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Crystal Structure of Ordered Li_4SiO_4

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Abstract

Ordered Li_4SiO_4 is monoclinic with space group $P2_1/m$ and $a = 11{\cdot}546$ (3), $b = 6{\cdot}090$ (2), $c = 16{\cdot}645$ (3) Å, $\beta = 99{\cdot}5$ (1)°. The substructure is identical to the previously refined structure of Li_4SiO_4 [Völlenkle, Wittman & Nowotny (1968). *Monatsh. Chem.* **99**, 1360–1371]. The superstructure was solved and refined to $R_w = 6\%$ for 1390 independent reflections. The Li atoms are ordered and occupy 19 of 42 sites in the sevenfold supercell. The LiO_4, LiO_5 and LiO_6 polyhedra are linked by edge- and corner-sharing. There is good three-dimensional connectivity between Li sites at distances of 2·9 Å from one another; most Li atoms share edges with at least two adjacent polyhedra. The ordered nature of Li_4SiO_4 is consistent with the low ionic conductivity of pure Li_4SiO_4 whereas good conductivity of $Li_{4-x}Si_{1-x}P_xO_4$, $Li_{4-2x}Si_{1-x}S_xO_4$ and $Li_{4+x}Si_{1-x}Al_xO_4$ is consistent with the good Li site connectivity and the introduction of either Li vacancies or Li interstitials.

Introduction

Compositions of the type $Li_{4-x}Si_{1-x}P_xO_4$, $Li_{4-2x}Si_{1-x}S_xO_4$ and $Li_{4+x}Si_{1-x}Al_xO_4$ have good Li^+ ion mobility (Shannon, Taylor, English & Berzins, 1977; Hu, Raistrick & Huggins, 1976; Shannon & Taylor, 1977). The structure of the parent compound Li_4SiO_4 is of interest in order to explain the high Li conductivity of the substituted compounds. Völlenkle, Wittman & Nowotny (1968) reported the structure of Li_4SiO_4 with the monoclinic unit cell $a = 5{\cdot}14$, $b = 6{\cdot}10$, $c = 5{\cdot}30$ Å, $\beta = 90{\cdot}5°$ and space group $P2_1/m$.

The structure was reported to contain six crystallographically different Li atoms. All the Li sites were partially occupied with occupancy factors ranging from $\frac{1}{3}$ to $\frac{2}{3}$. This structure is inconsistent with the knowledge that: (1) pure Li_4SiO_4 is a poor ionic conductor with $\sigma(RT) < 10^{-5}\ (\Omega m)^{-1}$ (West, 1973; Gratzer, Bittner, Nowotny & Seifert, 1971; Hodge, Ingram & West, 1976); (2) creation of Li vacancies or interstitials raises the conductivity by a factor of $\sim 10^3$–10^4.

These discrepancies led us to suspect that the Li positions were incorrect. An infrared absorption study by Lazarev, Kolesova, Solntseva, & Mirgorodskii (1973) suggested that the space group is really $P2_1$ rather than $P2_1/m$. A second harmonic generation (SHG) test, however, showed Li_4SiO_4 to be most likely centrosymmetric and this means that space group $P2_1$ is not probable. Finally, electron diffraction patterns of certain crystals revealed weak superstructure reflections and a unit cell much larger than that found by Völlenkle, Wittman & Nowotny (1968). This paper describes the structure of ordered Li_4SiO_4.

Experimental

Crystals of Li_4SiO_4 were grown by the Czochralski method from a melt at ~ 1523 K. Starting materials were $LiOH.H_2O$ and SiO_2. Emission spectrographic analysis showed $\sim 0{\cdot}5\%$ total impurities (Shannon, Taylor, English & Berzins, 1977). A powder diffraction pattern taken with a Hägg–Guinier camera (298 K, Cu $K\alpha$ radiation and a KCl internal standard) was indexed using the Völlenkle, Wittman & Nowotny (1968) cell. Refined cell dimensions of this subcell are $a = 5{\cdot}148$ (1), $b = 6{\cdot}099$ (1), $c = 5{\cdot}296$ (1) Å, $\beta = 90{\cdot}31°$, and $V = 166{\cdot}3$ Å^3. No superlattice lines were observed even with a 12 h exposure.

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Specimens were prepared for electron diffraction (ED) by grinding a crystal in an agate mortar. Small fragments (0·1–1 μm diameter) were then collected onto specimen grids. Crystal fragments with orientations having low-index zone axes with respect to the incident electron-beam directions were chosen and aligned with a goniometer stage in the microscope (100 kV). ED patterns with various orientations were collected from nearly 100 fragments. Interpretable electron micrographs could not be obtained because the crystals decomposed very quickly under intense electron-beam irradiation. Therefore, only ED patterns were studied.

Figs. 1(*a*) and 1(*b*) show two different reciprocal-lattice sections with zone axes of [010] and [211], respectively. Weak extra spots in both patterns indicate a superstructure. The a_s and b_s axes of the superstructure cell are parallel to [30$\bar{1}$] and [102], respectively, with lengths of $\frac{1}{7}$[301] and $\frac{1}{7}$[102]. All the patterns could be indexed by the X-ray diffraction data, confirming that the crystal had not changed structurally in the process of specimen preparation (mechanical deformation) nor during electron-beam irradiation. Approximate unit-cell parameters determined from these photos were $a = 11{\cdot}35$, $b = 6{\cdot}10$, $c = 16{\cdot}5$ Å and $\beta = 98°$. The superstructure was not always observed, suggesting that the superstructure does not occur in an entire crystal, but forms probably as domains. The domain size must not be smaller than an order of 1 μm. Li_4SiO_4 must, therefore, exist in both an ordered and a disordered state.

