Zeitschrift für Kristallographie, Bd. 126, S. 46—65 (1968)

The crystal structure of $LiAlSi_2O_6$-II ("β spodumene")

By **Chi-Tang Li**

Owens-Illinois Technical Center, Toledo, Ohio

and **Donald R. Peacor**

Department of Geology and Mineralogy, University of Michigan
Ann Arbor, Michigan

(Received October 27, 1966, and in revised form January 19, 1967)

Auszug

$LiAlSi_2O_6$-II (β-Spodumen) hat die Raumgruppe $P4_32_12$ (oder $P4_12_12$) und die Gitterkonstanten $a = 7{,}541 \pm 0{,}001$, $c = 9{,}156 \pm 0{,}002$ Å; es ist $Z = 4$, $D_{\text{beob.}} = 2{,}365$ und $D_{\text{ber.}} = 2{,}374$ g/cm³. Für R wurde als Endwert $6{,}2\,^0/_0$ erreicht. Die Struktur beruht auf einem Alumosilikat-Gerüst, das isotyp mit Keatit ist. Si- und Al-Atome sind ungeordnet verteilt; jedes Li-Atom ist von vier Sauerstoffatomen umgeben. Die Struktur wird beherrscht von miteinander verknüpften Fünferringen von (Si,Al)-Tetraedern. Alle Fünferringe liegen annähernd parallel (010) oder (100), wodurch Kanäle gebildet werden ähnlich denen der Zeolithe. Die Fähigkeit von $LiAlSi_2O_6$-II, Ionen auszutauschen, läßt sich durch das Vorhandensein der Kanäle erklären. Die vier Li-Atome einer Zelle sind auf die Punkte eines 8-zähligen Komplexes allgemeiner Lage verteilt. Es wird eine Erklärung für die ungewöhnlich geringe Wärmeausdehnung von $LiAlSi_2O_6$-II gegeben.

Abstract

$LiAlSi_2O_6$-II ("β spodumene") was found to be tetragonal, space group $P4_32_12$ (or $P4_12_12$), $a = 7.541 \pm 0.001$, $c = 9.156 \pm 0.002$ Å, $Z = 4$, $D_o = 2.365$ and $D_c = 2.374$ g/cm³. The bond lengths were determined with an accuracy of 0.006 Å for (Si,Al)—O bonds and 0.041 Å for Li—O bonds. The final R value was $6.2\,^0/_0$. The structure consists of a three-dimensional aluminosilicate framework. The framework was confirmed to be isotypic with keatite. The Li atoms were found to be coordinated to four oxygen atoms. The distribution of Si and Al in the tetrahedra is random. The structure is dominated by interlocking 5-membered rings of (Si,Al) tetrahedra. All the five-membered rings run approximately parallel to either (010) or (100), and thus help to create zeolite-like channels. These channels account for the ion-exchange properties of $LiAlSi_2O_6$-II. Lithium atoms are stuffed in interstitial positions but occupy a general eight-fold site.

The four lithium atoms per unit cell are distributed among four sets of paired sites of the eight-fold positions. An explanation for the unusually low thermal expansion behavior of $LiAlSi_2O_6$-II is given.

Introduction

Spodumene is the only naturally occurring polymorph of $LiAlSi_2O_6$ and is the stable low-temperature form. In some work on this compound this phase has been called α spodumene while the high-temperature tetragonal modification is called β spodumene. Mellor (1925) reviewed the early literature on these phases. A third high-temperature form, which is a stuffed derivative of β quartz, is now widely known as γ spodumene. All three polymorphs of $LiAlSi_2O_6$ are related by reconstructive transformations. The prefixes α, β and γ to the mineral name spodumene imply that displacive transformations relate these phases, however. We therefore propose that the phases be referred to as $LiAlSi_2O_6$-I (monoclinic, low-temperature form), $LiAlSi_2O_6$-II (high-temperature, tetragonal form) and $LiAlSi_2O_6$-III (hexagonal, stuffed derivative of β quartz). This nomenclature is consistent with the known structural relations, and may be readily applied to other members of those solid-solutions series of which these phases are members.

In many low-expansion lithium-bearing glass and ceramic materials, $LiAlSi_2O_6$-II is found to be the principal crystalline phase. Phase equilibrium studies of $LiAlSi_2O_6$-II were made by Hatch (1943), Roy, Roy and Osborn (1950), and Skinner and Evans (1960). However, there were some conflicting reports in the preliminary study of the $LiAlSi_2O_6$-II structure. Skinner and Evans (1960) reported that it was tetragonal and was isotypic with keatite, while Saalfeld (1961) indicated that it was orthorhombic and had a structure similar to that of high or β quartz. Thus, a complete crystal-structure analysis of $LiAlSi_2O_6$-II seemed necessary in order to clarify the controversy over structural relations and to explain the unusually low thermal-expansion behavior.

Experimental

The crystals were grown from the glass melt as follows: Glass of composition Li_2O—Al_2O_3—$4SiO_2$ was heated to above the liquidus (1425 °C) in a platinum crucible. The temperature was reduced and held at about 25° to 50 °C below the liquidus to allow crystals to grow. The glass melt was nucleated by gently touching the surface with a platinum rod. Then the whole platinum crucible was put into a water bath to quench it rapidly to room temperature. Most of the glass crystallized. About one gram of crystals was isolated with the help of a polarizing microscope for a chemical analysis. The analysis showed that the chemical composition of the crystals was 0.98 Li_2O—Al_2O_3—$4SiO_2$ which is close to a 1-1-4 mole ratio. Most of the crystals showed sharp extinction when examined under a polarizing microscope. Several single crystals were selected and analyzed using a Weissenberg camera. The lattice constants were precisely determined by using powder-diffractometer data with silicon as internal standard, and refined by the least-squares program LCLSQ written by Burnham (1962). The refined lattice parameters obtained thereby, plus some other constants are as follows:

Space group: $P4_32_12$ (or its enantiomorph $P4_12_12$)
$a = 7.541 \pm 0.001$, $c = 9.156 \pm 0.002$ Å
$Z = 4$ for $LiAlSi_2O_6$
$D_o = 2.365$, $D_c = 2.374$ g/cm^3
$\mu = 74.02$ cm^{-1} for Cu$K\alpha$ radiation.

A tiny crystal, approximately a parallelepiped with dimensions $1.39 \times .85 \times .46 \times 10^{-3}$ mm^3, mounted on the a axis, was used to collect the intensity data. The intensities were measured with a manually operated Supper diffractometer (equi-inclination Weissenberg) with a scintillation counter and Cu$K\alpha$ radiation. The associated electronics were standard Norelco equipment and included pulse-height analysis circuitry. Both the *hkl* and *khl* reflections were collected from the zero up to the eighth levels, and the average, after correction for Lorentz-polarization and absorption factors, was calculated. In general, *hkl* data agreed well with *khl* data except for the pair 201 and 021. Because of the great difference in primary and secondary extinction, this pair was not included in the final refinement. After the completion of the intensity measurement, a spherical grinder was made available to us. A very small spherical crystal (diameter = 0.192 mm) mounted on the c axis was used to check the symmetry of $LiAlSi_2O_6$-II, especially the relation between the reflections 201 and 021. The intensity values of 201 and 021 were equal within the estimated error, as were the rest of the reflection pairs tested. There were a total of 400 independent reflections, of which 348, or 87 %, were collected. Among the 348 reflections collected, 13 were extinct and 6 unobserved. Since $LiAlSi_2O_6$-II is non-centrosymmetric, the structure factors for the unobserved reflections were taken to be two thirds that of the minimum observed reflection.

The following ionic states were assigned to each element in $LiAlSi_2O_6$-II: for lithium: Li^{+1}; for oxygen: O^{-1}; and for both aluminum and silicon: $\frac{1}{3}(2\,Si^{+2} + Al^{+1})$. These assignments were based on the following considerations: (1) The overall charges remain balanced for $LiAlSi_2O_6$-II. (2) The bonding in $LiAlSi_2O_6$-II was assumed to be half ionic and half covalent. (3) Since $LiAlSi_2O_6$-II was formed at high temperature and rapidly quenched to room temperature, silicon and aluminum were assumed to be completely disordered over the two available equipoints. This was later verified by the refinement.

Determination and refinement of structure

The F_o values in $LiAlSi_2O_6$-II were compared with the corresponding F_c values in keatite (SHROPSHIRE *et al.*, 1959). A fairly reasonable agreement was obtained. Thus, a least-squares refinement on the positional parameters alone was started by using the atomic positions from keatite, omitting the Li atoms and assuming complete disorder for silicon and aluminum. The overall temperature coefficient was taken to be $B = 0.5$.

