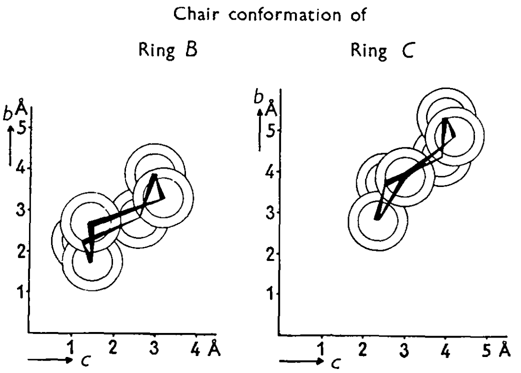

Fig. 8. Chairconfiguration of ring B and C.

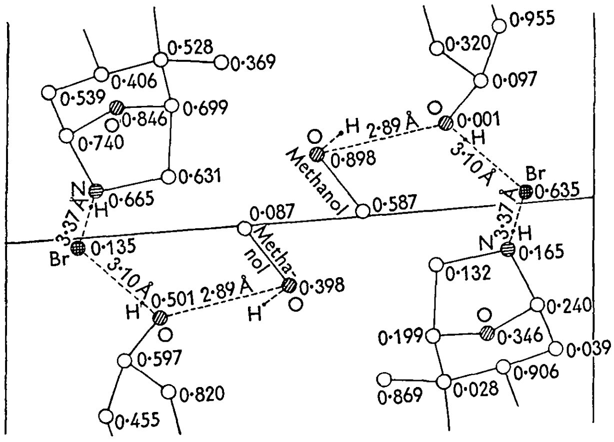

Fig. 9. Connection of the molecules to each other in the structure of samandarine.

shown in Fig. 9. There is a hydrogen bridge of 3·37 Å between the nitrogen of the oxazolidine ring and Br^- and another hydrogen bridge of 3·10 Å between Br^- and the oxygen atom of the ring D of the neighbouring molecule. This shows that the molecules are linked together via hydrogen bridges. The linkage of the methanol to the OH-group is schematically shown in Fig. 9, the O–O distance being 2·89 Å.

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References

Schöpf, C., Blödorn, H.-K., Klein, D. & Seitz, G. (1950). *Chem. Ber.* **83**, 372.

Schöpf, C. & Braun, W. (1934). *Liebigs. Ann. Chem.* **514**, 69.

Schöpf, C. & Klein, D. (1954). *Chem. Ber.* **II**, 1638.

Wölfel, E., Schöpf, C., Weitz, G. & Habermehl, G. (1961). *Chem. Ber.* **94**, 2361.

Acta Cryst. (1962). **15**, 491

A Reinvestigation of the Crystal Structure of Thortveitite $Sc_2Si_2O_7$

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With 252 $F_o(hkl)$, least-squares solutions for the structure of $Sc_2Si_2O_7$ have been found in each of the space groups Cm, $C2$ and $C2/m$. After discussion, the correct space group is concluded to be $C2/m$ and the Si–O–Si angle is therefore 180° [in agreement with Zachariasen (1930)]. The Si–O distances are all close to 1·62 Å; the Sc–O distances average 2·13 Å.

1. Introduction

Following some preliminary work by Gossner & Mussgnug (1929), the crystal structure of thortveitite, $Sc_2Si_2O_7$, was investigated by Zachariasen (1930), who derived a structure in the space group $C2/m$ with a linear Si–O–Si link in the Si_2O_7 pyrosilicate group. Barclay, Cox & Lynton (1956) called attention to the wide range from 131° to 180° in the reported Si–O–Si angles for the pyrosilicate groups in various minerals and suggested that reinvestigations were needed, particularly of those structures in which 180° angles had

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been suggested. Hemimorphite, $Zn_4(OH)_2Si_2O_7.H_2O$, was one of these and in new work Barclay & Cox (1960), with data for the *hk*0 and 0*kl* projections, found the Si–O–Si angle to be 133°, in contrast to the 180° reported by Ito & West (1932). A reinvestigation of thortveitite was therefore imperative and this is described in the present paper.

The problem has proved much more subtle than we expected. We have found formal solutions, that is to say minima for the least-squares function, in each of the three space groups *Cm*, *C*2 and *C*2/*m* allowed by the diffraction symmetry. In *C*2/*m* the Si–O–Si angle is necessarily 180°; in each of the other space groups this link is slightly bent to 166° and the whole structure deviates only slightly from the *C*2/*m* form. It is not easy to lay down principles which will distinguish whether such deviations are spurious or not; a lower least-squares minimum can always be found in a low-symmetry space group than in a more symmetrical one on account of the extra variables allowed. A genuine very small deviation from high symmetry, which did not change the diffraction symmetry, would be very difficult to detect. On the balance of the evidence, we consider that the space group in thortveitite is almost certainly *C*2/*m* and that the Si–O–Si link is linear.

The matter could probably have been settled quite definitely if very high-precision data had been available. The data, which we actually collected, were sufficiently extensive (252 *F*(*hkl*) for a small face-centred cell) and sufficiently accurate (final discrepancy factors for each space group of about 13%) to have solved all the problems expected at the start of the work; it was not quite accurate enough to have absolutely settled the problem finally encountered. Unfortunately as the two authors (G. A. B. and H. L.) concerned with the experimental work had left Leeds by the time the third author (D. W. J. C.) had found putative structures in all three space groups, it was impracticable to collect new and more accurate data.

2. Experimental

The present experimental work was done with specimens of thortveitite, from the British Museum (BM, 1914, 1379), which came from Iveland, Saetersdalen, Nedenäs, Norway. Zachariasen (1930), whose work was done with a specimen from the same region, reported chemical analyses by an earlier worker, J. Sterba, as showing: SiO_2 45·45%, Sc_2O_3 42·06%, Y_2O_3 8·89%, Fe_2O_3 2·83%, BeO 0·51%, *ign*. 0·59%. Thus there is evidently appreciable replacement of Sc by Y and Fe.