Intensity data were obtained on a crystal approximately 0·2 × 0·3 × 0·3 mm with a Picker FACS-I diffractometer. The crystal was oriented with the spindle parallel to **b**. Although the superstructure was not observed in all crystals using electron diffraction, it was observed in two separate crystals chosen for X-ray analysis. With nine subcell reflections, least-squares refinement gave $a = 5{\cdot}147\,(2)$, $b = 6{\cdot}094\,(2)$, $c = 5{\cdot}293\,(2)$ Å and $\beta = 90{\cdot}33\,(4)°$. The supercell dimensions can be obtained from the transformation:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix}_{\text{supercell}} = [T] \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{subcell}},$$

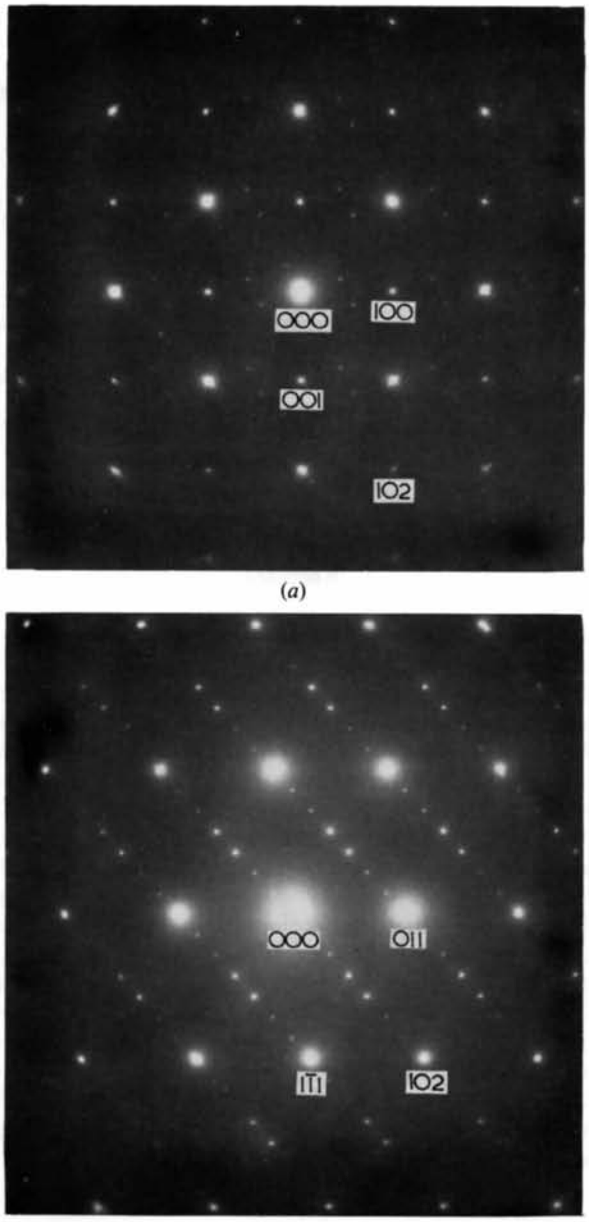
with

$$[T] = \begin{pmatrix} 2 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & \bar{3} \end{pmatrix},$$

and the atomic parameters can be derived by:

$$x_{\text{supercell}} = [\tilde{T}]^{-1}\, x_{\text{subcell}};$$

$$[\tilde{T}]^{-1} = \frac{1}{7} \begin{pmatrix} 3 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & \bar{2} \end{pmatrix}.$$



(*a*)

(*b*)

Fig. 1. (*a*) Electron diffraction pattern showing reciprocal-lattice section with zone axis [010]. (*b*) Electron diffraction pattern showing reciprocal-lattice section with zone axis [211].

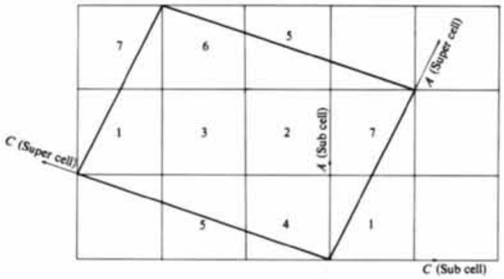


Fig. 2. Relationship of subcell to supercell.

Fig. 2 shows the relationship of the subcell to the supercell. Using the transformation matrix, we obtained the supercell parameters: $a = 11\cdot551$, $b = 6\cdot094$, $c = 16\cdot719$ Å, $\beta = 99\cdot03°$. The volume of this supercell is seven times that of the subcell. Table 1 shows the powder pattern of Li_4SiO_4 indexed on this supercell. Refined cell dimensions from these data are: $a = 11\cdot546$ (3), $b = 6\cdot090$ (2), $c = 16\cdot645$ (3) Å and $\beta = 99\cdot5$ (1)°. These parameters were used for all calculations involving bond lengths and angles. Zero and upper level precession photographs along the b axis confirmed the supercell found from electron diffraction. The space group was assumed to be $P\,2_1/m$.

Table 1. *Powder diffraction data for* Li_4SiO_4

	d_{obs}	d_{calc}	I/I_0
−103	5·279	5·284	30
201	5·121	5·123	20
−113	3·988	3·991	65
211	3·922	3·920	60
−302	3·693	3·685	15
104	3·669	3·672	50
203		3·654	
−204	3·623	3·625	20
020	3·045	3·045	15
−304		3·049	
−206	2·643	2·642	90
−123	2·640	2·638	100
221	2·620	2·617	50
−222		2·613	
−411		2·608	
106	2·571	2·565	70
410		2·579	
402		2·561	
304		2·581	
−216	2·427	2·424	5
−405	2·352	2·351	40
−322	2·348	2·347	40
007		2·345	
124		2·344	
223		2·339	
501	2·201	2·206	5
017	2·191	2·188	20
−415		2·194	
−406	2·159	2·159	5
−511		2·158	
−307		2·161	
315		2·153	
−416	2·032	2·034	5
−505		2·035	
−317		2·036	
−423		2·026	
031	2·013	2·014	10
−133	1·897	1·895	10
415		1·894	
−326		1·893	
−603		1·892	
033		1·903	
513		1·890	
504	1·866	1·864	10
118		1·868	
307		1·862	
−425		1·861	

A total of 4001 reflections from the upper half of the sphere (with $3 < 2\theta < 50°$) were collected with Mo $K\overline{\alpha}$ radiation with a Zr filter. The intensities were measured by scanning in the $2\theta/\omega$ mode at 0·4° min^{-1} and a scan range of $\Delta\theta = 1\cdot40 + 0\cdot02 \tan\theta$. Background was obtained by stationary counting at the scan extremes for 40 s each. The $62\bar{3}$ reflection was chosen as an internal standard and measured every 50 reflections. No significant deviation in its intensity was observed. A ψ scan on the 060 reflection indicated that the effects of absorption were small. Therefore, no absorption correction was made. Although the number of variables is somewhat high, no measurements of intensities with $2\theta > 50$ were collected because at high angles the superstructure reflections became very weak. The 4001 nonunique reflections corresponded to 1390 unique reflections for which $I > 3\sigma(I)$. Intensities were corrected for Lorentz and polarization factors. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

The subcell contains two Li_4SiO_4 formula units. The first refinement using only the subcell reflections with the starting atomic parameters given by Völlenkle, Wittman & Nowotny (1968) quickly converged to $R = 0\cdot05$. The Si—O lengths and O—Si—O angles are only slightly different from those of Völlenkle, Wittman & Nowotny (1968). In this refinement, the eight Li atoms per unit cell were allowed to occupy statistically three sets of general equivalent positions (multiplicity of four) and three sets of special equivalent positions (multiplicity of two) for a total of 18 individual atomic sites per subcell.