Table 1. *Final atom parameters together with those of keatite* (in parentheses)

Atom	x	y	z
Si(1)	.3323 ± 2 (.326)	.1121 ± 2 (.120)	.2384 ± 2 (.248)
Si(2)	.4178 ± 3 (.410)	(.4178) (.410)	(0) (0)
O(1)	.4432 ± 9 (.445)	.1207 ± 8 (.132)	.3931 ± 6 (.400)
O(2)	.1245 ± 7 (.117)	.1159 ± 7 (.123)	.2994 ± 6 (.296)
O(3)	.3637 ± 9 (.344)	.3046 ± 9 (.297)	.1459 ± 7 (.143)
Li	.0705 ± 54	.1953 ± 62	.5011 ± 45

Table 2. *Isotropic temperature factors and atom parameters at the end of isotropic refinement*

Atom	x	y	z	B
Si(1)	.3324 ± 3	.1221 ± 3	.2384 ± 3	.26 ± .03
Si(2)	.4182 ± 3	(.4182)	(0)	.23 ± .04
O(1)	.4436 ± 10	.1190 ± 9	.3926 ± 7	1.50 ± .10
O(2)	.1254 ± 8	.1154 ± 8	.2999 ± 7	1.08 ± .09
O(3)	.3628 ± 9	.3024 ± 10	.1454 ± 8	2.01 ± .11
Li	.0644 ± 38	.1880 ± 38	.4964 ± 31	1.79 ± .37

Table 3. *Final anisotropic temperature factors**

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B**
Si(1)	.0012 ± 3	.0013 ± 3	0 ± 2	.0001 ± 3	.0002 ± 2	—.0003 ± 2	.19 Å^2
Si(2)	.0011 ± 2	(.0011)	.0005 ± 3	—.0003 ± 3	—.0005 ± 2	(.0005)	.22
O(1)	.0102 ± 12	.0091 ± 11	.0037 ± 6	—.0022 ± 9	—.0044 ± 8	.0008 ± 8	1.88
O(2)	.0031 ± 9	.0080 ± 12	.0020 ± 6	.0006 ± 8	0 ± 6	—.0006 ± 6	1.07
O(3)	.0129 ± 13	.0080 ± 12	.0068 ± 8	.0006 ± 11	.0033 ± 10	.0033 ± 8	2.34
Li	.0195 ± 76	.0245 ± 97	.0083 ± 44	—.0130 ± 72	.0066 ± 59	—.0091 ± 63	4.26

* By symmetry, $\beta_{22} = \beta_{11}$, and $\beta_{23} = -\beta_{13}$ for Si_2.

** An equivalent isotropic temperature factor defined by Hamilton (1959).

Refinement of the structure was carried out on the IBM 7090 using the SFLSQ2 least-squares program of Prewitt (1962). A modified weighting scheme of Hughes (1941) was used, namely, $(W)^{1/2} = 1/F_0(1 + 3\sigma_F)$, where σ_F is the relative probable error of F_0. All the reflections measured were used except for those intensities which were zero as required by symmetry.

The refinement converged at $R = 14.9\,^0/_0$. Three-dimensional difference and electron-density syntheses were then computed. The difference synthesis failed to show the Li atom unambiguously since several possible Li peaks were found. These included the correct Li location later determined, and one of four possible Li positions predicted from geometrical considerations by Skinner and Evans (1960). This Li position predicted by Skinner and Evans also happened to show up as a very small peak in the electron-density synthesis. A test on this and the three other possible Li positions of Skinner and Evans was made, but the R value increased slightly for all four cases. When one cycle of isotropic refinement was carried out, the temperature factor of Li increased from 0.5 to 3.06. Further attempts to locate the Li atom were, therefore, made. The Li was excluded from the refinement while the isotropic temperature factors as well as the positional parameters of the rest of the atoms were refined. The weighting scheme recommended by CRUICKSHANK (1965) was used. The 021 reflection was excluded from the refinement because of the primary and secondary extinction. The R value dropped to 8.9%. Both the difference and electron-density syntheses were again computed. The correct Li position was located unambiguously from the difference synthesis, which was featureless except for the Li peaks. This correct Li position also showed up as a small peak in the electron-density synthesis, but the peak height was of the order of magnitude of the background fluctuation. The R value dropped from 8.9 to 8.4% when the correct Li position was introduced and refined on the positional parameters alone. Both isotropic and anisotropic refinements were subsequently carried out. The isotropic temperature factor of Li was 1.78. The final R value was 6.2% at the completion of anisotropic refinement.

A comparison of final F_c and F_o revealed that several reflections were affected by the primary and secondary extinctions. The 040 reflection was found to be affected most, other than the 021 reflection. Practically no change of the final results could be found on one more

Table 4. *Thermal motion data*

Atom	Principal thermal axes	Root mean square displacement	Direction cosines of the principal axes in xyz system of the crystal		
			α	β	γ
Si(1)	1	.013 ± .034 Å	.199	−.301	.932
	2	.061 ± .007	.926	−.254	−.281
	3	.064 ± .007	−.321	−.919	−.228
Si(2)	1	.022 ± .026	−.384	.384	.840
	2	.049 ± .012	.707	.707	.0
	3	.074 ± .009	.593	−.593	.543
O(1)	1	.073 ± .017	.555	−.061	.830
	2	.153 ± .011	.294	.919	.262
	3	.206 ± .010	−.779	.389	−.492
O(2)	1	.090 ± .013	.061	−.151	.987
	2	.093 ± .014	.992	−.099	−.077
	3	.154 ± .011	−.110	−.984	−.144
O(3)	1	.112 ± .014	.272	.690	.670
	2	.169 ± .012	.652	−.645	.399
	3	.220 ± .011	−.707	−.329	.627
Li	1	.128 ± .068	.049	−.483	.874
	2	.160 ± .055	.821	.517	.240
	3	.346 ± .059	.568	−.706	−.421

Table 5. *Observed and calculated structure factors*

h k l	F_o	$0.1818\|F_c\|$	A_c	B_c
0 2 0	1.33	1.11	6.09	0.00
4	80.91	90.23	-496.32	0.00
6	5.19	4.12	- 22.68	0.00
8	4.89	5.56	30.60	0.00
0 1 1	11.23	9.24	- 35.92	35.92
3	5.94	6.04	- 23.48	23.48
4	0.95	1.09	- 4.22	- 4.22
5	7.39	5.95	- 23.15	23.15
6	26.16	24.90	96.85	96.85
7	24.93	23.03	89.59	- 89.59
8	3.24	1.84	7.16	7.16
9	7.15	8.29	32.24	- 32.24
0 1 2	46.81	49.96	-274.79	0.00
2	3.83	2.65	0.00	14.58
3	5.49	4.23	- 23.25	0.00
4	23.26	21.00	0.00	115.54
5	56.47	58.09	319.53	0.00
6	1.56	3.00	0.00	- 16.49
7	9.89	9.09	50.02	0.00
8	6.50	7.28	0.00	- 40.06
9	24.55	26.63	-146.49	0.00
0 1 3	8.24	7.20	- 28.02	- 28.02
2	1.28	0.46	1.79	- 1.79
3	51.04	48.81	189.83	189.83
4	6.78	6.29	24.45	- 24.45
5	23.06	21.44	83.38	83.38
6	1.47	0.51	1.97	- 1.97
7	28.66	28.66	-111.48	-111.48
8	3.19	3.60	- 14.01	14.01
0 0 4	38.50	40.56	223.13	0.00
1	21.72	20.88	0.00	-114.88
2	5.00	2.09	11.49	0.00
3	14.80	13.80	0.00	75.93
4	38.26	37.03	-203.68	0.00
5	10.31	9.45	0.00	52.01
6	4.04	4.35	- 23.91	0.00
7	8.69	8.46	0.00	- 46.53
8	0.95	0.20	1.09	0.00
0 1 5	5.09	6.09	- 23.67	23.67
2	51.13	51.67	-200.98	-200.98
3	37.87	36.75	-142.94	142.94
4	1.36	0.88	3.42	3.42
5	10.36	8.37	- 32.56	32.56
6	5.26	3.04	11.81	11.81
7	18.88	18.73	72.85	- 72.85
8	0.95	1.50	5.85	5.85
0 1 6	24.47	23.05	-126.80	0.00
2	2.93	2.96	0.00	16.29
3	1.38	1.99	10.94	0.00
4	16.74	15.82	0.00	- 87.03
5	34.33	33.15	182.33	0.00
6	5.07	4.46	0.00	- 24.55
7	6.82	7.58	41.67	0.00
0 1 7	8.59	8.55	33.24	33.24
2	44.17	44.10	171.54	-171.54
3	24.65	23.94	93.10	93.10
4	5.43	6.30	24.51	- 24.51
5	4.65	4.76	18.52	18.52
6	8.32	8.49	- 33.02	33.02
7	26.08	27.19	-105.75	-105.75
0 0 8	53.36	55.07	302.90	0.00
1	4.03	3.35	0.00	- 18.44
2	5.29	1.87	10.31	0.00
3	16.73	15.86	0.00	87.24
4	22.16	22.17	-121.93	0.00
5	7.92	6.40	0.00	- 35.19
6	2.16	2.27	- 12.49	0.00
0 1 9	9.51	8.92	- 34.71	34.71
2	28.05	28.90	-112.40	-112.40
3	13.80	13.72	- 53.36	53.36
4	6.41	5.42	21.10	21.10
5	1.47	0.83	- 3.24	3.24
0 1 10	5.98	6.05	- 33.28	0.00
2	7.15	7.27	0.00	40.01
3	18.32	18.14	- 99.76	0.00
4	0.95	0.71	0.00	- 3.91
0 1 11	13.54	13.73	- 53.39	- 53.39
2	19.73	19.07	74.18	- 74.18
1 1 0	7.96	6.39	35.13	0.00
2	5.37	4.07	22.39	0.00
3	4.84	4.19	23.05	0.00
4	12.39	12.46	- 68.51	0.00
5	16.06	14.59	- 80.26	0.00
6	32.33	31.50	173.24	0.00
7	22.16	21.68	-119.23	0.00
8	6.17	6.89	37.91	0.00
9	8.33	7.56	41.57	0.00
1 1 1	26.30	22.64	0.00	124.52
2	29.60	26.38	-127.30	69.69
3	11.33	10.62	- 2.76	- 58.32
4	4.82	4.77	- 11.17	23.77
5	27.65	25.31	- 76.35	-116.45
6	20.32	19.55	- 33.99	102.03
7	17.47	16.73	- 30.20	86.95
8	13.53	14.51	- 49.65	- 62.46
9	10.97	11.59	48.86	40.91
1 1 2	44.76	45.63	250.98	0.00
2	5.62	4.66	- 25.64	0.49
3	25.79	22.11	65.34	-102.60
4	23.00	20.74	110.41	28.69