The cell dimensions quoted by Gossner & Mussgnug

Table 1. *Structure factors* (×10) *for thortveitite*

The columns show *h*, *k*, *l*, $|F_o|$ and F_c. The $|F_o|$ include the scale factor determined in the LS refinement. The F_c have been calculated for the space group *C*2/*m* with the parameters shown in Tables 2 and 3. Note that the true $|F_o|$ probably differ from those shown here by a factor of the order of $\exp\{-0{\cdot}030{\cdot}8\pi^2(\sin\theta/\lambda)^2\}$

2	0	0	91	-69
4	0	0	949	1133
6	0	0	283	163
3	0	0	1009	1008
1	1	0	257	228
3	1	0	348	273
5	1	0	419	-347
7	1	0	566	578
0	2	0	96	162
2	2	0	535	-524
4	2	0	439	-330
6	2	0	616	-547
8	2	0	358	-353
1	3	0	510	-526
3	3	0	717	-629
5	3	0	999	-840
7	3	0	424	-386
0	4	0	479	498
2	4	0	136	110
4	4	0	141	106
1	5	0	685	576
3	5	0	787	580
5	5	0	202	91
7	5	0	939	921
0	6	0	1014	1213
2	6	0	207	-158
4	6	0	802	716
1	7	0	394	-327
3	7	0	222	-230
5	7	0	924	-852
0	8	0	115	11
2	8	0	858	-750
4	8	0	474	-414
0	10	0	939	880
2	10	0	540	522
0	0	1	368	232
2	0	1	409	363
4	0	1	550	522
6	0	1	550	458
-2	0	1	767	1152
-4	0	1	267	165
-6	0	1	792	822
-8	0	1	106	137
1	1	1	631	714
3	1	1	368	-348
5	1	1	858	777
-1	1	1	96	32
-3	1	1	581	757
-5	1	1	293	205
0	2	1	752	-1068
2	2	1	479	-477
4	2	1	787	-703
6	2	1	424	-317
-2	2	1	56	10
-4	2	1	828	-779
-6	2	1	358	-354
-8	2	1	772	-833
1	3	1	717	-761
3	3	1	722	-614
5	3	1	323	-204
7	3	1	636	-630
-1	3	1	151	-55
-3	3	1	666	-582
-5	3	1	207	-94
-7	3	1	908	-958
0	4	1	429	-432
2	4	1	177	127
4	4	1	283	-247
6	4	1	298	241
-2	4	1	505	519
-4	4	1	273	-244
-6	4	1	262	188
1	5	1	793	795
3	5	1	252	121
5	5	1	1161	1043
-1	5	1	702	531
-3	5	1	949	852
-5	5	1	747	629
-7	5	1	409	409
2	6	1	323	199
4	6	1	343	239
6	6	1	257	292
-2	6	1	717	719
-6	6	1	546	563
3	7	1	994	-822
5	7	1	288	202
-1	7	1	621	-497
-5	7	1	464	-368
0	8	1	868	-885
2	8	1	591	-561
4	8	1	974	-759
-2	8	1	177	-134
-4	8	1	1055	-866
3	9	1	328	-268
2	10	1	414	584
-2	10	1	833	938
0	0	2	414	278
2	0	2	782	912
4	0	2	485	474
6	0	2	853	932
-2	0	2	712	728
-4	0	2	702	749
-6	0	2	631	572
-8	0	2	661	785
1	1	2	278	-212
3	1	2	520	490
7	1	2	283	297
-1	1	2	222	140
-5	1	2	434	352
-7	1	2	212	152
0	2	2	358	-257
2	2	2	520	-462
4	2	2	313	-233
6	2	2	227	-232
-2	2	2	838	-839
-4	2	2	182	192
-6	2	2	686	-690
1	3	2	1085	-1177
3	3	2	101	99
5	3	2	924	-921
-1	3	2	505	-360
-3	3	2	802	-806
-5	3	2	399	-323
-7	3	2	474	-493
0	4	2	419	317
4	4	2	318	262
6	4	2	267	255
-2	4	2	439	-392
-4	4	2	707	709
-6	4	2	313	-268
1	5	2	212	84
3	5	2	919	877
5	5	2	399	344
-1	5	2	747	563
-3	5	2	399	287
-5	5	2	747	678
-7	5	2	570	573
0	6	2	202	138
2	6	2	535	513
4	6	2	252	291
-2	6	2	283	276
-4	6	2	525	539
-6	6	2	298	343
1	7	2	591	-634
5	7	2	474	-445
-1	7	2	273	-305
-3	7	2	424	-501
-5	7	2	151	-150
0	8	2	449	-483
2	8	2	550	-516
4	8	2	485	-465
-2	8	2	737	-773
-4	8	2	116	-131
1	9	2	591	-556
3	9	2	439	400
3	9	2	313	-301
0	10	2	656	589
0	0	3	575	401
2	0	3	616	545
4	0	3	485	514
6	0	3	288	345
-2	0	3	651	554
-4	0	3	187	112
-6	0	3	712	776
-8	0	3	313	339
1	1	3	707	583
3	1	3	177	91
5	1	3	328	287
-1	1	3	111	36
-3	1	3	373	277
-5	1	3	121	86
-7	1	3	434	378
0	2	3	399	-257
2	2	3	545	-516
4	2	3	197	-142
6	2	3	702	-946
-2	2	3	550	-545
-4	2	3	555	-568
-6	2	3	197	-171
1	3	3	313	216
3	3	3	792	-725
5	3	3	308	-295
-1	3	3	1004	-970
-3	3	3	105	8
-5	3	3	863	-874
-7	3	3	101	-21
0	4	3	333	240
2	4	3	187	-121
4	4	3	429	363
-2	4	3	111	-112
-4	4	3	247	-199
-6	4	3	343	282
1	5	3	848	916
3	5	3	520	393
5	5	3	521	666
-1	5	3	434	248
-3	5	3	702	651
-5	5	3	444	343
0	0	4	626	533
2	0	4	641	615
4	0	4	207	202
-2	0	4	626	535
-4	0	4	551	638
-6	0	4	207	206
1	1	4	202	-138
3	1	4	283	251
-1	1	4	702	590
-3	1	4	278	-213
-5	1	4	414	385
-7	1	4	252	-179
0	2	4	530	-469
2	2	4	111	-95
4	2	4	792	-778
-2	2	4	116	-52
-4	2	4	414	-432
-6	2	4	444	-437
1	3	4	550	-453
3	3	4	676	-636
-1	3	4	338	-234
-3	3	4	631	-599
-5	3	4	409	-350
0	4	4	146	-89
2	4	4	424	328
4	4	4	323	-319
-2	4	4	434	387
-4	4	4	105	-68
1	5	4	348	256
3	5	4	585	513
-1	5	4	878	813
-3	5	4	207	161
-5	5	4	757	669
0	0	5	696	755
2	0	5	116	-40
-2	0	5	106	102
-4	0	5	651	766
-6	0	5	298	301
1	1	5	187	149
-3	1	5	575	512
0	2	5	247	-247
2	2	5	565	-648
-2	2	5	459	-470
-4	2	5	182	-194
1	3	5	479	-510
-1	3	5	404	-428
-3	3	5	227	-221
-5	3	5	454	-458
0	4	5	106	93
-4	4	5	278	174
1	5	5	424	446
-1	5	5	288	328
-3	5	5	732	775
-2	0	5	505	658