The atomic coordinates of the SiO_4 group found in the previous refinement are in fact the average positions of the seven crystallographically independent groups in the superstructure and the 56 Li atoms per supercell are in 18 individual sites of the subcell. The problem was to locate 56 Li atoms among 126 (= 7 × 18) possible individual atomic sites in the unit cell of the superstructure. Of these 126 potential sites, some pairs cannot be occupied simultaneously because their distances would be too short. Based on such geometrical restrictions, 12 Li occupation models were found. Refinements varying only scale factor, overall temperature factor and population factor of Li atoms led to the six most probable models with the lowest R (0·25–0·26). Refining the six models by varying positional and isotropic temperature factors of all atoms did not lower R significantly. Difference Fourier maps had too many residual peaks of the same order of magnitude to find the remaining Li positions. However, once the Si—Si, Si—O and O—O peaks were located on the Patterson map there were still some non-zero density regions on this map. All possible Si—Li vectors were computed and some Si—Li peaks were identified, especially those in the planes $b = 0, \frac{1}{2}$. By trial and error and using the Patterson map and distance constraints, we obtained a structure model with R = 0·18. The five Li atoms still missing were located by successive Fourier analyses.

A refinement with isotropic temperature factors including all atoms of the structure reduced R_w from 0·14 to 0·06 after eight cycles of full-matrix refinement. The 255 substructure reflections alone with a mean F_{obs} of 168 yielded an R_w of 0·023, while the 1135 superstructure reflections alone with a mean F_{obs} of 28 had an R_w of 0·082. A refinement with anisotropic temperature factors for the heavy atoms improved R, but the determinant of the anisotropic coefficients had become non-positive for two Si and three O atoms. This was due either to poor diffraction data or to remaining errors in the resolution of the superstructure. A difference Fourier map showed that the residual background was generally within ±0·2 e and there was only one residual peak with a value above 0·5 e. This residual peak located at (0·95, 0·05, 0·16) had a magnitude less than one third of a Li atom. Since it was only 0·8 Å from Li(51), it was considered to be caused by one of the factors mentioned above. The scatter in the values of the isotropic temperature factors, the inability to refine meaningful anisotropic temperature factors and the relatively high R value for the superstructure reflections all indicate that this refinement is not as precise as we might wish. Table 2 contains the final atomic and isotropic thermal parameters. The bond distances and angles are listed in Table 3*.

Table 2. *Positional* ($\times 10^4$) *and thermal* ($\times 10^2$) *parameters*

	x	y	z	B (Å^2)
Si(11)	3416 (2)	2500	0056 (2)	82 (6)
Si(12)	7540 (2)	2500	1386 (2)	74 (5)
Si(13)	4772 (2)	2500	7152 (2)	37 (5)
Si(14)	2003 (2)	2500	2924 (2)	33 (5)
Si(15)	0406 (2)	2500	5773 (2)	83 (6)
Si(16)	8941 (2)	2500	8567 (2)	30 (5)
Si(17)	6145 (2)	2500	4280 (2)	48 (5)
O(11)	3560 (3)	0265 (8)	0579 (3)	53 (9)
O(12)	7860 (4)	0342 (8)	1956 (3)	145 (10)
O(13)	4994 (3)	0305 (8)	7715 (3)	125 (10)
O(14)	2185 (3)	0283 (8)	3484 (3)	70 (9)
O(15)	0668 (4)	0316 (8)	6344 (3)	136 (10)
O(16)	9269 (3)	0330 (7)	9175 (2)	38 (9)
O(17)	6530 (3)	0283 (7)	4811 (2)	37 (8)
O(21)	1998 (5)	2500	9638 (4)	92 (14)
O(22)	6186 (5)	2500	0977 (4)	60 (13)
O(23)	3352 (5)	2500	6744 (4)	45 (13)
O(24)	0626 (5)	2500	2447 (4)	93 (14)
O(25)	9082 (5)	2500	5278 (4)	71 (13)
O(26)	7611 (5)	2500	8143 (4)	95 (14)
O(27)	4745 (5)	2500	3985 (4)	87 (14)
O(31)	4194 (4)	2500	9341 (4)	9 (12)
O(32)	8436 (5)	2500	0682 (4)	88 (14)
O(33)	5526 (6)	2500	6386 (4)	140 (15)
O(34)	2842 (5)	2500	2228 (4)	120 (14)
O(35)	1308 (5)	2500	5114 (4)	83 (13)
O(36)	9918 (5)	2500	7957 (4)	73 (13)
O(37)	6967 (5)	2500	3561 (4)	49 (13)
Li(12)	3823 (8)	0072 (19)	4068 (6)	88 (21)
Li(15)	8123 (8)	0006 (20)	5448 (6)	108 (21)
Li(16)	6605 (8)	0112 (20)	8270 (6)	103 (22)
Li(17)	5255 (8)	9981 (20)	1173 (6)	126 (23)
Li(21)	2722 (15)	2500	8558 (12)	226 (40)
Li(23)	4176 (15)	2500	5491 (12)	258 (42)
Li(24)	1321 (11)	2500	1464 (9)	20 (28)
Li(25)	9695 (18)	2500	4271 (14)	355 (50)
Li(32)	4490 (12)	2500	2780 (10)	122 (33)
Li(36)	7272 (12)	2500	6977 (10)	90 (31)
Li(37)	5940 (13)	2500	9794 (10)	113 (32)
Li(41)	1962 (7)	9631 (17)	0192 (6)	33 (19)
Li(43)	3309 (8)	9681 (20)	7279 (7)	143 (23)
Li(46)	9515 (9)	0298 (20)	7108 (7)	168 (24)
Li(51)	0790 (14)	0278 (33)	8663 (10)	479 (40)
Li(53)	2373 (9)	0379 (20)	5977 (7)	173 (24)
Li(61)	1407 (15)	2500	7360 (12)	231 (40)
Li(64)	0082 (16)	2500	0076 (12)	230 (39)
Li(65)	8701 (19)	2500	2956 (15)	404 (54)

Description of the structure

The unit cell of our Li_4SiO_4 crystals contains 14 formula units, seven times as large as the cell described by Völlenkle, Wittman & Nowotny (1968). Because electron diffraction showed only certain crystals to have a superstructure, we cannot say that the Völlenkle, Wittman & Nowotny (1968) structure is, in fact, in error. They may have solved only the substructure or they may have indeed found a disordered crystal. Table 4 shows reasonable agreement between their Li occupation factors and the ratio of occupied Li sites over the number of available sites for ordered Li_4SiO_4. We looked at two different crystals; both clearly showed superstructure reflections. Although it seems possible that Völlenkle, Wittman & Nowotny (1968) determined the structure of disordered Li_4SiO_4, the question then still remains as to why disordered Li_4SiO_4 is not a good conductor. Perhaps only a small fraction of polycrystalline Li_4SiO_4 is disordered.