h k l	F_o	$0.1818\|F_c\|$	A_c	B_c
1 5 2	39.21	39.05	-213.93	19.30
6	12.85	12.47	19.38	65.80
7	4.54	3.12	- 10.61	13.49
8	12.68	14.01	74.07	- 21.29
9	14.52	15.00	81.97	9.30
1 1 3	20.04	18.96	0.00	104.29
2	24.29	22.53	81.40	93.47
3	42.61	41.37	-116.77	-195.33
4	5.39	5.71	- 17.29	26.25
5	25.21	24.68	114.33	- 73.24
6	7.50	6.49	- 23.83	- 26.60
7	18.90	17.56	46.91	84.42
8	10.71	11.69	42.63	- 48.17
1 1 4	21.32	20.05	110.27	0.00
2	20.99	18.54	-101.54	- 9.32
3	25.83	24.54	134.29	- 13.65
4	7.91	7.54	- 18.20	- 37.28
5	24.59	24.73	-135.29	- 13.89
6	14.21	13.71	74.52	11.41
7	21.22	21.09	-113.08	- 25.81
8	3.17	3.74	17.48	- 10.82
1 1 5	10.41	8.64	0.00	- 47.52
2	14.70	14.08	37.99	- 67.50
3	24.59	24.46	- 0.69	-134.56
4	8.83	8.14	15.81	41.90
5	12.66	12.51	- 66.38	- 18.11
6	11.11	11.60	- 19.88	60.62
7	19.88	19.82	19.32	107.30
8	16.79	18.00	- 63.75	- 75.75
1 1 6	11.73	11.03	60.69	0.00
2	15.68	15.60	- 10.50	- 85.14
3	5.22	3.21	9.16	15.06
4	5.36	4.06	2.44	22.19
5	19.10	19.61	-100.67	38.76
6	1.69	2.46	11.20	7.58
7	1.37	2.67	14.19	3.69
1 1 7	12.27	12.44	0.00	68.40
2	25.62	25.99	99.74	102.41
3	16.75	15.44	- 80.18	- 27.97
4	4.30	4.68	- 21.43	14.26
5	13.70	14.38	68.49	- 39.62
6	2.17	3.06	15.19	7.21
7	12.59	13.11	66.19	28.69
1 1 8	7.66	6.97	- 38.32	0.00
2	12.76	13.44	70.57	- 22.05
3	22.04	21.34	101.26	59.39
4	5.92	6.42	- 15.09	- 31.93
5	5.46	4.02	- 21.74	3.99
6	9.92	10.56	47.24	33.78
1 1 9	10.68	9.38	0.00	51.57
2	4.20	5.09	- 27.91	- 2.31
3	16.10	15.25	- 9.42	- 83.34
4	8.75	8.84	- 47.49	10.57
5	16.35	15.60	- 41.32	- 75.22
1 1 10	6.66	7.39	40.67	0.00
2	15.09	15.02	- 9.91	- 82.01
3	8.70	9.30	- 41.85	- 29.39
4	4.53	6.71	2.87	36.81
1 1 11	1.73	0.99	0.00	- 5.44
2 2 0	10.71	9.35	51.43	0.00
3	11.42	9.98	54.89	0.00
4	6.12	4.49	24.71	0.00
5	10.88	10.50	57.78	0.00
6	10.58	10.42	- 57.29	0.00
7	28.38	27.13	-149.23	0.00
8	9.59	10.26	- 56.44	0.00
9	6.81	7.54	- 41.50	0.00
2 2 1	1.33	1.39	0.00	7.66
3	3.74	4.31	0.52	23.69
4	32.52	30.21	-143.97	82.94
5	36.09	33.93	-165.93	- 85.46
6	6.54	6.24	- 24.72	- 23.78
7	4.80	5.18	- 25.67	- 12.34
8	6.90	7.30	2.50	40.10
9	16.38	17.34	90.07	31.39
2 2 2	34.60	32.27	-177.52	0.00
3	27.15	24.09	- 52.17	-121.81
4	4.74	3.10	14.86	8.42
5	5.70	4.74	17.01	- 19.74
6	5.31	4.36	20.05	13.11
7	13.31	13.24	69.84	20.68
8	3.71	1.62	- 5.78	- 6.76
2 2 3	7.47	6.67	0.00	36.67
3	10.16	9.14	- 8.98	49.45
4	15.57	14.60	62.16	50.81
5	34.83	34.01	159.44	- 97.89
6	10.32	10.78	17.68	- 56.60
7	4.69	5.73	25.21	- 18.91
8	6.12	5.47	14.92	26.16
2 2 4	2.01	0.01	- 0.04	0.00
3	35.26	33.65	184.67	- 12.27
4	9.59	9.32	31.28	- 40.59
5	27.42	27.38	150.16	- 11.47
6	11.20	10.22	- 24.82	50.42
7	26.54	25.37	-139.29	8.44
8	11.97	12.31	- 64.06	21.93
2 2 5	2.92	3.84	0.00	- 21.10
3	23.96	23.31	89.77	91.52
4	42.93	43.50	-179.78	157.88
5	14.70	14.41	- 78.99	6.59