(1929) were 6·56, 8·58, 4·74 Å and $\beta=103° 8'$. New measurements, kindly made by D. Holey and Dr Mary R. Truter, with the Straumanis method give

$$a=6·542,\ b=8·519,\ c=4·669\ \text{Å}\ (\text{all}\ \pm 0·005\ \text{Å});\\ \beta=102° 33'\pm 10'.$$

The intensities were determined visually from multiple-film Weissenberg photographs of the zero, first and second layers about the c axis and of the zero to fifth layers about the b axis. Absorption corrections, particularly necessary for the b axis data since the crystals had (001) as the needle axis, were applied only in a simple empirical fashion sufficient to give the b and c axis data similar apparent absorption effects. This matching of the two sets of data was done in the following way. Plots were made of $\log (I_b/I_c)/\sin^2\theta$ for the reflections of the types ($h00$), ($h10$), ..., ($h50$) which were common to the intensities I_c obtained from the zero layer of the c axis and the corresponding intensities I_b obtained from the six b axis layers. These showed that the b-axis intensities were decreasing much more slowly with $\sin\theta$ than the c-axis intensities. The correlation factor was $\exp\{4·74 (\sin\theta/\lambda)^2\}$, which for computational convenience was applied to the zero-layer c axis intensities rather than to the b axis intensities. A similar comparison of the intensities of the c-axis first layer with the b-axis intensities yielded a factor

$$\exp\{7·20 (\sin\theta/\lambda)^2\},$$

which was applied to the c-axis intensities. A comparison of the c-axis second layer with the b-axis intensities suggested that no exponential factor was necessary. After these adjustments, the layers were scaled together in the usual way and the 252 structure factors $|F_o(hkl)|$, listed in Table 1, were obtained. A trivial consequence of the application of the exponential factors with positive arguments to the c-axis data rather than with negative arguments to the b-axis data is that the $|F_o(hkl)|$ have artificially been given negative temperature factors. The true $|F(hkl)|$ probably differ by a factor of the order of $\exp\{-\frac{1}{2}(4·74)(\sin\theta/\lambda)^2\}$, which corresponds to an apparent atomic mean square vibration amplitude of $U=0·030$ Å^2. The U_{ij} listed later in Table 3 differ from the U_{ij} appropriate to the $|F_o(hkl)|$ of Table 1 by this amount.

3. Structure analysis

As a first step in the attempt to discover whether the space group could be Cm or $C2$ in place of the $C2/m$ taken by Zachariasen, the intensity statistics for the 35($hk0$) and 38($h0l$) reflections were examined. These suggested that both projections were acentric and hence that the space group was probably Cm (Barclay, Cox & Lynton, 1956). After unsuccessful attempts at finding a structure of this symmetry from the Patterson syntheses for these two projections, a three-dimensional Patterson synthesis was calculated with the 252$|F_o(hkl)|$. This was interpreted by G. A. B. and H. L. in terms of a Cm structure, though as mentioned by Barclay & Cox (1960) its symmetry was nearly $C2/m$. This Cm structure was then refined by successive observed and calculated Fourier syntheses for the (001) and (010) projections to discrepancy factors of 9·4% and 18%.

When several years later the problem was taken up by D. W. J. C., this improved Cm structure was used as the starting point for a series of least-squares refinements with the 252$|F_o(hkl)|$. These calculations were carried out on the Leeds University Ferranti Pegasus computer with the structure-factor least-squares (SFLS) program described by Cruickshank *et al.* (1961). The Sc^{3+} f values were derived by interpolation from the values for K^+, Ca and Cr^{2+} given by Berghuis *et al.* (1955). The Si f values were those given by Tomiie & Stam (1958), though it was assumed that their value of 9·20 at $\sin\theta/\lambda=0·125$ a.u. was a misprint for 9·00, and the O f values were those of Berghuis *et al.* The SFLS program was designed to minimize the function

$$R_1=\Sigma w_1\Delta^2/\Sigma w_1|F_o|^2.$$

The weights were taken as

$$w_1=1/(10+|F_o|+|F_o|^2/50),$$

where the $|F_o|$ values were without the scale factor 1·04 eventually determined by the LS process. These weights gave nearly constant average values of $w\Delta^2$ in groups of increasing $|F_o|$.