In this refinement of ordered Li_4SiO_4, the Li atoms are referenced by two digits. The first indexes the atom in a particular subcell, whereas the second indexes the subcell. Thus, Li(34) refers to the third Li atom in the fourth subcell.

The general features of the SiO_4^{4-} arrangement are identical to those found by Völlenkle, Wittman & Nowotny (1968). Seven isolated SiO_4^{4-} tetrahedra are located in the mirror plane at $y = \frac{1}{4}, \frac{3}{4}$ and are related by the 2_1 axes along [010]. The SiO_4 tetrahedra are more distorted than in most orthosilicates. Individual Si—O distances and O—Si—O angles range from 1·58 to 1·69 Å and from 103 to 116°, respectively. Mean Si—O distances range from 1·623 to 1·646 Å. Such

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* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34374 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

scatter is consistent with the variation of mean bond lengths of SiO_4 tetrahedra observed in a sample of 50 precisely determined orthosilicates (Baur, 1978). The distortions correspond approximately to the bond-strength distributions (Table 5). By and large, longer Si—O distances are associated with greater total Li—O

Table 3. *Bond distances* (Å) *and angles* (°) *in* Li_4SiO_4

Si(11)–O(11) ×2	1·609 (5)	Si(11)–O(21)	1·670 (6)	Si(11)–O(31)	1·605 (8)
Si(12)–O(12) ×2	1·627 (5)	Si(12)–O(22)	1·599 (6)	Si(12)–O(32)	1·686 (6)
Si(13)–O(13) ×2	1·628 (5)	Si(13)–O(23)	1·668 (5)	Si(13)–O(33)	1·658 (7)
Si(14)–O(14) ×2	1·634 (5)	Si(14)–O(24)	1·656 (6)	Si(14)–O(34)	1·628 (7)
Si(15)–O(15) ×2	1·634 (5)	Si(15)–O(25)	1·612 (6)	Si(15)–O(35)	1·632 (6)
Si(16)–O(16) ×2	1·670 (4)	Si(16)–O(26)	1·581 (6)	Si(16)–O(36)	1·638 (6)
Si(17)–O(17) ×2	1·635 (4)	Si(17)–O(27)	1·610 (5)	Si(17)–O(37)	1·646 (6)
Average	1·634 (5)	Average	1·628 (6)	Average	1·642 (6)
Values obtained by refinement of the substructure	1·637 (1)		1·634 (1)		1·641 (1)

Li(12)–O(27)	1·84 (1)	Li(15)–O(14)	1·88 (1)	Li(16)–O(26)	1·90 (1)	Li(17)–O(31)	1·90 (1)
Li(12)–O(33)	1·94 (1)	Li(15)–O(25)	1·93 (1)	Li(16)–O(13)	1·94 (1)	Li(17)–O(13)	1·93 (1)
Li(12)–O(14)	1·98 (1)	Li(15)–O(35)	1·96 (1)	Li(16)–O(34)	1·95 (1)	Li(17)–O(22)	1·93 (1)
Li(12)–O(17)	1·99 (1)	Li(15)–O(17)	1·97 (1)	Li(16)–O(11)	1·97 (1)	Li(17)–O(11)	2·05 (1)
Li(21)–O(31)	1·96 (2)	Li(23)–O(17) ×2	1·91 (1)	Li(24)–O(24)	1·94 (1)	Li(25)–O(25)	1·92 (2)
Li(21)–O(12) ×2	2·00 (1)	Li(23)–O(33)	1·97 (2)	Li(24)–O(34)	1·99 (1)	Li(25)–O(15) ×2	2·01 (2)
Li(21)–O(21)	2·10 (2)	Li(23)–O(23)	2·43 (2)	Li(24)–O(16) ×2	2·08 (1)	Li(25)–O(35)	2·14 (2)
Li(32)–O(34)	1·97 (1)	Li(36)–O(26)	1·92 (2)	Li(37)–O(11) ×2	1·92 (1)	Li(41)–O(11)	1·89 (1)
Li(32)–O(27)	1·98 (2)	Li(36)–O(14) ×2	2·00 (1)	Li(37)–O(22)	1·94 (2)	Li(41)–O(16)	1·90 (1)
Li(32)–O(13) ×2	2·03 (1)	Li(36)–O(33)	2·09 (1)	Li(37)–O(31)	2·03 (1)	Li(41)–O(32)	1·95 (1)
						Li(41)–O(21)	1·98 (1)
Li(43)–O(37)	1·92 (1)	Li(46)–O(24)	1·88 (1)	Li(51)–O(36)	1·96 (2)	Li(53)–O(17)	2·01 (1)
Li(43)–O(23)	1·94 (1)	Li(46)–O(36)	1·95 (1)	Li(51)–O(12)	2·04 (2)	Li(53)–O(37)	2·01 (1)
Li(43)–O(13)	2·00 (1)	Li(46)–O(15)	1·99 (1)	Li(51)–O(16)	2·08 (2)	Li(53)–O(23)	2·03 (1)
Li(43)–O(12)	2·00 (1)	Li(46)–O(14)	2·08 (1)	Li(51)–O(32)	2·13 (2)	Li(53)–O(15)	2·16 (1)
				Li(51)–O(21)	2·38 (2)	Li(53)–O(35)	2·16 (1)
Li(61)–O(36)	2·12 (2)	Li(64)–O(16) ×2	2·10 (1)	Li(65)–O(15) ×2	2·13 (2)		
Li(61)–O(12) ×2	2·17 (1)	Li(64)–O(16) ×2	2·19 (1)	Li(65)–O(12) ×2	2·22 (2)		
Li(61)–O(15) ×2	2·21 (2)	Li(64)–O(32)	2·29 (2)	Li(65)–O(37)	2·39 (2)		
Li(61)–O(23)	2·62 (2)	Li(64)–O(21)	2·44 (2)	Li(65)–O(24)	2·51 (2)		