h k l	F_o	$0.1818\|F_c\|$	A_c	B_c
2 6 5	4.67	6.76	- 36.94	4.26
7	15.45	15.94	- 74.08	- 46.87
8	13.34	13.05	57.67	- 42.77
2 2 6	62.73	68.15	-374.88	0.00
3	17.57	18.16	- 47.86	87.68
4	5.47	2.46	- 3.54	13.08
5	8.41	8.27	15.10	- 42.93
6	14.13	13.14	71.93	- 7.01
7	10.87	11.09	60.63	6.51
2 2 7	2.98	3.99	0.00	21.93
3	17.83	17.90	91.05	- 37.52
4	15.36	14.21	72.52	29.10
5	23.21	23.27	106.43	- 71.07
6	7.34	8.01	8.26	- 43.25
2 2 8	5.26	4.68	25.75	0.00
3	29.40	28.71	156.89	- 17.81
4	10.42	9.81	13.37	- 52.26
5	5.49	4.98	16.40	- 21.93
6	5.89	6.67	- 36.43	- 4.55
2 2 9	6.60	8.67	0.00	- 47.70
3	20.91	19.47	76.98	74.42
4	13.95	14.23	- 69.29	36.39
5	20.97	19.93	-100.30	- 44.23
2 2 10	30.73	31.23	-171.78	0.00
3	5.27	6.20	- 25.95	22.09
3 3 0	0.95	1.91	- 10.50	0.00
4	7.49	7.89	43.39	0.00
5	4.23	2.10	- 11.57	0.00
6	23.13	22.27	122.50	0.00
7	8.50	8.36	46.01	0.00
8	3.60	2.10	- 11.56	0.00
3 3 1	4.76	4.43	0.00	24.38
4	11.66	11.48	- 46.27	43.01
5	19.58	19.17	- 18.08	103.88
6	23.50	22.57	77.51	- 96.96
7	10.51	11.09	- 53.62	29.03
8	13.99	14.49	- 29.10	- 74.19
3 3 2	18.57	17.28	- 95.03	0.00
4	10.51	10.01	49.93	23.26
5	31.42	30.73	-149.24	- 79.34
6	13.39	13.70	75.33	0.75
7	15.10	15.07	80.07	21.40
8	14.32	14.32	- 78.49	- 6.70
3 3 3	33.35	31.08	0.00	-170.96
4	31.27	29.53	147.89	- 67.16
5	32.85	32.25	- 33.18	174.25
6	6.49	6.25	13.10	- 31.77
7	17.32	17.61	22.25	94.26
8	6.80	7.83	- 30.79	- 30.08
3 3 4	39.20	39.19	-215.56	0.00
4	5.86	6.17	22.70	25.25
5	3.30	4.96	- 22.97	- 14.76
6	7.35	6.17	- 32.01	- 11.19
7	15.87	15.09	79.80	- 22.93
8	3.70	3.31	- 16.96	6.56
3 3 5	12.79	12.07	0.00	- 66.41
4	14.39	14.03	- 73.91	- 22.23
5	21.46	20.99	- 19.35	113.85
6	12.11	11.97	47.08	- 46.06
7	10.11	11.22	- 53.69	30.39
3 3 6	13.49	13.68	- 75.22	0.00
4	11.16	10.83	52.57	27.97
5	16.52	17.22	- 92.30	- 21.15
6	11.75	11.99	65.48	7.84
7	14.44	13.62	74.74	- 5.38
3 3 7	23.97	24.31	0.00	-133.69
4	14.12	13.76	74.10	15.36
5	11.99	12.81	- 4.05	70.33
6	8.92	9.57	29.23	- 43.78
3 3 8	18.93	16.94	- 93.17	0.00
4	16.77	16.67	45.61	79.58
5	13.12	12.53	- 47.02	50.39
3 3 9	5.42	4.98	0.00	27.39
4	7.33	7.00	- 34.59	- 16.85
3 3 10	21.62	23.78	-130.78	0.00
4 4 0	38.36	35.61	195.86	0.00
5	24.24	22.76	125.18	0.00
6	7.32	6.36	- 34.97	0.00
7	2.08	0.84	4.62	0.00
8	2.76	3.28	18.02	0.00
4 4 1	8.48	8.27	0.00	- 45.51
5	9.11	8.95	3.66	- 49.08
6	10.40	10.15	- 54.98	9.53
7	20.15	19.95	-109.63	- 4.20
8	12.13	12.98	- 36.36	61.41
4 4 2	12.31	10.29	- 56.62	0.00
5	34.75	33.47	-184.06	3.52
6	15.57	16.46	- 89.84	11.35
7	6.83	6.59	- 32.12	16.84
8	7.90	7.19	38.87	7.17
4 4 3	5.03	4.76	0.00	- 26.19
5	15.62	15.26	- 62.22	- 56.33
6	8.03	7.93	41.50	13.51
7	23.80	24.52	132.87	23.12
4 4 4	29.27	29.94	164.70	0.00
5	18.20	18.84	103.23	- 9.36
6	8.47	8.63	- 38.42	- 27.86
7	6.27	6.65	30.23	20.57
4 4 5	11.32	11.39	0.00	- 62.64
5	12.22	12.55	33.87	- 60.16

Table 5. *(Continued)*

h	k	l	F_o	$0.1818\|F_c\|$	A_c	B_c	h	k	l	F_o	$0.1818\|F_c\|$	A_c	B_c	h	k	l	F_o	$0.1818\|F_c\|$	A_c	B_c
4	6	5	9.52	10.09	- 55.43	2.70	5	6	0	20.34	19.80	-108.88	0.00	5	5	4	27.51	27.88	153.37	0.00
	7		13.44	12.18	- 65.27	- 15.08		7		9.32	10.01	55.07	0.00		6		13.84	13.60	- 73.47	- 14.03
4	4	6	11.59	10.76	- 59.18	0.00	5	5	1	21.87	21.12	0.00	116.17	5	5	5	5.89	5.60	0.00	30.82
	5		13.90	14.24	- 71.89	31.08		6		15.37	15.10	- 57.90	- 59.55		6		15.22	15.51	- 66.57	- 53.38
	6		12.06	12.48	- 63.37	26.38		7		14.97	15.55	- 46.26	- 71.96	5	5	6	5.81	6.22	34.21	0.00
4	4	7	0.98	0.62	0.00	3.39	5	5	2	19.03	18.41	101.24	0.00	5	5	7	5.39	5.41	0.00	29.78
	5		9.10	7.50	- 26.03	- 32.00		6		9.39	10.10	- 22.24	- 50.92	6	6	0	12.02	11.99	65.97	0.00
	6		8.03	7.77	18.73	38.42		7		9.49	9.72	42.18	- 32.85	6	6	1	12.84	14.53	0.00	79.93
4	4	8	5.90	4.92	27.07	0.00	5	5	3	8.45	9.39	0.00	51.64	6	6	2	5.25	4.88	26.82	0.00
	5		13.79	13.84	72.03	24.67		6		16.39	17.14	94.23	- 2.22	6	6	3	18.41	20.02	0.00	110.12
5	5	0	30.02	28.85	158.72	0.00		7		12.67	12.23	28.50	- 60.94	6	6	4	9.48	9.82	54.01	0.00

cycle of anisotropic refinement with the 040 reflection being excluded. The final positional parameters for all atoms, together with those for keatite, are listed in Table 1. The final isotropic temperature factors and the atom parameters at the end of isotropic refinement are listed in Table 2. The individual anisotropic temperature factors are listed in Table 3, the thermal-motion data are listed in Table 4, and the observed and calculated structure factors are listed in Table 5.

Discussion of the structure

The bond distances, angles, and their standard deviations were computed with Busing, Martin and Levy's function-and-error program (1964). The results are listed in Tables 6 and 7. The projections of the structure on (001) and (100) are shown in Figs. 1 and 2.

