56 Å. If the coordination is taken as nine such that six near neighbours each contribute 2/9 and the six next each contribute 1/9, Pauling's rule is approximately obeyed. The assumption of a ratio of 2:1 for the two 'shells' seems reasonable on the basis of an inverse square relationship between force and distance.

The surroundings of $\mathrm{O_{I}}$ and $\mathrm{O_{II}}$ are; two $\mathrm{Ca_{II}}$, each contributing $\frac{1}{4}$, one close $\mathrm{Ca_{I}}$ giving 2/9, and two more remote $\mathrm{Ca_{I}}$ giving 1/9 each. The total is thus 0·94. $\mathrm{O_{III}}$ and $\mathrm{O_{IV}}$ have as nearest neighbours two $\mathrm{Ca_{II}}$ ($\frac{1}{4}$ each), next nearest two $\mathrm{Ca_{I}}$ (2/9 each) and, more remote, one $\mathrm{Ca_{I}}$ (1/9). The total is 1·06. After satisfying the valency requirements of silicon each oxygen has one free valency and Pauling's electrostatic valency rule is thus obeyed.

A table of bond lengths in the final structure is given in Table 3. Since the oxygen positions could not be

Table 3. *Interatomic distances*

Atom	No. of neighbours	Neighbour	Distance (Å)
$\mathrm{Ca_{I}}$	6 nearest	$\mathrm{O_{I}}$	2·30
		$\mathrm{O_{III}}$	2·37
		$\mathrm{O_{IV}}$	2·40
		$\mathrm{O_{III}}$	2·48
		$\mathrm{O_{II}}$	2·54
		$\mathrm{O_{IV}}$	2·75
	6 next nearest	$\mathrm{O_{II}}$	2·98
		$\mathrm{O_{IV}}$	3·08
		$\mathrm{O_{II}}$	3·22
		$\mathrm{O_{III}}$	3·30
		$\mathrm{O_{I}}$	3·48
		$\mathrm{O_{I}}$	3·56
$\mathrm{Ca_{II}}$	8	$\mathrm{O_{II}}$	2·36
		$\mathrm{O_{IV}}$	2·40
		$\mathrm{O_{II}}$	2·43
		$\mathrm{O_{IV}}$	2·48
		$\mathrm{O_{I}}$	2·48
		$\mathrm{O_{III}}$	2·49
		$\mathrm{O_{I}}$	2·50
		$\mathrm{O_{III}}$	2·80
Si	4	$\mathrm{O_{I}}$	1·57
		$\mathrm{O_{II}}$	1·60
		$\mathrm{O_{III}}$	1·60
		$\mathrm{O_{IV}}$	1·64
$\mathrm{O_{I}}$		$\mathrm{O_{II}}$	2·59
		$\mathrm{O_{III}}$	2·64
		$\mathrm{O_{IV}}$	2·64
		$\mathrm{O_{I}}$ next cell	2·32
$\mathrm{O_{II}}$		$\mathrm{O_{III}}$	2·64
		$\mathrm{O_{IV}}$	2·64
$\mathrm{O_{III}}$		$\mathrm{O_{IV}}$	2·65

fixed exactly from the experimental data, no particular significance can be attached to these values.

Relation to orthorhombic and trigonal symmetry

It will be seen in Fig. 2 that the Si, $\mathrm{Ca_{I}}$ and $\mathrm{Ca_{II}}$ positions lie very near the $x = \frac{1}{4}$ planes. These atoms need only a small shift of the order of 0·05 Å, accompanied by a small rotation of the tetrahedra, the β angle being reduced from 94°33′ to 90°, to produce orthorhombic symmetry and the space group *Pmcn* of β potassium sulphate. This close approach to orthogonal symmetry explains the ease with which the polysynthetic or inversion twinning, always associated with the mineral, occurs. The crystal can twin about the pseudo glide plane, or the pseudo mirror plane, twin planes (001) and (100) respectively, as shown in Fig. 2.

A rather larger distortion is required to produce trigonal symmetry. Movements of the order of 0·5 Å are needed to bring the $\mathrm{Ca_{II}}$ ions to the $(\frac{1}{4}, 0, -\frac{1}{4})$ positions and to bring $\mathrm{Ca_{I}}$ and Si to the $(\frac{1}{4}, y, 0{\cdot}417)$ positions necessary for trigonal symmetry. A larger rotation of half of the tetrahedra is also required, of the order of 75°. The structure would be of the glaserite type, with space group $C\bar{3}m$.

It seems likely that these small adjustments of the lattice actually take place in the phase changes β to α' and α' to α. The energy change in the latter inversion is known to be larger than in the former.

Although the coordination of the Ca ions is irregular, there are no open spaces as in Ca_3SiO_5 (Jeffrey, 1950) which would allow ready attack by hydroxyl ions. This would account for the fact that although both compounds have valuable cementing properties Ca_3SiO_5 is very rapidly hydrated, and Ca_2SiO_4 only slowly. These aspects will be discussed further elsewhere.

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