O(11)–Si(11)–O(21) ×2	103·4 (2)	O(12)–Si(12)–O(22) ×2	111·1 (2)	O(13)–Si(13)–O(23) ×2	106·6 (2)
O(11)–Si(11)–O(31) ×2	112·4 (2)	O(12)–Si(12)–O(32) ×2	107·4 (2)	O(13)–Si(13)–O(33) ×2	112·9 (2)
O(11)–Si(11)–O(11)	115·5 (2)	O(12)–Si(12)–O(12)	107·7 (3)	O(13)–Si(13)–O(13)	110·4 (3)
O(21)–Si(11)–O(31)	108·7 (3)	O(22)–Si(12)–O(32)	111·9 (4)	O(23)–Si(13)–O(33)	107·0 (4)
O(14)–Si(14)–O(24) ×2	107·2 (2)	O(15)–Si(15)–O(25) ×2	111·5 (2)	O(16)–Si(16)–O(26) ×2	112·2 (2)
O(14)–Si(14)–O(34) ×2	111·7 (2)	O(15)–Si(15)–O(35) ×2	108·3 (2)	O(16)–Si(16)–O(36) ×2	105·4 (2)
O(14)–Si(14)–O(14)	111·4 (3)	O(15)–Si(15)–O(15)	109·0 (3)	O(16)–Si(16)–O(16)	104·7 (3)
O(24)–Si(14)–O(34)	107·2 (4)	O(25)–Si(15)–O(35)	108·2 (4)	O(26)–Si(16)–O(36)	116·2 (4)
O(17)–Si(17)–O(27) ×2	109·6 (2)	O(17)–Si(17)–O(37) ×2	104·8 (2)	O(17)–Si(17)–O(17)	111·4 (3)
O(27)–Si(17)–O(37)	116·7 (4)				
O(14)–Li(12)–O(27)	115·3 (6)	O(25)–Li(15)–O(17)	111·2 (6)	O(13)–Li(16)–O(26)	117·3 (6)
O(14)–Li(12)–O(33)	105·1 (5)	O(25)–Li(15)–O(35)	107·3 (6)	O(13)–Li(16)–O(34)	101·7 (5)
O(14)–Li(12)–O(17)	98·1 (4)	O(25)–Li(15)–O(14)	114·6 (6)	O(13)–Li(16)–O(11)	103·4 (5)
O(27)–Li(12)–O(17)	111·6 (6)	O(17)–Li(15)–O(14)	102·2 (5)	O(26)–Li(16)–O(11)	110·9 (6)
O(27)–Li(12)–O(33)	110·7 (5)	O(17)–Li(15)–O(35)	99·6 (5)	O(26)–Li(16)–O(34)	109·2 (5)
O(17)–Li(12)–O(33)	115·5 (6)	O(14)–Li(15)–O(35)	120·7 (6)	O(34)–Li(16)–O(11)	114·2 (6)
O(11)–Li(17)–O(22)	111·4 (6)	O(21)–Li(21)–O(31)	81·7 (8)	O(23)–Li(23)–O(33)	74·0 (7)
O(11)–Li(17)–O(31)	102·4 (5)	O(21)–Li(21)–O(12) ×2	102·3 (7)	O(23)–Li(23)–O(17) ×2	90·9 (7)
O(11)–Li(17)–O(13)	100·9 (5)	O(31)–Li(21)–O(12) ×2	118·5 (5)	O(33)–Li(23)–O(17) ×2	116·7 (5)
O(22)–Li(17)–O(13)	114·2 (6)	O(12)–Li(21)–O(12)	120·1 (9)	O(17)–Li(23)–O(17)	124·9 (9)
O(22)–Li(17)–O(31)	108·6 (4)				
O(13)–Li(17)–O(31)	118·4 (7)				
O(24)–Li(24)–O(34)	84·6 (6)	O(25)–Li(25)–O(35)	80·5 (9)	O(27)–Li(32)–O(34)	116·3 (9)
O(24)–Li(24)–O(16) ×2	106·6 (5)	O(25)–Li(25)–O(15) ×2	111·6 (7)	O(27)–Li(32)–O(13) ×2	114·0 (5)
O(34)–Li(24)–O(16) ×2	120·4 (3)	O(35)–Li(25)–O(15) ×2	114·9 (6)	O(34)–Li(32)–O(13)	97·8 (5)
O(16)–Li(24)–O(16)	111·9 (6)	O(15)–Li(25)–O(15)	117·5 (11)	O(13)–Li(32)–O(13)	114·8 (7)
O(26)–Li(36)–O(33)	119·8 (8)	O(22)–Li(37)–O(31)	110·3 (8)	O(11)–Li(41)–O(21)	83·4 (5)
O(26)–Li(36)–O(14) ×2	111·3 (5)	O(22)–Li(37)–O(11) ×2	109·1 (5)	O(11)–Li(41)–O(32)	119·2 (5)
O(33)–Li(36)–O(14)	111·3 (5)	O(31)–Li(37)–O(11) ×2	102·3 (5)	O(11)–Li(41)–O(16)	125·8 (6)
O(33)–Li(36)–O(14)	99·1 (5)	O(11)–Li(37)–O(11)	123·0 (8)	O(21)–Li(41)–O(16)	108·8 (5)
O(14)–Li(36)–O(14)	115·6 (8)			O(21)–Li(41)–O(32)	105·1 (5)
				O(16)–Li(41)–O(32)	108·4 (5)

Table 3 (*cont.*)

O(13)–Li(43)–O(23)	84·3 (5)	O(36)–Li(46)–O(15)	110·8 (6)	O(16)–Li(51)–O(36)	81·4 (6)
O(13)–Li(43)–O(37)	115·6 (6)	O(36)–Li(46)–O(24)	111·4 (6)	O(16)–Li(51)–O(32)	96·6 (8)
O(13)–Li(43)–O(12)	119·2 (6)	O(36)–Li(46)–O(14)	123·8 (6)	O(12)–Li(51)–O(36)	100·7 (8)
O(23)–Li(43)–O(12)	111·7 (6)	O(15)–Li(46)–O(14)	112·2 (6)	O(12)–Li(51)–O(32)	79·7 (8)
O(23)–Li(43)–O(37)	107·0 (6)	O(15)–Li(46)–O(24)	111·6 (6)	O(21)–Li(51)–O(16)	98·7 (7)
O(12)–Li(43)–O(37)	114·2 (6)	O(14)–Li(46)–O(24)	84·0 (6)	O(21)–Li(51)–O(36)	101·6 (8)
				O(21)–Li(51)–O(12)	92·2 (6)
				O(21)–Li(51)–O(32)	87·3 (5)
				O(36)–Li(51)–O(32)	171·0 (10)
				O(12)–Li(51)–O(16)	168·3 (11)