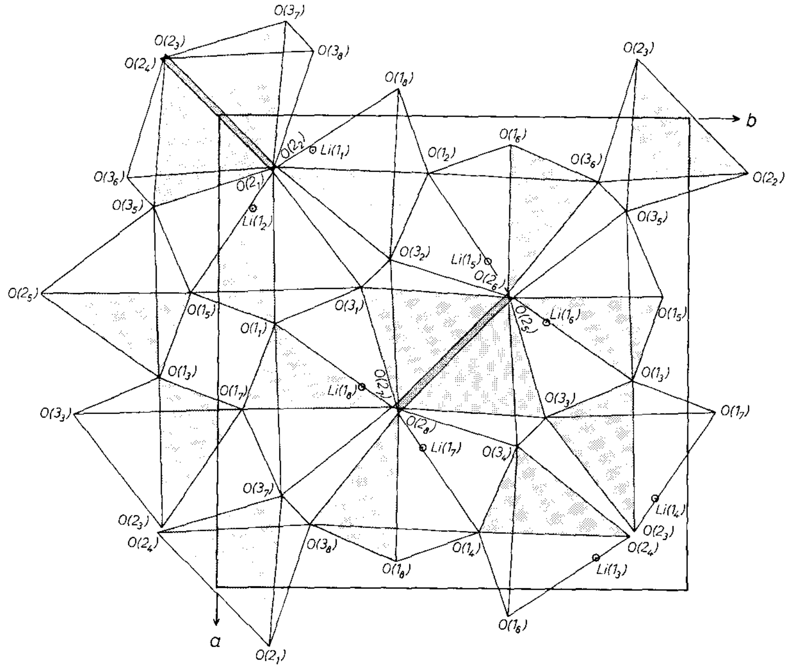

Fig. 1. The projection of $LiAlSi_2O_6$-II down the c axis

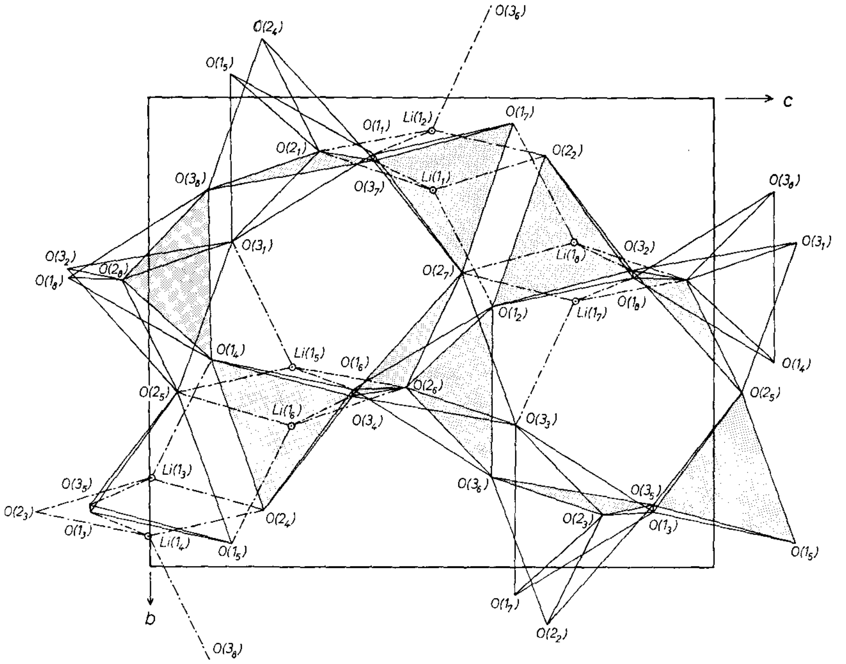

Fig. 2. The projection of $LiAlSi_2O_6$-II down the *a* axis

The (Si,Al) tetrahedra

The structure consists of a three-dimensional aluminosilicate framework. The distribution of Si and Al in the tetrahedra is random. There are two symmetry-independent (Si,Al) tetrahedra. The Si(1) atom is in the general equipoint of rank 8, while the Si(2) atom is on a two-fold axis and occupies an equipoint of rank 4. The average Si(1)—O bond distance is 1.647 Å and the average Si(2)—O bond distance is 1.640 Å. The overall average of (Si,Al)—O bond distances is 1.643 Å. According to Smith and Bailey (1963), the average (Si,Al)—O bond distance for a site containing $\frac{1}{3}$ Al + $\frac{2}{3}$ Si is 1.655 Å, as compared with our value of 1.643 Å. Whether the high-temperature nature of $LiAlSi_2O_6$-II is responsible for the deviation remains to be seen. The Si(2) tetrahedron shares vertices with four Si(1) tetrahedra, while the Si(1) tetrahedron shares vertices with two Si(2) and two Si(1) tetrahedra. According to the aluminum avoidance rule (Loewenstein, 1954; Goldsmith and Laves, 1955), the Si(2) tetrahedron would become Al rich if a partial ordering of Al and Si occurs.

Table 6. *Interatomic distances in* $LiAlSi_2O_6$-II

Atom pair	Distance	Standard deviation
(a) Si(1) tetrahedron		
Si(1_1)–O(1_1)	1.644 Å	.006 Å
Si(1_1)–O(1_5)	1.646	.006
Si(1_1)–O(2_1)	1.665	.005
Si(1_1)–O(3_1)	1.633	.006
O(1_1)–O(1_5)	2.695	.005
O(1_1)–O(2_1)	*2.552*	.008
O(1_1)–O(3_1)	2.721	.009
O(1_5)–O(2_1)	2.728	.008
O(1_5)–O(3_1)	2.728	.011
O(2_1)–O(3_1)	2.694	.008
(b) Si(2) tetrahedron		
Si(2_1)–O(2_5)	1.643	.005
Si(2_1)–O(2_8)	1.643	.005
Si(2_1)–O(3_1)	1.637	.006
Si(2_1)–O(3_2)	1.637	.006
O(2_5)–O(2_8)	2.719	.010
O(2_5)–O(3_1)	*2.574*	.008
O(2_5)–O(3_2)	2.725	.008
O(2_8)–O(3_1)	2.725	.008
O(2_8)–O(3_2)	*2.574*	.008
O(3_1)–O(3_2)	2.746	.013
(c) Lithium tetrahedron		
Li(1_1)–O(1_2)	2.139	.038
Li(1_1)–O(2_1)	1.984	.035
Li(1_1)–O(2_2)	1.933	.048
Li(1_1)–O(3_7)	2.269 Å	.043 Å
O(1_2)–O(2_1)	3.744	.009
O(1_2)–O(2_2)	*2.552*	.008
O(1_2)–O(3_7)	3.843	.010
O(2_1)–O(2_2)	3.674	.011
O(2_1)–O(3_7)	*2.574*	.008
O(2_2)–O(3_7)	3.647	.009
(d) 5-membered ring of (Si, Al) tetrahedra		
(i) oxygen-pentagon (nearly coplanar)		
O(1_3)–O(3_3)	2.721	.009
O(3_3)–O(2_6)	2.725	.008
O(2_6)–O(3_6)	2.694	.008
O(3_6)–O(3_5)	2.746	.013
O(3_5)–O(1_3)	2.728	.011
(ii) Si pentagon (not coplanar)		
Si(1_5)–Si(1_3)	3.183	.002
Si(1_3)–Si(2_2)	3.186	.003
Si(2_2)–Si(1_6)	3.142	.003
Si(1_6)–Si(2_3)	3.186	.003
Si(2_3)–Si(1_5)	3.186	.003
(e) closest distance between Li and (Si, Al)		
Li(1_5)–Si(1_6)	2.628	.037
Li(1_5)–Si(2_1)	2.710	.040

Table 7. *Interatomic angles in* $LiAlSi_2O_6$-II

Atoms	Angle	Standard deviation
(*a*) Si(1) tetrahedron		
O(1_1)–Si(1_1)–O(1_5)	110.0°	.4°
O(1_1)–Si(1_1)–O(2_1)	100.9	.3
O(1_1)–Si(1_1)–O(3_1)	112.2	.4
O(1_5)–Si(1_1)–O(2_1)	111.0	.3
O(1_5)–Si(1_1)–O(3_1)	112.6	.4
O(2_1)–Si(1_1)–O(3_1)	109.5	.3
average	109.4	.3

Table 7. *(Continued)*

Atoms	Angle	Standard deviation
(*b*) Si(2) tetrahedron		
O(2_5)—Si(2_1)—O(2_8)	111.6	.4
O(2_5)—Si(2_1)—O(3_1)	103.4	.3
O(2_5)—Si(2_1)—O(3_2)	112.4	.3
O(2_8)—Si(2_1)—O(3_1)	112.4	.3
O(2_8)—Si(2_1)—O(3_2)	103.4	.3
O(3_1)—Si(2_1)—O(3_2)	114.0	.5
average	109.5	.4
(*c*) Lithium tetrahedron		
O(1_2)—Li(1_1)—O(2_1)	130.5	2.1
O(1_2)—Li(1_1)—O(2_2)	77.4	1.3
O(1_2)—Li(1_1)—O(3_7)	121.3	2.3
O(2_1)—Li(1_1)—O(2_2)	139.4	2.8
O(2_1)—Li(1_1)—O(3_7)	74.1	1.4
O(2_2)—Li(1_1)—O(3_7)	120.2	1.7
average	110.5	1.9
(*d*) 5-membered ring of (Si,Al) tetrahedra		
(*i*) oxygen-pentagon (nearly coplanar)		
O(1_3)—O(3_3)—O(2_6)	120.0	.3
O(3_3)—O(2_6)—O(3_6)	91.4	.2
O(2_6)—O(3_6)—O(3_5)	119.0	.2
O(3_6)—O(3_5)—O(1_3)	99.2	.3
O(3_5)—O(1_3)—O(3_3)	101.9	.3
average	106.3	.2
(*ii*) Si-pentagon (not coplanar)		
Si(1_5)—Si(1_3)—Si(2_2)	106.16	.08
Si(1_3)—Si(2_2)—Si(1_6)	96.38	.04
Si(2_2)—Si(1_6)—Si(2_3)	106.93	.08
Si(1_6)—Si(2_3)—Si(1_5)	100.74	.10
Si(2_3)—Si(1_5)—Si(1_3)	88.05	.04
average	99.65	.07
(*e*) Si—O—Si		
Si(1_5)—O(1_3)—Si(1_3)	150.7°	.5°
Si(1_3)—O(3_3)—Si(2_2)	154.0	.5
Si(2_2)—O(2_6)—Si(1_6)	143.6	.4

The (Si,Al) tetrahedra form interconnecting 5-, 7-, and 8-membered rings. The structure is predominated and essentially made up by interlocking 5-membered rings. Each 5-membered ring contains two Si(2) and three Si(1) tetrahedra with alternation of Si(2) and Si(1) tetrahedra. Each Si(2) tetrahedron contributes to the forming of three 5-membered rings, while each Si(1) tetrahedron contributes to the forming of two 5-membered rings. The neighboring 5-membered rings share one, two, or three common tetrahedra. Within each 5-membered ring the silicon atoms are not coplanar, while the five bridging oxygens are almost coplanar. All the 5-membered rings run approximately parallel to either (100) or (010) and thus help to create the zeolite-like channels. The channels parallel to both the *a* and *b* axes have a free diameter of about 3 Å and are appreciably wider than those parallel to the *c* axis. Thus, $LiAlSi_2O_6$-II is endowed with ion-exchange properties. White and McVay (1958) exchanged Li^{+1} for H^{+1}. According to Zoltai's classification of silicates (1960), $LiAlSi_2O_6$-II is similar to the following silicates: keatite (Shropshire *et al.*, 1959), petalite (Zemann-Hedlik *et al.*, 1955; Liebau, 1961), mordenite (Meier, 1961), dachiardite (Gottardi and Meier, 1963), and marialite scapolite (Papike and Zoltai, 1965). Each of them has a sharing coefficient of 2.0 and 5-membered rings of tetrahedra. It is interesting to note that they all have approximately the same Si—O—Si angles. The comparison is listed in Table 8.