The structure factors calculated from the projection coordinates gave an initial discrepancy factor of 20·0% for the 252$|F(hkl)|$.

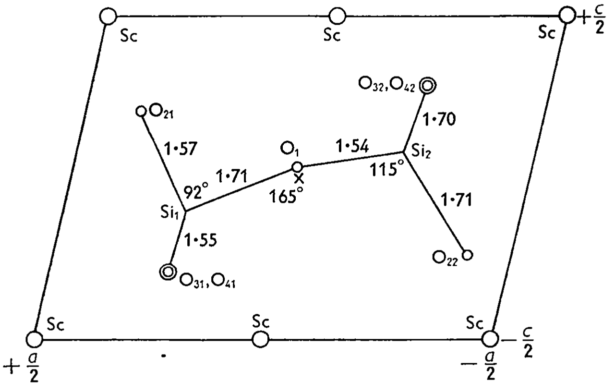

Fig. 1. Projection on b-face of result of Cm refinement by minimization of R_1. The cross marks the centre of the cell defined by the scandium atoms.

After four cycles of LS refinement, the last two with anisotropic vibrations, the discrepancy reduced apparently satisfactorily to 13·0%. However calculation of the dimensions and configuration of the pyrosilicate ion revealed the unsatisfactory results shown in Fig. 1. The striking feature is that the sets of chemically equivalent bond lengths show unreasonable discrepancies: the pair Si_1–O_1, Si_2–O_1 are 1·71, 1·54 Å; Si_1–O_{21}, Si_2–O_{22} are 1·57, 1·71 Å; Si_1–O_{31}, Si_2–O_{32} are 1·55, 1·70 Å; and there are similar inconsistencies among the angles, O_{21}–Si_1–O_1 being 92° but O_{22}–Si_2–O_1 115°. These discrepancies are much greater than the nominal e.s.d.'s, which are about 0·03–0·04 Å for a Si–O bond length. As can be seen from Fig. 1, in which the Si_1–O_1–Si_2 angle is 165°, the putative structure very nearly possesses a two-fold axis of symmetry passing through a point near O_1. Most plausibly the discordant dimensions are due to the neglect of this symmety element in the refinement and the space group is properly *C*2/*m*.

An initial set of coordinates for *C*2/*m* refinement was easily derived by appropriate averaging of pairs of coordinates of the *Cm* structure; O_1 was moved to (0, 0, 0). Three cycles of LS refinement sufficed, as these initial coordinates were all within 0·01 Å of the final values. The final discrepancy factor was 13·8%. This is to be expected to be slightly greater than the 13·0% for the less symmetrical *Cm* structure, since the latter has more parameters. The only chemically equivalent bond lengths in the *C*2/*m* structure are Si_1–O_{21} and Si_1–O_{31} which had values 1·62 and 1·63 Å. The Si_1–O_1 length was 1·62 Å, and the Si–O_1–Si angle necessarily 180°. These results for the pyrosilicate group were very similar to the corresponding dimensions in the Si_5O_{16} group in zunyite (Kamb, 1960). The evidence therefore suggested that the *C*2/*m* structure was a very reasonable one.

We were however strongly pressed by Dr F. Liebau of Germany (private communication), on account of his experiences with layer silicates (Liebau, 1961*a*, *b*, *c*), to examine the possibility of keeping the two-fold axis but removing the mirror plane of symmetry, so making the space group *C*2. Two initial structures for refinement in this space group were tried; in each the central O_1 was shifted 0·3 Å above the former mirror plane and the two independent Sc were displaced by 0·05 Å from their *C*2/*m* positions, but in different senses in the two trial structures. As expected the LS refinement then led to movements of all other atoms from their former positions. Of the two trial combinations of the Sc and O_1 displacements, one proved a little better than the other and this better structure was refined to convergence with a final discrepancy factor of 12·2%. The effect of the refinement was to reduce the displacement of O_1 from the trial 0·3 Å to 0·19 Å, to leave the Sc positions within 0·01 Å of those postulated and to change the coordinates of the other atoms by less than 0·04 Å. The Si–O_1–Si angle was 166°.

The problem of deciding whether this *C*2 solution was spurious was rather more difficult than for the *Cm* solution. First, the differences within the trio of chemically equivalent bond lengths did not exceed 0·05 Å and so might reasonably be attributed to experimental error. Second, the discrepancy factor of 12·2% was lower than the 13·0% of *Cm*, though not so decisively lower than the 13·8% of *C*2/*m* as to settle the matter. A more thorough examination of the space-group problem was therefore needed.

4. Space group

Although the anisotropic vibration amplitudes determined in the various LS refinements have little absolute significance due to the lack of proper absorption corrections, it might nevertheless be hoped that they, as well as the coordinates, would offer some hints as to the correct space group. However the results on the vibrations in the different space groups, which had been obtained at this stage of the analysis, were not properly comparable because of the uncertainties in the phase angles of the $|F_o|$. As is well-known (Cochran, 1948; Cruickshank, 1952) LS refinement with the function

$$R_1 = \Sigma w_1(|F_o| - |F_c|)^2 / \Sigma w_1 |F_o|^2$$

is closely related to the determination of a structure from the Fourier series for the electron density. If the phase angles are wrong, as they must be for two of the three space groups, the electron-density peak shapes will be distorted and misleading vibration amplitudes will be obtained. This difficulty can be avoided by minimizing the function

$$R_2 = \Sigma w_2(|F_o|^2 - |F_c|^2)^2 / \Sigma w_2 |F_o|^4,$$

which is related to the determination of a structure directly from the Patterson synthesis, so that phase-angle uncertainties are irrelevant.