O(15)–Li(53)–O(23)	105·9 (6)	O(12)–Li(61)–O(15) ×2	89·4 (2)	O(16)–Li(64)–O(16)	78·0 (7)	O(12)–Li(65)–O(37) ×2	91·3 (7)
O(15)–Li(53)–O(35)	75·7 (4)	O(12)–Li(61)–O(12)	106·1 (8)	O(16)–Li(64)–O(16)	104·1 (8)	O(12)–Li(65)–O(24) ×2	92·8 (8)
O(15)–Li(53)–O(37)	100·5 (5)	O(15)–Li(61)–O(15)	74·0 (6)	O(16)–Li(64)–O(16) ×2	89·0 (2)	O(12)–Li(65)–O(15) ×2	90·0 (2)
O(23)–Li(53)–O(35)	103·6 (6)	O(36)–Li(61)–O(12) ×2	91·7 (7)	O(16)–Li(64)–O(16) ×2	166·9 (7)	O(12)–Li(65)–O(12)	72·8 (7)
O(23)–Li(53)–O(37)	100·3 (5)	O(36)–Li(61)–O(15) ×2	96·8 (6)	O(32)–Li(64)–O(16) ×2	90·5 (6)	O(15)–Li(65)–O(15)	107·0 (10)
O(23)–Li(53)–O(17)	101·1 (5)	O(23)–Li(61)–O(12) ×2	85·4 (5)	O(32)–Li(64)–O(16) ×2	88·9 (7)	O(15)–Li(65)–O(24) ×2	86·7 (7)
O(35)–Li(53)–O(17)	92·1 (6)	O(23)–Li(61)–O(15) ×2	87·0 (7)	O(21)–Li(64)–O(16) ×2	96·1 (8)	O(15)–Li(65)–O(37) ×2	90·2 (8)
O(15)–Li(53)–O(17)	152·3 (6)	O(15)–Li(61)–O(12) ×2	162·1 (9)	O(21)–Li(64)–O(16) ×2	85·9 (6)	O(24)–Li(65)–O(37)	174·9 (11)
O(35)–Li(53)–O(37)	156·0 (6)	O(23)–Li(61)–O(36)	175·2 (9)	O(21)–Li(64)–O(32)	171·4 (9)	O(15)–Li(65)–O(12) ×2	162·8 (9)
O(17)–Li(53)–O(37)	80·5 (4)						

Table 4. *Comparison of occupancies between ordered* Li_4SiO_4 *and* Li_4SiO_4 *refined by Völlenkle, Wittman & Nowotny* (1968)

	Number of occupied sites	Number of available sites	Occupied sites/available sites	Occupation factor from Völlenkle *et al.* (1968)
Li(1)	4 × 4	7 × 4	0·57	0·67
Li(2)	4 × 2	7 × 2	0·57	0·50
Li(3)	3 × 2	7 × 2	0·42	0·50
Li(4)	3 × 4	7 × 4	0·42	0·33
Li(5)	2 × 4	7 × 4	0·28	0·33
Li(6)	3 × 2	7 × 2	0·42	0·33

bond strengths surrounding individual oxygen atoms. Table 5 shows that this is only approximately valid both for Pauling (1929) and Brown–Shannon (Brown & Shannon, 1973) bond strengths. The poor correlation is probably partly due to the insufficient accuracy of the Li—O distances (see the relatively large e.s.d.'s of 0·01 to 0·02 Å) and partly to the low overall accuracy of the refinement. Most likely, the e.s.d.'s are systematically too low. It is notable that the average Si—O distance (over the seven independent SiO_4 groups) of 1·635 Å is very similar to the Si—O distance of 1·637 Å obtained by our refinement of the substructure.

Of the 42 sets of equivalent positions which could be occupied in the supercell, only 19 are occupied. These 19 sets can be divided into two groups. The first is made up of ten sets of special equivalent positions [Li(2*i*), Li(3*i*), Li(6*i*)] with a multiplicity of two which are located on the mirror planes as are the Si atoms ($y = \frac{1}{4}, \frac{3}{4}$). The second group consists of nine sets of general equivalent positions with a multiplicity of four [Li(1*i*), Li(4*i*), and Li(5*i*)] which are located near the planes $y = 0$. Thus, two times ten and four times nine add up to the 56 Li atoms occupying 56 out of a possible 126 individual atomic sites per supercell. Fourteen Li atoms are tetrahedrally coordinated. In most of these tetrahedra, the Li—O distances vary between 1·84 and 2·15 Å. The Li(23) tetrahedron is particularly distorted with Li—O distances ranging from 1·91 to 2·43 Å. Actually this tetrahedron could also be viewed as a trigonal coordination with a nearby fourth neighbor. Li(51) and Li(53) are surrounded by five O atoms with Li—O distances ranging from 1·96 to 2·38 Å. Li(61), Li(64), and Li(65) are octahedrally coordinated (2·10 < Li—O < 2·62 Å).

As in Li_2CO_3, Li_3BO_3 and Li_5AlO_4, the atoms in ordered Li_4SiO_4 form a three-dimensional network with edge- and corner-shared LiO_4, LiO_5 and LiO_6 polyhedra (Fig. 3) (Shannon, Taylor, English & Berzins, 1977). In order to understand the good conductivity of substituted Li silicates such as $Li_{4-x}Si_{1-x}P_xO_4$, it is useful to analyze the connectivity of the Li sites. If we consider Li–Li distances of less than 2·9 Å, a

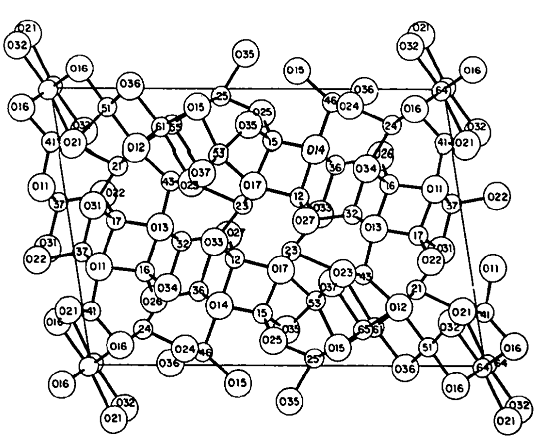

Fig. 3. Projection along **b** of the LiO_n polyhedra.