Table 8. *A comparison of* Si—O—Si *angles among similar silicate structures*

	$LiAlSi_2O_6$-II	Keatite	Petalite	Marialite scapolite	Mordenite	Dachiardite
Sharing coefficients	2.0	2.0	2.0	2.0	2.0	2.0
Repeat-units and loops of tetrahedra	5—7—8	5—7—8	5—6	4—5—8	4—5—6—8	4—5—6—8
Si—O—Si angles						
(1) for oxygens at general positions	143.6°	149.3°	149.8°	138.3°	146.5°	142.7°
	150.7	155.3	153.0	139.0	152.6	146.7
	154.0	155.8				
(2) for oxygens at special positions	—	—	163.4	156.8	173.6	177.1
			166.0			

Lithium coordination

The structure is a stuffed derivative of the keatite structure. The Li atom is stuffed in an interstitial position but occupies a general 8-fold site. There are only four Li atoms per unit cell. They are distributed among four sets of paired sites of the 8-fold positions. Each Li atom occupies either of the two sites in each pair. The distance between the two sites in each pair is only 1.33 ± 0.10 Å, which is too short, for the Li atoms to occupy both sites simultaneously. If Li distribution among the eight sites is ordered rather than random, twinning may occur. At the present time we have no way to tell whether this kind of twinning exists or not. However, even if the twinning exists, it does not interfere with the structure analysis. The x-ray data merely shows that there is half a Li atom at each the 8-fold positions. It is interesting to note that the center of each pair of sites

Table 9. *Irregular lithium octahedron*

Atoms	Distances or angles	Atoms	Distances or angles
Li—O (Li$_1$ is at the center of each pair of sites of Li atoms)			
Li$_1$—O(1$_5$)	2.54 Å	Li$_1$—O(2$_6$)	1.84 Å
Li$_1$—O(1$_6$)	2.54	Li$_1$—O(3$_1$)	2.65
Li$_1$—O(2$_5$)	1.84	Li$_1$—O(3$_4$)	2.65
O—O (same length for regular octahedron)			
O(2$_5$)—O(1$_5$)	2.55 Å	O(1$_5$)—O(3$_4$)	3.84 Å
O(2$_5$)—O(1$_6$)	3.74	O(1$_5$)—O(1$_6$)	3.96
O(2$_5$)—O(3$_1$)	2.57	O(3$_1$)—O(3$_4$)	4.02
O(2$_5$)—O(3$_4$)	3.65		
O—Li—O (90°)			
O(1$_6$)—Li$_1$—O(2$_6$)	116.6°	O(1$_6$)—Li$_1$—O(3$_1$)	95.5°
O(1$_6$)—Li$_1$—O(2$_6$)	69.2	O(1$_6$)—Li$_1$—O(1$_5$)	102.4
O—Li—O (90°)			
O(2$_5$)—Li$_1$—O(3$_1$)	67.1°	O(2$_5$)—Li$_1$—O(3$_4$)	107.1°
O(2$_5$)—Li$_1$—O(1$_5$)	69.2		
O—Li—O (180°)			
O(1$_6$)—Li$_1$—O(3$_4$)	136.2°	O(2$_5$)—Li$_1$—O(2$_6$)	171.6°

of Li (a special 4-fold site) has distorted octahedral coordination. The three principal axes of the octahedron are approximately parallel to the *a*, *b* and *c* axes. The details of the geometry of the distorted octahedron are reported in Table 9 and illustrated in Fig. 3. The Li—O distances corresponding to the 6-fold site are 1.84 Å along the *c* axis, and 2.54 and 2.65 Å along the *a* and *b* axes. However, Li may occupy this octahedral position with rise in temperature. As discussed later, the *c* axis may expand, and both the *a* and *b* axes contract upon heating. This would probably adjust the Li—O distances to suit the 6-fold coordination. Besides, not much thermal energy would be required to move lithium just 0.66 Å from the present 4-fold to the new 6-fold coordination position.

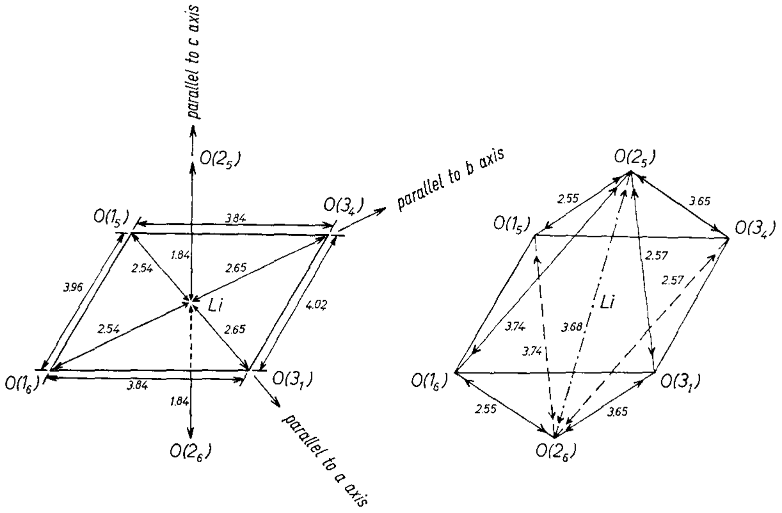

Fig. 3. The irregular lithium octahedron

The Li tetrahedron is irregular. The Li—O bond distances range from 1.933 to 2.269 Å with an average of 2.081 ± 0.041 Å. The O—Li—O tetrahedral angles range from 74.1° to 139.4° with an average of 110.5°. The mean Li—O bond distance of 2.10 Å is somewhat longer than other accurate tetrahedral Li—O values reported in the literature. For example, in Li_2CO_3 ZEMANN (1957) reported a distance of 1.97 Å, in $LiGaO_2$ and γ $LiAlO_2$ MAREZIO (1965) reported 1.99 and 2.00 Å, and in $Li_2SO_4 \cdot H_2O$ LARSON (1965) reported 1.95 Å. The average tetrahedral Li—O distance given in International tables for x-ray crystallography, Vol. III (1962) is 1.98 Å. The larger-than-average value of the Li—O bond distance may be caused by the fact that Li occupies an interstitial position.

Each Li tetrahedron shares two edges—one with Si(1) and one with Si(2) tetrahedra. The Si(1) tetrahedron shares only one edge with one Li tetrahedron, while the Si(2) tetrahedron shares two edges with two Li tetrahedra. As would be expected, the shared edges are the shortest for the Li tetrahedron and the (Si,Al) tetrahedra, i.e., 2.552 and 2.574 Å, as shown in italics in Table 6. The short shared edges permit reasonable (Si,Al)—Li distances of 2.628 and 2.710 Å, which are very close to the minimum Al—Li distance of 2.656 Å reported in γ $LiAlO_2$ by MAREZIO (1965). This edge shortening agrees