Table 2. *Coordinates for the three possible space groups*

	x (Å)	*y* (Å)	*z* (Å)
Space group *Cm*			
Sc_1	0	2·621	2·3345 (= $\frac{1}{2}c$)
Si_1	1·511	0	−0·464
Si_2	−1·391	0	0·382
O_1	0·090	0	0·170
O_{21}	2·471	0	0·982
O_{22}	−2·645	0	−1·100
O_{31}	1·582	1·297	−1·350
O_{32}	−1·510	1·376	1·325
Space group *C*2/*m*			
Sc_1	0	2·621	2·3345 (= $\frac{1}{2}c$)
Si_1	1·461	0	−0·421
O_1	0	0	0
O_{21}	2·556	0	1·034
O_{31}	1·535	1·336	−1·337
Space group *C*2			
Sc_1	0	2·620	2·3345 (= $\frac{1}{2}c$)
Sc_2	0	−2·620	2·3345
Si_1	1·461	−0·077	−0·428
O_1	0	0·124	0
O_{21}	2·560	−0·009	1·041
O_{31}	1·508	1·262	−1·301
O_{41}	1·573	−1·435	−1·366

Table 3. *Components in Å² of the vibration tensors in the three possible space groups*

To obtain the F_c for $C2/m$ given in Table 1, an isotropic contribution of 0·030 Å² should be subtracted

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Space group Cm						
Sc_1	0·006	0·005	0·019	−0·006	−0·005	0·000
Si_1	0·003	0·026	0·029	0	0	0·003
Si_2	0·019	0·019	0·023	0	0	0·007
O_1	0·013	0·020	0·026	0	0	−0·008
O_{21}	0·034	0·002	0·022	0	0	−0·013
O_{22}	0·012	−0·001	0·020	0	0	−0·001
O_{31}	0·033	0·033	0·023	0·003	0·017	0·004
O_{32}	0·016	0·014	0·036	−0·007	0·013	0·002
Space group $C2/m$						
Sc_1	0·004	0·006	0·017	0	0	0·001
Si_1	0·013	0·020	0·027	0	0	0·003
O_1	0·018	0·019	0·059	0	0	0·015
O_{21}	0·022	0·000	0·026	0	0	0·000
O_{31}	0·020	0·022	0·030	0·002	0·002	0·005
Space group $C2$						
Sc_1	0·006	0·011	0·016	0	0	0·005
Sc_2	0·003	0·002	0·020	0	0	−0·002
Si_1	0·012	0·021	0·030	−0·005	0·016	0·002
O_1	0·015	0·032	0·054	0	0	0·013
O_{21}	0·025	0·002	0·029	−0·014	−0·005	0·002
O_{31}	0·016	0·026	0·025	−0·008	0·013	0·002
O_{41}	0·018	0·020	0·038	−0·013	0·010	0·010

The refinements in each of the three space groups were therefore continued by LS calculations on the function R_2, with $w_2 = w_1/4|F_o|^2$. The parameter changes from those obtained with R_1 were in fact quite small and three cycles in each space group sufficed for satisfactory convergence. The results for the coordinate and anisotropic vibration parameters are given in Tables 2 and 3. The latter parameters have been listed after adding the crude absorption correction equivalent to $U = 0{\cdot}030$ Å² mentioned at the end of § 2. The $|F_o|$ scale factors changed from about 1·04 in the R_1 refinements to about 1·115 for all three space groups with R_2.

The final values of R_2 were 0·0325 in $C2/m$, 0·0283 in Cm and 0·0279 in $C2$. If the extra parameters introduced in the lower symmetry refinements are spurious, it would be plausible to expect their values of R_2 to be lower than the $C2/m$ value by a factor of n_c/n_s, where n_s is the difference between the numbers of observations and parameters in $C2/m$ and n_c is this difference in Cm or $C2$. On this basis the expected values of R_2 are

$$Cm\colon\ 0{\cdot}0325(252-58)/(252-33) = 0{\cdot}0288;$$
$$C2\colon\ 0{\cdot}0325(252-54)/(252-33) = 0{\cdot}0294.$$

These are sufficiently close to the actual values of 0·0283 and 0·0279 for it to seem very unlikely that either of the lower-symmetry space groups has yielded any significant reduction of R_2.

The coordinates listed in Table 2 may now be examined in some detail. In Cm the arbitrary origin of the x and z coordinates has been chosen to put Sc at $(0, y, \frac{1}{2})$; in $C2$ the arbitrary origin of the y coordinates has been chosen to put the two distinct Sc at $(0, y, \frac{1}{2})$ and $(0, -y, \frac{1}{2})$. [This origin differs by about 0·05 Å from that implicit in the description of the $C2$ refinement in § 3]. We notice first that when an atom in $C2/m$ gives rise to two distinct atoms in Cm or $C2$, the mean coordinates of the two atoms in Cm or $C2$ are very close to the single value in $C2/m$. Thus in Cm, the mean y coordinate of O_{31} and O_{32}, $\frac{1}{2}(1{\cdot}297 + 1{\cdot}376) = 1{\cdot}336$ Å, is the same as the y coordinate of O_{31} in $C2/m$, while the mean numerical values of the x and z coordinates of these atoms, 1·546 and 1·338 Å, are close to the corresponding coordinates, 1·535 and 1·337 Å, in $C2/m$. Similarly in $C2$, the equal y coordinates of the two Sc, 2·620 Å, are practically the same as the single value, 2·621 Å, in $C2/m$. The splittings of pairs of coordinates in Cm or $C2$ are of similar magnitude; thus the largest splitting in Cm is the 0·174 Å difference in the x coordinates of O_{21} and O_{22}, and the largest in $C2$ is the 0·173 Å difference in the y coordinates of O_{31} and O_{41}. For atoms which do not multiply in the lower space groups, the situation is a little different. Thus Si_1, which has coordinates of the type $(x, 0, z)$ in $C2/m$ and (x, y, z) in $C2$, has virtually the same x and z coordinates in the two space groups, but in the latter the y coordinate becomes $-0{\cdot}077$ Å. Similarly for O_{21}, except that its $C2$ y coordinate is puite small, $-0{\cdot}009$ Å. For the vital O_1 the changes in coordinates between the different space groups are about as large as the largest pair splittings. Thus its Cm x and z coordinates differ by 0·090 and 0·170 Å from the $C2/m$ special position, while the $C2$ y coordinate differs by 0·124 Å. In $C2$ it is the difference of the Si_1 and O_1 y coordinates which determines the Si–O–Si angle;

this difference is 0·201 Å. Since the space groups *Cm* and *C*2 cannot both be correct, the general similarities of their coordinate displacements and pair splittings seem further indications that neither is correct.