Table 5. *Coordinations of* Li *around* O, *observed and calculated* Si–O *bond lengths* (Å) *and bond strengths at oxygen atoms*

	Number of Li atoms about each oxygen	d(Si–O) obs.	d(Si–O) calc.*	Sum of Li–O bond strengths about O		Si–O bond strengths	Total bond strengths
				†	‡	‡	‡
O(11)	4	1·609	1·615	1·000	0·97	1·04	2·01
O(12)	5	1·627	1·641	1·033	0·95	0·99	1·93
O(13)	4	1·628	1·638	1·000	0·94	0·98	1·92
O(14)	4	1·634	1·640	1·000	0·92	0·97	1·89
O(15)	5	1·634	1·632	1·033	0·92	0·97	1·89
O(16)	5	1·670	1·646	1·033	0·98	0·88	1·86
O(17)	4	1·635	1·634	0·950	0·94	0·97	1·91
O(21)	6	1·670	1·646	1·333	0·95	0·88	1·84
O(22)	3	1·599	1·615	0·750	0·75	1·06	1·82
O(23)	6	1·668	1·669	1·333	1·09	0·89	1·98
O(24)	4	1·656	1·632	0·917	0·91	0·92	1·82
O(25)	3	1·612	1·606	0·750	0·77	1·03	1·80
O(26)	3	1·581	1·620	0·750	0·81	1·12	1·93
O(27)	3	1·610	1·616	0·750	0·85	1·03	1·88
O(31)	4	1·605	1·615	1·000	0·99	1·05	2·04
O(32)	5	1·686	1·644	1·067	0·96	0·85	1·81
O(33)	4	1·658	1·638	1·000	0·91	0·91	1·82
O(34)	4	1·628	1·640	1·000	0·95	0·98	1·93
O(35)	5	1·632	1·642	1·150	0·97	0·97	1·94
O(36)	5	1·638	1·649	1·067	1·14	0·96	2·10
O(37)	5	1·646	1·645	1·067	1·06	0·94	2·00

* Baur (1971).
† Pauling (1929).
‡ Brown & Shannon (1973), universal curves.

Table 6. Li–Li *distances along* [010]

The distances m_1 and m_2 between Li polyhedra are related by a mirror plane and c by a center of symmetry.

	m_1	m_2		c
Li(12)	3·13	2·96	Li(25)	3·89
Li(15)	3·05	3·04	Li(37)	3·87
Li(16)	3·18	2·91	Li(64)	3·06
Li(17)	3·07	3·02		
Li(41)	3·49	2·60		
Li(43)	3·43	2·66		
Li(46)	3·41	2·68		
Li(51)	3·38	2·71		
Li(53)	3·51	2·58		

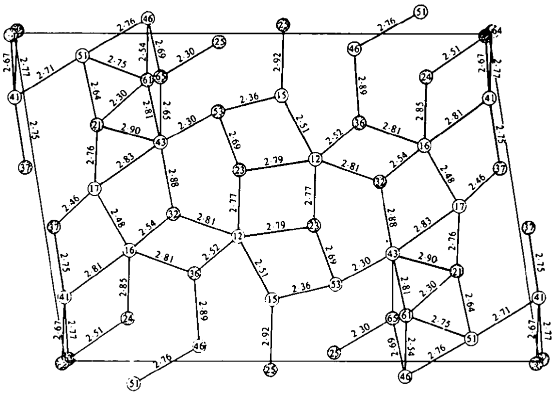

Fig. 4. Projection along **b** of all Li atoms in the unit cell. Open circles are at $y \simeq 0$; shaded circles are at $y = \frac{1}{4}$ or $\frac{3}{4}$. All Li–Li distances indicated are less than 2·9 Å. Average e.s.d.'s of Li–Li distances are ±0·02 Å.

continuous network can be constructed. Fig. 4 is a projection of all the Li atoms in the unit cell. It shows all Li–Li connections less than 2·9 Å except those parallel to **b**. If we look at Li in planes at $y \simeq 0$, there are continuous two-dimensional pathways such as Li(41)–Li(16)–Li(17)–Li(43)–Li(53)–Li(15)–Li(46)–Li(51)–Li(41) [these atoms are all within 2·9 Å of one another with the exception of Li(15)–Li(46) at 2·96 Å]. The Li polyhedra at $y \simeq 0$, in addition to being connected to other Li atoms in the plane and in directions on diagonals between planes at 0 and $\frac{1}{4}$, are linked to other Li atoms equivalent by the mirror plane along [010]. These atoms lie within distances of 3·1 Å (see Fig. 5 and Table 6). If we consider the Li atoms at $y = \frac{1}{4}, \frac{3}{4}$, there are no direct pathways in the plane. The Li atoms equivalent by centers of symmetry form Li–Li chains in the **b** direction [Li(2*i*)–Li(2*i*), Li(3*i*)–Li(3*i*) and Li(6*i*)–Li(6*i*)]. The Li(2)–Li(2) and Li(3)–Li(3) distances are quite long (3·9 Å), but the Li(6)–Li(6) pairs are close enough (3·06 Å) to provide a path for mobile Li atoms. Clearly mobile Li atoms can follow many pathways both within the $y \simeq 0$ planes

Table 7. *Edge- and corner-sharing between polyhedra in* Li_4SiO_4

Mult. = multiplicity of element per polyhedron, *E* = edge, *C* = corner, *t* = tetrahedron, *f* = five coordination, *o* = octahedron, CN = coordination number.