Table 10. *Additional four-fold tetrahedral sites for lithium*

Atoms	Distances or angles
(1) Special site 1 (0.64, 0.64, 0)	
Li_1—$O(1_3)$	2.147 Å
Li_1—$O(2_5)$	1.985
$O(1_3)$—$O(1_4)$	3.957
$O(1_3)$—$O(2_5)$	2.727
$O(1_3)$—$O(2_8)$	3.806
$O(2_5)$—$O(2_8)$	2.719
$O(1_3)$—Li_1—$O(1_4)$	134.4°
$O(1_3)$—Li_1—$O(2_5)$	82.5
$O(1_3)$—Li_1—$O(2_8)$	134.1
$O(2_5)$—Li_1—$O(2_8)$	86.4
(2) Special site 2 (0.80, 0.80, 0)	
Li_2—$O(2_3)$	2.025 Å
Li_2—$O(1_3)$	2.163
$O(1_3)$—$O(1_4)$	3.957
$O(1_3)$—$O(2_3)$	2.552
$O(1_3)$—$O(2_4)$	3.744
$O(2_3)$—$O(2_4)$	3.675
$O(1_3)$—Li_2—$O(1_4)$	132.3°
$O(1_3)$—Li_2—$O(2_3)$	75.0
$O(1_3)$—Li_2—$O(2_4)$	126.7
$O(2_3)$—Li_2—$O(2_4)$	130.3
(3) Special site 3 (0.95, 0.95, 0)	
Li_3—$O(2_3)$	1.984 Å
Li_3—$O(3_5)$	2.181
(3) Special site 3 (0.95, 0.95, 0)	
$O(2_3)$—$O(2_4)$	3.675 Å
$O(2_3)$—$O(3_5)$	2.574
$O(2_3)$—$O(3_8)$	3.647
$O(3_5)$—$O(3_8)$	4.018
$O(2_3)$—Li_3—$O(2_4)$	135.7°
$O(2_3)$—Li_3—$O(3_5)$	76.2
$O(2_3)$—Li_3—$O(3_8)$	122.2
$O(3_5)$—Li_3—$O(3_8)$	134.2
(4) General site (0.84, 0.49, 0.68)	
Li_4—$O(1_2)$	2.248 Å
Li_4—$O(1_8)$	1.981
Li_4—$O(2_7)$	2.243
Li_4—$O(3_3)$	2.204
$O(1_2)$—$O(1_8)$	2.695
$O(1_2)$—$O(2_7)$	3.877
$O(1_2)$—$O(3_3)$	4.134
$O(1_8)$—$O(2_7)$	3.744
$O(1_8)$—$O(3_3)$	3.843
$O(2_7)$—$O(3_3)$	2.574
$O(1_2)$—Li_4—$O(1_8)$	78.9°
$O(1_2)$—Li_4—$O(2_7)$	179.4
$O(1_2)$—Li_4—$O(3_3)$	136.4
$O(1_8)$—Li_4—$O(2_7)$	124.7
$O(1_8)$—Li_4—$O(3_3)$	133.3
$O(2_7)$—Li_4—$O(3_3)$	70.7

well with PAULING's rules (1960). According to PAULING, this is evidence that the structure has appreciable ionic character.

Several additional 4-fold tetrahedral sites other than the one which is occupied by Li are available. These sites include the three special positions ($x = 0.95$, 0.80, or 0.64) and one general position ($x = 0.85$, $y = 0.49$, $z = 0.68$). All of them are close to the sites indicated by SKINNER and EVANS (1960). The Li tetrahedra corresponding to these sites are listed in Table 10. Most of these Li tetrahedra are similar in geometry. The reasons why Li prefers the present site to the others are explained as follows: There are three independent oxygens, i.e., O(1), O(2), and O(3) and two independent (Si,Al), i.e., Si(1) and Si(2). Si(1) is coordinated to two O(1), one O(2), and one O(3) and Si(2) to two O(2) and two O(3). The Li is coordinated to two O(2), one O(1), and one O(3). Thus, all three independent oxygens have the same coordination number of three. If the Li atom occupies a special 4-fold site instead of the present general site, only two out of three independent oxygens will be used to coordinate the Li atoms. There will always be one independent oxygen whose negative charge is left unbalanced by Li^{+1}. In order to achieve better charge balance, no Li may occupy a special site. This leaves only the general site for consideration. Since the present Li site is coordinated to two O(2), one O(1), and one O(3), it is reasonable to assume that Li may occupy a general site so as to be coordinated either to two O(1), one O(2), and one O(3) or to two O(3), one O(1), and one O(2). No tetrahedral site could be found for the latter case. The Li tetrahedron corresponding to the former case is described in Table 10. This site was found to be less favorable because of the longer mean Li—O bond distance of 2.20 Å.

It is noted that each Li tetrahedron forms two 5-membered and one 6-membered rings with (Si,Al) tetrahedra. There are two independent 6-membered rings and three independent 5-membered rings formed by Li and (Si,Al) tetrahedra. They are listed in Table 11. All the 5-membered rings resembled the one made up by all (Si,Al) tetrahedra. It seems that the forming of 5- and 6-membered rings help to stabilize the lithium position. The isotropic temperature factor for lithium was found to be 1.79 Å^2 which falls between those of the oxygen atoms (1.08 to 2.01). This is also found to be the case for $Li_2SO_4 \cdot H_2O$ (LARSON 1965): Li: 1.45, oxygens: 1.23 to 2.62; for $LiC_6O_7H_7$ (GLUSKER *et al.*, 1965): Li: 2.04, oxygens: 1.44 to 2.20.

Table 11. *Five- and six-membered rings formed by* Li *and* (Si,Al) *tetrahedra*

Atoms	Distances or angles
(1) Li and (Si,Al) pentagon No. 1	
Li(1_2)—Si(1_2)	3.161 Å
Li(1_2)—Si(1_7)	3.302
Si(1_7)—Si(2_2)	3.142
Si(2_2)—Si(1_6)	3.142
Si(1_6)—Si(1_2)	3.183
Si(1_2)—Li(1_2)—Si(1_7)	93.1°
Li(1_2)—Si(1_7)—Si(2_2)	97.3
Si(1_7)—Si(2_2)—Si(1_6)	101.1
Si(2_2)—Si(1_6)—Si(1_2)	93.8
Si(1_6)—Si(1_2)—Li(1_2)	82.1
(2) Li and (Si,Al) pentagon No. 2	
Li(1_6)—Si(2_2)	2.710 Å
Li(1_6)—Si(2_1)	3.095
Si(2_1)—Si(1_1)	3.186
Si(1_1)—Si(1_7)	3.183
Si(1_7)—Si(2_2)	3.142
Si(2_2)—Li(1_6)—Si(2_1)	115.1°
Li(1_6)—Si(2_1)—Si(1_1)	88.6
Si(2_1)—Si(1_1)—Si(1_7)	106.1
Si(1_1)—Si(1_7)—Si(2_2)	93.8
Si(1_7)—Si(2_2)—Li(1_6)	109.0
(3) Li and (Si,Al) pentagon No. 3	
Li(1_6)—Si(2_2)	2.710 Å
Li(1_6)—Si(1_1)	3.302
Si(1_1)—Si(1_7)	3.183
Si(1_7)—Si(1_3)	3.183
Si(1_3)—Si(2_2)	3.186
Si(2_2)—Li(1_6)—Si(1_1)	115.2°
Li(1_6)—Si(1_1)—Si(1_7)	86.1
(3) Li and (Si,Al) pentagon No. 3	
Si(1_1)—Si(1_7)—Si(1_3)	121.1°
Si(1_7)—Si(1_3)—Si(2_2)	88.1
Si(1_3)—Si(2_2)—Li(1_6)	116.6
(4) Li and (Si,Al) hexagon No. 1	
Li(1_1)—Si(1_2)	2.627 Å
Li(1_1)—Si(1_1)	3.161
Si(1_1)—Si(1_7)	3.183
Si(1_7)—Si(2_2)	3.142
Si(2_2)—Si(1_6)	3.142
Si(1_6)—Si(1_2)	3.183
Si(1_2)—Li(1_1)—Si(1_1)	131.8°
Li(1_1)—Si(1_1)—Si(1_7)	82.1
Si(1_1)—Si(1_7)—Si(2_2)	93.8
Si(1_7)—Si(2_2)—Si(1_6)	101.1
Si(2_2)—Si(1_6)—Si(1_2)	93.8
Si(1_6)—Si(1_2)—Li(1_1)	68.5
(5) Li and (Si,Al) hexagon No. 2	
Li(1_5)—Si(1_5)	3.161 Å
Li(1_5)—Si(2_2)	3.095
Si(2_2)—Si(1_3)	3.186
Si(1_3)—Si(1_7)	3.183
Si(1_7)—Si(1_1)	3.183
Si(1_1)—Si(1_5)	3.183
Si(1_5)—Li(1_5)—Si(2_2)	115.1°
Li(1_5)—Si(2_2)—Si(1_3)	131.4
Si(2_2)—Si(1_3)—Si(1_7)	88.1
Si(1_3)—Si(1_7)—Si(1_1)	121.1
Si(1_7)—Si(1_1)—Si(1_5)	121.1
Si(1_1)—Si(1_5)—Li(1_5)	82.1