Table 4. *Pyrosilicate ion dimensions obtained by minimization of the function* R_2

	Cm	*C*2/*m*	*C*2
Si–O_2	1·55, 1·72 Å	1·62 Å	1·63 Å
Si–O_3	1·58, 1·69	1·63	1·60, 1·67
Si–O_1	1·54, 1·68	1·61	1·62
O_1–Si–O_2	93, 115°	104°	103°
O_1–Si–O_3	105, 111	108	100, 115
O_2–Si–O_3	111, 115	114	111, 115
O_3–Si–O_4	109, 110	110	111
Si–O_1–Si	166	180	166

A related approach to the problem is to consider the plausibility of the pyrosilicate ion dimensions given in Table 4. As at the earlier stage of the analysis, *Cm* is clearly to be rejected on the grounds of the considerable variation of the chemically equivalent bond lengths. The three pairs of equivalent bonds show internal differences of 0·17, 0·11 and 0·14 Å as compared with LS estimates for the e.s.d.'s of individual bonds of 0·03–0·04 Å. Similarly the pairs of equivalent angles show internal differences of 22, 4, 6 and 1°. There are fewer distinct bond lengths and angles in *C*2. The one pair of equivalent bonds shows an internal difference of 0·07 Å and the two pairs of angles show differences of 4 and 15°. The latter difference makes *C*2 unlikely to be the correct space group, since it is implausible for the angles O_1–Si_1–O_{31} and O_1–Si_1–O_{41} to differ from the tetrahedral value of $109\frac{1}{2}$° in opposite senses.

We now consider whether the nominal anisotropic vibration amplitudes listed in Table 3 offer any guidance on the space group problem. In all three space groups, the apparent average vibrations of Si and the O_2 and O_3 type of oxygens are of similar magnitudes. The apparent vibrations of Sc are rather smaller (this is partly due to the neglect of the Y and Fe impurities in the 'Sc' *f* curve), and, in the space groups *C*2/*m* and *C*2, the vibrations of O_1 are rather larger. For those atoms which are single in *C*2/*m* but double in *Cm* or *C*2, a splitting of the pairs of U_{ij} values tends to occur. Thus the U_{11} component for Si_1, which is 0·013 Å² in *C*2/*m*, splits to 0·003 and 0·019 Å² in *Cm*; the average however is close to the *C*2/*m* value. The general behaviour of these averages and splittings is rather similar in *Cm* and *C*2. For O_1, the values in *Cm* of U_{11} and especially U_{33} are much less than those in *C*2/*m*. This can be correlated directly with the large displacement of O_1 from (0, 0, 0) in *Cm*. A relation

$$U_{33}(C2/m) \sim U_{33}(Cm) + (\Delta z)^2$$

would be expected to hold approximately, since U_{33} is a measure of the mean square peak breadth in the *z* direction, and indeed the relation

$$0{\cdot}059 \sim 0{\cdot}026 + (0{\cdot}17)^2 = 0{\cdot}055$$

does hold roughly. (The validity of this relation is unaffected by the likely systematic errors in the experimental data, since it is simply a formal consequence of the fact that Patterson peaks can be interpreted either as single peaks or as pairs of slightly displaced peaks but with reduced vibrations.) Similarly the value of U_{22} for O_1 in *C*2 ought to be rather less than that in *C*2/*m* due to the 0·12 Å *y* displacement. In fact it is not. No satisfactory explanation has been found for this, but the fact that the O_1 peak is actually most diffuse in *C*2 is hardly evidence in favour of this space group. Summarizing this discussion of the nominal vibration amplitudes, we conclude that they offer no decisive guidance, though the general similarity of the pair splittings in *Cm* and *C*2 is again an indication that *C*2/*m* is the correct space group. (In *C*2/*m* the excess of the apparent average vibration of O_1 over the vibrations of other atoms may be due to experimental errors, as the LS estimates of the e.s.d.'s of the U_{ij} for O_1 are rather large, ~ 0·015 Å².)

The final method considered for the space-group discrimination was an examination of the worst discrepancies between the $|F_o|$ and the $|F_c|$. Of the 12 worst discrepancies, 10 were insensitive to the choice of space group, the small *F*(080) favoured *C*2 and the small $F(2\bar{2}1)$ tended to favour *Cm* or *C*2. The general insensitiveness of the bad reflections to the choice of space group shows that the test is not a critical one. Some poor fits between the $|F_o|$ and the $|F_c|$ were inevitable with the rough method used to allow for absorption in the correlation of the layer lines.

To summarize the discussion of this section, we conclude that the correct space group of thortveitite is *C*2/*m* on the following grounds:

(*a*) the reductions of the residual R_2 in *Cm* or *C*2 are about those expected for additional spurious parameters;

(*b*) the displacements and pair splittings in the coordinates and vibration parameters in the two lower-symmetry space groups are of similar magnitude;

(*c*) the dimensions of the pyrosilicate group in *Cm* are manifestly absurd and those in *C*2 show large discrepancies in the O–Si–O bond angles;

(*d*) the worst discrepancies between the $|F_o|$ and the $|F_c|$ do not markedly favour anyone space group.