Atom	CN	Atom	Mult.	Distance	Shared elements
Li(12)	IV	Li(15)		2·51 Å	*E*, *tt*
		Li(36)		2·52	*E*, *tt*
		Li(23)		2·77	*C*, *tt*
		Li(23)		2·79	*C*, *tt*
		Li(32)		2·81	*C*, *tt*
		Li(12)		2·96	*C*, *tt*
Li(15)	IV	Li(53)		2·36	*E*, *tf*
		Li(12)		2·51	*E*, *tt*
		Li(25)		2·91	*C*, *tt*
		Li(46)		2·96	*C*, *tt*
		Li(15)		3·04	*C*, *tt*
		Li(15)		3·05	*C*, *tt*
Li(16)	IV	Li(17)		2·48	*E*, *tt*
		Li(32)		2·54	*E*, *tt*
		Li(36)		2·81	*C*, *tt*
		Li(41)		2·81	*C*, *tt*
		Li(24)		2·85	*C*, *tt*
		Li(16)		2·91	*C*, *tt*
Li(17)	IV	Li(37)		2·46	*E*, *tt*
		Li(16)		2·48	*E*, *tt*
		Li(21)		2·76	*C*, *tt*
		Li(43)		2·83	*C*, *tt*
		Li(37)		2·97	*C*, *tt*
		Li(17)		3·02	*C*, *tt*
		Li(17)		3·07	*C*, *tt*
Li(21)	IV	Li(61)		2·30	*E*, *to*
		Li(51)	(×2)	2·64	*E*, *tf*
		Li(17)	(×2)	2·76	*C*, *tt*
		Li(43)	(×2)	2·90	*C*, *tt*
Li(23)	IV	Li(53)	(×2)	2·69	*E*, *tf*
		Li(12)	(×2)	2·77	*C*, *tt*
		Li(12)	(×2)	2·79	*C*, *tt*
Li(24)	IV	Li(64)		2·51	*E*, *to*
		Li(16)	(×2)	2·85	*C*, *tt*
		Li(41)	(×2)	2·93	*C*, *tt*
		Li(51)	(×2)	2·95	*C*, *tf*
Li(25)	IV	Li(65)		2·30	*E*, *to*
		Li(15)	(×2)	2·92	*C*, *tt*
		Li(53)	(×2)	2·94	*C*, *tf*
Li(32)	IV	Li(16)	(×2)	2·54	*E*, *tt*
		Li(12)	(×2)	2·81	*C*, *tt*
		Li(43)	(×2)	2·88	*C*, *tt*
Li(36)	IV	Li(12)	(×2)	2·52	*E*, *tt*
		Li(16)	(×2)	2·81	*C*, *tt*
		Li(46)	(×2)	2·89	*C*, *tt*
Li(37)	IV	Li(17)	(×2)	2·46	*E*, *tt*
		Li(41)	(×2)	2·75	*C*, *tt*
		Li(17)	(×2)	2·97	*C*, *tt*
Li(41)	IV	Li(41)		2·60 Å	*C*, *tt*
		Li(64)		2·67	*E*, *to*
		Li(51)		2·71	*E*, *tf*
		Li(37)		2·75	*C*, *tt*
		Li(64)		2·77	*E*, *to*
		Li(16)		2·81	*C*, *tt*
		Li(24)		2·93	*C*, *tt*
Li(43)	IV	Li(53)		2·30	*E*, *tf*
		Li(65)		2·65	*E*, *to*
		Li(43)		2·66	*C*, *tt*
		Li(61)		2·81	*E*, *to*
		Li(17)		2·83	*C*, *tt*
		Li(32)		2·88	*C*, *tt*
		Li(21)		2·90	*C*, *tt*
Li(46)	IV	Li(61)		2·54	*E*, *to*
		Li(46)		2·68	*C*, *tt*
		Li(65)		2·69	*E*, *to*
		Li(51)		2·76	*C*, *tf*
		Li(36)		2·89	*C*, *tt*
		Li(15)		2·96	*C*, *tt*
Li(51)	V	Li(21)		2·64	*E*, *ft*
		Li(51)		2·71	*C*, *ft*
		Li(41)		2·71	*E*, *ft*
		Li(61)		2·75	*E*, *fo*
		Li(46)		2·76	*C*, *ft*
		Li(64)		2·94	*E*, *fo*
		Li(24)		2·95	*C*, *ft*
		Li(64)		3·00	*E*, *fo*
Li(53)	V	Li(43)		2·30	*E*, *ft*
		Li(15)		2·36	*E*, *ft*
		Li(53)		2·58	*C*, *ft*
		Li(23)		2·69	*E*, *ft*
		Li(65)		2·91	*E*, *fo*
		Li(25)		2·94	*C*, *ft*
		Li(61)		3·01	*E*, *fo*
Li(61)	VI	Li(21)		2·30	*E*, *ot*
		Li(46)	(×2)	2·54	*E*, *ot*
		Li(51)	(×2)	2·75	*E*, *of*
		Li(43)	(×2)	2·81	*E*, *ot*
		Li(53)	(×2)	3·01	*E*, *of*
		Li(65)	(×2)	3·09	*E*, *oo*
Li(64)	VI	Li(24)		2·51	*E*, *ot*
		Li(41)	(×2)	2·67	*E*, *ot*
		Li(41)	(×2)	2·77	*E*, *ot*
		Li(51)	(×2)	2·94	*E*, *of*
		Li(51)	(×2)	3·00	*E*, *of*
		Li(64)	(×2)	3·06	*E*, *oo*
Li(65)	VI	Li(25)		2·30	*E*, *ot*
		Li(43)	(×2)	2·65	*E*, *ot*
		Li(46)	(×2)	2·69	*E*, *ot*
		Li(53)	(×2)	2·91	*E*, *of*
		Li(61)	(×2)	3·09	*E*, *oo*

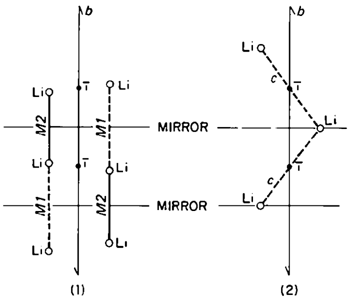

Fig. 5. Li–Li distances along [010].

and between the $y \simeq 0$ and $\frac{1}{4}$ planes. Although two-dimensional connectivity is sufficient for good conductivity, as is apparent from the excellent conductivity of β-Al_2O_3, Li_4SiO_4 clearly contains paths allowing three-dimensional conductivity.

Li connectivity can also be analyzed by studying the Li polyhedral linkage. Geller (1973) has associated good conductivity in AgI-based solid electrolytes with networks of face-shared anion polyhedra. In oxides, face-sharing of tetrahedra is not observed and for other polyhedra it is rare. The next best arrangement is a continuous network of edge-shared polyhedra. In Li_4SiO_4 we have extensive edge-sharing of polyhedra and no face-sharing of LiO_n polyhedra as found by Völlenkle, Wittman & Nowotny (1968). It is likely that the good conductivity arises from the extensive edge-sharing. Table 7 summarizes all Li–Li distances <3·01 Å and lists shared polyhedral elements. As anticipated, the shortest Li–Li distances are associated with shared polyhedral edges. All Li^+ ions except Li(24) and Li(25) share edges with at least two other polyhedra. The shortest distances (down to 2·30 Å) and, therefore, the best possibilities for Li^+ ion transfer from one site to an adjacent site are associated with edges shared between tetrahedra and five- or six-coordinated polyhedra. The next shortest distances (2·46–2·54 Å) are those associated with edges shared between tetrahedra. Shared edges between five- and six-coordinated polyhedra result in Li–Li distances of 2·75 to 3·01 Å. Extensive Li^+ ion transfer between corner-shared polyhedra probably does not occur because the path would be more indirect. Consistent with the structure of the ordered phase as described here, Li_4SiO_4 has very low ionic conductivity. Introducing either Li vacancies as in $Li_{4+x}Si_{1-x}P_xO_4$ or $Li_{4-2x}Si_{1-x}S_xO_4$ or Li interstitials as in $Li_{4+x}Si_{1-x}Al_xO_4$ at levels of $x = 0{\cdot}2$ increases σ by factors of 10^3–10^4 (Shannon, Taylor, English & Berzins, 1977). Location of the vacancies or interstitials in the substituted phases cannot be determined without refining the structure of one of these phases.

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