Thermal behavior

HUMMEL (1951) observed that $LiAlSi_2O_6$-II has the unusually small but positive mean thermal expansion coefficient of $9 \cdot 10^{-7}/°C$ between 20 and 1000 °C for polycrystalline aggregates. This small thermal-expansion coefficient may now be rationalized as follows: Each Li (or each pair of two half Li atoms) is located between two 5-membered rings of (Si,Al) tetrahedra, one oriented up, approximately parallel to (010), and one down, approximately parallel to (100). The five bridging oxygens within each 5-membered ring are almost coplanar and form a fairly regular pentagon. The two oxygens (one up and one down, and parallel to *c* axis) which are closest to the Li, form the minimum O—O—O angle of 91° in the oxygen pentagon. The minimum angle of 91° deviates appreciably from the ideal pentagon angle of 108°. This may indicate the existence of some strain in the 5-membered rings. Upon heating, thermal energy is used to relieve the strain by increasing the minimum O—O—O angle of 91° which, in turn, causes the raising and lowering of the two oxygen atoms (parallel to the *c* axis) closest to the Li atom. Thus, the *c* axis expands. As the four corresponding (Si,Al) tetrahedra change orientation, the two pairs of oxygen (parallel to the *a* and *b* axes, respectively) around the Li contract, and the *a* and *b* axes contract, as is illustrated in Fig. 4. As a result of this, the overall volume remains almost unchanged. The bond lengths and angles within each (Si,Al) tetrahedron change very little during heating. The only significant changes occur in the angles between the neigh-

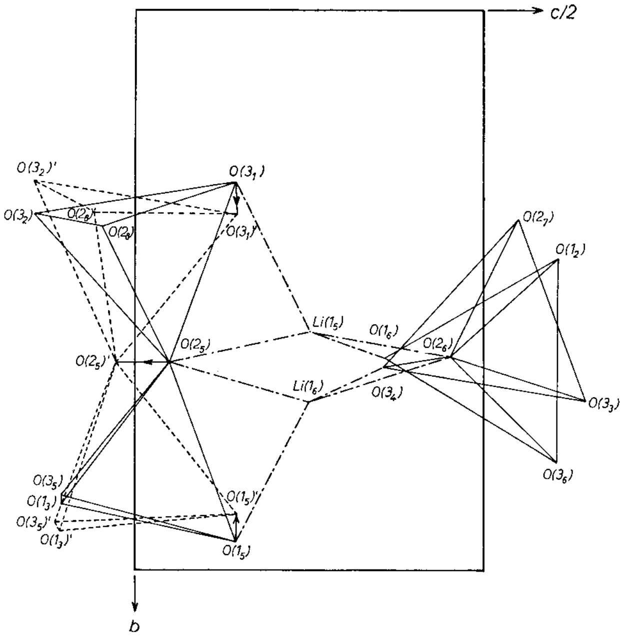

Fig. 4. Diagram illustrating the thermal expansion changes, with expansion of the *c* axis and contraction of the *a* axis

boring tetrahedra. As a further result of this expansion behavior, Li atoms are free to move from the present position of 4-fold coordination to the position of 6-fold coordination as described earlier.

$LiAlSi_2O_6$-II is a stuffed derivative of the keatite structure. In keatite, Keat (1954) found that, upon heating, the *c* axis expands up to 550 °C, and both the *a* and *b* axes contract up to about 250 °C. This observation may provide some evidence for the rationalization just described.

Acknowledgments

Most of the computation was done on the IBM 7090 at the University of Michigan. Part of the computation was done on an IBM 1620 at Owens-Illinois Technical Center in Toledo. Dr. F. R. Ahmed kindly supplied the 1620 computer programs. Thanks are due also to Dr. M. A. Conrad who supplied the $LiAlSi_2O_6$-II single crystals.

References

C. W. Burnham (1962), LCLSQ, Crystallographic lattice-constant least-squares refinement program. Carnegie Institute Washington Yearbook **61**, 132—135.

C. W. Burnham (1962), Absorption corrections for prismatic crystals and evaluation of end effect. Abstract, 1962 Meeting of the American Crystallographic Society, 19.

W. R. Busing, K. O. Martin and H. A. Levy (1964), ORFFE, A Fortran crystallographic function and error program. U.S. Atomic Energy Commission Publication, ORNL-TM-306.

D. W. J. Cruickshank (1965), Errors in least-squares methods in computing methods in crystallography. Edited by J. S. Rollett, Pergamon Press, New York, N.Y., 112—116.

J. P. Glusker, D. van der Helm, W. E. Love, M. L. Dornberg, J. A. Minkin, C. K. Johnson and A. L. Patterson (1965), The structures of sodium and lithium dihydrogen citrates. Acta Crystallogr. **19**, 561—572.

J. R. Goldsmith and F. Laves (1955), Cation order in anorthite ($CaAl_2Si_2O_8$) as revealed by gallium and germanium substitutions. Z. Kristallogr. **106**, 213—226.

G. Gottardi and W. M. Meier (1963), The crystal structure of dachiardite. Z. Kristallogr. **119**, 53—64.

W. C. Hamilton (1959), On the isotropic temperature factor equivalent to a given anisotropic temperature factor. Acta Crystallogr. **12**, 609—610.

R. A. Hatch (1943), Phase equilibrium in the system $Li_2O—Al_2O_3—SiO_2$. Amer. Mineralogist **28**, 471—496.

E. W. Hughes (1941), The crystal structure of melamine. J. Amer. Chem. Soc. **63**, 1737—1752.

F. A. Hummel (1951), Thermal expansion properties of some synthetic lithia minerals. J. Amer. Ceram. Soc. **34**, 235—239.

International tables for x-ray crystallography (1962), Vol. III, Birmingham: Kynoch Press.

P. P. Keat (1954), A new crystalline silica. Science **120**, 328—330.

A. C. LARSON (1965), The crystal structure of $Li_2SO_4 \cdot H_2O$, a three-dimensional refinement. Acta Crystallogr. **18**, 717—724.

F. LIEBAU (1961), Zur Kristallstruktur von Petalit $LiAlSi_4O_{10}$. Acta Crystallogr. **14**, 339—406.

W. LOEWENSTEIN (1954), The distribution of aluminum in the tetrahedra of silicates and aluminates. Amer. Mineralogist **39**, 92—96.

M. MAREZIO (1965), The crystal structure of $LiGaO_2$. Acta Crystallogr. **18**, 481—484.

M. MAREZIO (1965), The crystal structure of γ-$LiAlO_2$. Acta Crystallogr. **19**, 396—400.

W. M. MEIER (1961), The crystal structure of mordenite. Z. Kristallogr. **115**, 439—450.

J. W. MELLOR (1925), Treatise on inorganic and theoretical chemistry. Vol. **6**, 640—643, Longmans Green Co., London.

J. J. PAPIKE and T. ZOLTAI (1965), The crystal structure of a marialite scapolite. Amer. Mineralogist **50**, 641—655.

L. PAULING (1960), The nature of the chemical bond. Third Ed., Cornell University Press, Ithaca, N.Y., pp. 561—562.

C. T. PREWITT (1962), SFLSQ2, An IBM 7090 program for least-squares refinement, PhD thesis, M.I.T.

R. ROY, D. M. ROY and E. F. OSBORN (1950), Compositional and stability relationships among the lithium aluminosilicates: eucryptite, spodumene and petalite. J. Amer. Ceram. Soc. **33**, 152—159.

H. SAALFELD (1961), Zur thermischen Umwandlung und Kristallographie von Petalit und Spodumen. Z. Kristallogr. **115**, 420—432. — B. J. SKINNER and H. T. EVANS, Discussion of the paper „Zur thermischen Umwandlung und Kristallographie von Petalit und Spodumen" by H. SAALFELD. Z. Kristallogr. **117** (1962) 227—230. — H. SAALFELD, Erwiderung auf die Diskussionsbemerkung von B. J. SKINNER und H. T. EVANS über meine Veröffentlichung: „Zur thermischen Umwandlung und Kristallographie von Petalit und Spodumen". Z. Kristallogr. **117** (1962) 231—232.

H. SAALFELD (1961), Struktur und Ausdehnungsverhalten von Li—Al-Silicaten. Berichte Deutschen Keram. Gesellschaft **38**, 281—338.

J. SHROPSHIRE, P. P. KEAT and P. A. VAUGHAN (1959), The crystal structure of keatite, a new form of silica. Z. Kristallogr. **112**, 409—413.

B. J. SKINNER and H. T. EVANS (1960), Crystal chemistry of β-spodumene solid solutions on the join $Li_2O \cdot Al_2O_3 \cdot SiO_2$. Amer. Journ. Science, Bradley Vol. **238**-A, 312—324.

J. V. SMITH and S. W. BAILEY (1963), Second review of Al—O and Si—O tetrahedral distances. Acta Crystallogr. **16**, 801—811.

G. D. WHITE and T. N. MCVAY (1958), Some aspects of the recovery of lithium from spodumene. U.S. Atomic Energy Comm., ORNL-2450.

J. ZEMANN (1957), Die Kristallstruktur von Li_2CO_3. Acta Crystallogr. **10**, 664—666.

A. ZEMANN-HEDLIK and J. ZEMANN (1955), Die Kristallstruktur von Petalit $LiAlSi_4O_{10}$. Acta Crystallogr. **8**, 781—787.

T. ZOLTAI (1960), Classification of silicates and other minerals with tetrahedral structures. Amer. Mineralogist **45**, 960—973.