The possibility of a superlattice was discounted by the lack of any extra reflections on oscillation and Weissenberg photographs. There is also the possibility that the crystal consists of some random array of slightly bent Si_2O_7 ions with *C*2/*m* as the space group of the average structure, but we think this to be unlikely.

Perhaps it should be added that the minima of R_2 in *Cm* and *C*2 represented by the parameters of

Tables 2 and 3 are almost certainly not the only spurious minima (indeed two minima were found in $C2$). If much more accurate data are ever obtained for thortveitite, it will be a sure indication that our Cm and $C2$ 'solutions' were spurious if the refinement of the new data converges to 'solutions' even closer to $C2/m$ than ours.

For the remainder of this paper, we shall regard $C2/m$ as the correct space group.

5. Discussion of the structure

After the use of the present cell dimensions, the coordinates given by Zachariasen (1930) are shown in Table 5. Comparison with the present results for the space group $C2/m$ given in Table 2 shows that the maximum discrepancy is 0·12 Å, which is very satisfactory considering the few $|F_o|$ used by Zachariasen. The general features of his description of the crystal structure of $Sc_2Si_2O_7$ are therefore unaltered, though the detailed dimensions are changed slightly. His diagram is reproduced here as Fig. 2. Each Sc lies on a two-fold axis and is octahedrally coordinated to six oxygens at distances Sc–O_2 2·12, Sc–O_3 2·20, Sc–O_3 2·08. The mean Sc–O distance of 2·13 Å is slightly less than the expected sum of the crystal radii, 0·81 + 1·40 = 2·21 Å (Pauling, 1960). The octahedron is somewhat distorted and there are three short shared edges, O_2–O_2 2·68 Å and O_3–O_3 2·59 Å (twice); there is also a pair of short unshared edges, O_2–O_3 2·75 Å. All other edges are greater than 3·00 Å. Apart from O_1 which is bonded to the two silicons of the pyrosilicate group, each oxygen, as well as being bonded to a silicon, is also coordinated to two Sc. Pauling's valence rule is consequently satisfied.

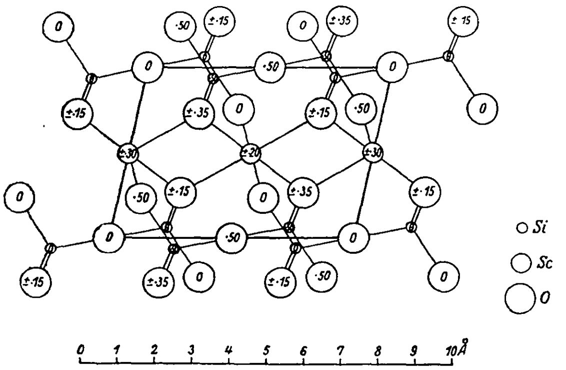

Fig. 2. The structure of thortveitite projected on the b-face. The numbers represent the approximate heights of atoms, expressed in fractions of the b-axis. [Diagram reproduced from Zachariasen (1930).]

Table 5. *Zachariasen's coordinates*

(Space group $C2/m$)

	x (Å)	y (Å)	z (Å)
Sc_1	0	2·56	2·33(= ½c)
Si_1	1·45	0	−0·30
O_1	0	0	0
O_{21}	2·63	0	1·09
O_{31}	1·63	1·28	−1·26

There is one set of inter-anionic distances of less than 3 Å which was not mentioned by Zachariasen. Along the a axis the pyrosilicate ions dovetail into one another in columns. An O_2 at $(1-x, 0, z)$ of the ion centered at (1, 0, 0) fits neatly into the base of the trigonal pyramid of the ion at (0, 0, 0), with distances Si–O_2 2·72, O_2–O_2 2·76 and O_3–O_2 (twice) 2·75 Å. (The latter pair of distances are the short unshared edges of the Sc octahedra referred to earlier.) Equally O_2 of the ion at (0, 0, 0) fits into the other base of the ion at (1, 0, 0). These contacts are relatively short and are presumably due to the Coulomb attraction between the negatively charged O_2 and the positively charged Si, which is evidently sufficiently great to balance the repulsions between oxygen atoms of different ions. However a simple assignment of formal charges does not seem to give a satisfactory balance. According to Pauling's (1960) relation between ionic character and electronegativity difference, a Si–O σ-bond has approximately 50% ionic character. If there are no π-bonds to consider the net charges in the $Si_2O_7^{6-}$ ion will be +2·0 on Si, −1·5 on O_2 and O_3, and −1·0 on the central O_1. In the contacts between adjacent bases of two pyramidal ions, there are two Si–O attractions and five O–O repulsions. A simple calculation then shows that an oxygen: silicon charge ratio of 1·5:2·0 gives a considerable repulsion, so that the oxygen charges need reducing. To this point the formal charge distribution between the ions of the crystal structure has been taken as $(Sc^{3+})_2Si_2O_7^{6-}$. However Pauling's electroneutrality principle, that the net charges on atoms are quite small and within the range −1 to +1, suggests that the effective charges on Sc should be rather less than the formal 3+. As little as 17% covalent character in the Sc–O bonds is needed to reduce the effective charge on Sc to $(+3{\cdot}0-6\times2\times0{\cdot}17)=+1{\cdot}0$. Since each O_2 or O_3 is coordinated to two Sc this would change the oxygen charges from −1·5 to $(-1{\cdot}5\times2\times2\times0{\cdot}17)=-0{\cdot}8$. Further the electroneutrality principle suggests that the charge on Si cannot be as large as +2·0. This fits in with the calculations of Jaffé (1954) and Cruickshank (1961) who show that the Si $d_{x^2-y^2}$ and d_{z^2} orbitals are suitable for π-bonds to the tetrahedrally coordinated oxygens. If we reduce the Si charge to +1·0 the charges on O_2 and O_3 diminish by perhaps a further 0·3 to −0·5 (while O_1 diminishes by 0·2 to −0·8). The resulting oxygen: silicon charge ratio of 0·5:1·0 then roughly balances the electrostatic attractions and repulsions between the bases of the two pyramids. These considerations are necessarily very speculative since a proper calculation would involve a great deal of work, but they serve to show some of the results hinted at by the ionic packing.

We now consider the dimensions of the pyrosilicate group itself. The results of the computer refinement for $C2/m$, rounded off to 0·01 Å, have already been given in Table 4. To a further place of decimals, the results are Si–O_1 1·607 ± 0·007, Si–O_2 1·620 ± 0·020, Si–O_3 1·630 ± 0·015 Å, where the e.s.d.'s are those obtained from the LS calculations. The e.s.d. for Si–O_1 is small because O_1 is in a fixed position. The weighted mean of the two outer bonds is 1·626 ± 0·012 Å; statistically this is not significantly longer than the inner Si–O bond of 1·607 ± 0·007 Å, but it is noteworthy that the inner oxygen actually makes two bonds to silicons, each as short as the one bond of the outer oxygens. The point is discussed by Cruickshank (1961) in his account of Si–O π-bonds and may be another hint that the charge on the bridge oxygen O_1 is actually greater than the charges on the outer oxygens O_2 and O_3.

The most important result of this study is the confirmation of the 180° Si–O–Si angle obtained by Zachariasen. Comparison with other structures containing the Si_2O_7 group is hampered by the fact that, so far as we are aware, there are no other fully refined three-dimensional analyses available. Apart from the hemimorphite analysis mentioned earlier, analyses carried out in the last ten years show angles ranging from 180° in seidozerite (Simonov & Belov, 1959) to 135° in lawsonite (Rumanova & Skipetrova, 1959). The reported dimensions in seidozerite (inner Si–O 1·63 Å, outer Si–O 1·635 Å) are in close agreement with those found in thortveitite; however, despite the satisfactory level of refinement [$R = 16·6\%$ for 378 $F(h0l)$, $R = 20·7\%$ for 331 $F(0kl)$], the 180° angle is not proven unambiguously as many of the key atoms lie in overlapping peaks in the projections, though it is clear that the angle must be close to 180°. In epidote (Ito, Morimoto & Sadanaga, 1954) though 1000 $F(hkl)$ were used, the discrepancy factor R of 27·5% indicates that by present standards considerable further refinement is needed before the reported angle of 155° can be taken as definite. In lawsonite [$R = 16·7\%$ for 172 $F(h0l)$], although the detailed dimensions have been obtained only from the $(h0l)$ projection (since all the atoms except one have special y coordinates), it is clear that the Si–O–Si angle cannot possibly be close to 180° and must be near the 135° reported by the authors. We have done some LS calculations with Barclay & Cox's data for hemimorphite, which have confirmed their low residuals [$R(0kl) = 0·09$, $R(hk0) = 0·10$]. However the calculations show that the e.s.d.'s of the z coordinates of the oxygens are as large as 0·1 Å, because of the absence of the centre of symmetry in the (100) projection. The accuracy of the 133° angle in hemimorphite is consequently rather less than that of the 135° angle in lawsonite and further experimental work is desirable to obtain a better accuracy.

Despite the lack of high-grade analyses, it seems clear that the Si–O–Si angles in pyrosilicate groups do vary between 180° and about 135°. Evidently the angle depends on the environment of the group, but it would be prudent at present not to speculate about the details of this but to wait until enough good three-dimensional analyses are available.

Note added in proof by D. W. J. Cruickshank.— In a recent article Liebau (1961*d*) has maintained that Si-O-Si angles of 180° do not normally occur in crystalline silicates. *Inter alia*, he discusses thortveitite, zunyite and coesite. I have nothing to add to the present discussion of thortveitite, and I feel that the 180° angles found by the original authors in zunyite and coesite, by analyses of fairly high quality, could only be discounted after very careful re-investigation.

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References

Barclay, G. A. & Cox, E. G. (1960). *Z. Kristallogr.* **113**, 23.

Barclay, G. A., Cox, E. G. & Lynton, H. (1956). *Chemistry and Industry*, p. 178.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.

Cochran, W. (1948). *Acta Cryst.* **1**, 138.

Cruickshank, D. W. J. (1952). *Acta Cryst.* **5**, 511.

Cruickshank. D. W. J. (1961). *J. Chem. Soc.*, p. 5486.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). *Computing Methods and the Phase Problem*, p. 32. Oxford: Pergamon Press.

Gossner, B. & Mussgnug, F. (1929). *Centr. Min. Abt.*, No. 1.

Ito, T., Morimoto, N. & Sadanaga, R. (1954). *Acta Cryst.* **7**, 53.

Ito, T. & West, J. (1932). *Z. Kristallogr.* **83**, 1.

Jaffé, H. H. (1954). *J. Phys. Chem.* **58**, 185.

Kamb, W. B. (1960). *Acta Cryst.* **13**, 5.

Liebau, F. (1961*a*). *Acta Cryst.* **14**, 389.

Liebau, F. (1961*b*). *Acta Cryst.* **14**, 395.

Liebau, F. (1961*c*). *Acta Cryst.* **14**, 399.

Liebau, F. (1961*d*). *Acta Cryst.* **14**, 1103.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Cornell: University Press.

Rumanova, I. M. & Skipetrova, T. I. (1959). *Doklady Akad. Nauk. SSR*, **124**, 324.

Simonov, V. I. & Belov, N. V. (1959). *Kristfya.* **4**, 163.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Zachariasen, W. H. (1930). *Z. Kristallogr.* **73**, 1.