THE LITHIUM SODIUM SILICIDE Li₃NaSi₆ AND THE FORMATION OF ALLO-SILICON*

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Summary

Metallic grey Li₃NaSi₆ is formed by heating the elements in stoichiometric amounts. The compound is the only stable ternary phase in the Li-Na-Si system, and does not belong to the tetrasilatetrahedrane derivatives. The novel complex layer structure is characterized by two-dimensional infinite ${}_{\infty}^{2}[Si_{6}^{4-}]$ polyanions showing polymerized tube-like structural units which are known from Hittorf's violet phosphorus and GeAs₂ respectively. The alkali metal atoms are inserted between the respective polyanionic layers (Pnma (62); a = 1797.2 pm, b = 378.8 pm, c = 1029.9 pm; 808 hkl; R = 0.025; d(Si-Si) = 237.2 - 244.9 pm; d(Li-Si) = 254.1 - 296.6 pm; d(Na-Si) = 312.0 - 347.1 pm). Li₃NaSi₆ is a diamagnetic semiconductor with a molar susceptibility χ_{mol} of -243×10^{-6} emu mol⁻¹, $R(300 \text{ K}) = 50 \Omega$ and $R(2 \text{ K}) = 3 \times 10^3 \Omega$. Li₃NaSi₆ reacts with protic solvents as well as with benzophenone (in tetrahydrofuran) topotactically yielding a new metastable silicon modification, namely allo-Si. The polyanionic block structure is decharged and is polymerized to a three-dimensional network ($\chi_{mol} = -38 \times$ 10^{-6} emu atom⁻¹). According to reflection electron microscopy, larger crystals show a pronounced lamellar structure which is responsible for the graphite-like mechanical behaviour. At 800 K, allo-Si transforms irreversibly into α -Si.

1. Introduction

During the last few years we have systematically investigated binary and ternary alkali metal silicides and germanides [1 - 20]. These studies were primarily meant to find derivatives with polyanionic Y_n^{q-} clusters, especially Si_4^{4-} and Ge_4^{4-} tetrahedranes, and to learn more about their topological changes on varying the cationic coordination. Besides NaSi, no other tetrahedrane structure exists in the ternary system Li-Na-Si [20]. The only

^{*}Dedicated to Professor Harald Schäfer on the occasion of his 75th birthday.

stable ternary phase that we found is the compound Li_3NaSi_6 , which is the long-searched-for starting material for the preparation of (metastable) allo-Si, comparable with $Li_{12}Ge_7$ for the preparation of allo-Ge [3]. A survey of these investigations is given below.

2. Preparation of Li₃NaSi₆

By changing the atomic ratio Li:Na:Si systematically, it was obvious that Li_3NaSi_6 is the only stable ternary phase [20] besides the binary NaSi and Na₈Si₄₆ and the four lithium silicides [1, 2, 16]. Li₃NaSi₆ was first identified by X-ray structure analysis and then synthesized in pure form.

The following procedure was used. Lithium (4.00 g; 150 mmol), sodium (1.15 g; 50 mmol) and silicon (8.42 g; 300 mmol) were loaded into a niobium ampoule under inert conditions and closed by arc welding. The ampoule was heated in a closed vertical quartz glass tube and then cooled down slowly (argon atmosphere; heating period, 4 h; reaction at 1075 K for 4 h; cooling period, 40 h). The product was isolated under inert conditions.

The starting materials were lithium (98% with 1% sodium, Merck Darmstadt), sodium (99%, Riedel de Haen) and silicon (99%, M2N5, Ventron).

All procedures were carried out under argon (99.996%, Messer-Griessheim), in a glove box (Braun, München) with an integrated gas cleaner (0.4 ppm H_2O , 1 - 2 ppm oxygen). An arc-welding system was used to heat-seal the niobium ampoules and the heat treatment was carried out in a resistance furnace.

The reaction procedure is not simplified by using binary starting materials for the synthesis.

3. Properties of Li₃NaSi₆

 Li_3NaSi_6 forms beautiful grey crystals with a metallic lustre. The rodshaped crystals can be easily cleaved. The growth direction is [010] and the cleavage plane is (100).

The compound is diamagnetic with a molar susceptibility χ_{mol} of -243×10^{-6} emu mol⁻¹. The electric resistance (four-point method) decreases with rising temperature ($R(2 \text{ K}) = 3 \times 10^{3} \Omega$, $R(300 \text{ K}) = 50 \Omega$). Therefore Li₃NaSi₆ is a semiconductor. The compound can be identified clearly by its characteristic X-ray diagram (Fig. 1, Table 1).

 Li_3NaSi_6 differs drastically from the other alkali metal silicides in its chemical behaviour (except for the clathrates Na_8Si_{46} etc.). Indeed, the compound shows a remarkably low reactivity against humidity and air. The reactivity depends also on the degree of crystallization; fine-grained powder samples react fast, but larger single crystals decompose only over a period of several hours. The reaction products are allo-Si, hydrogen and an alkali metal hydroxide, which were analysed quantitatively (Section 4).



Fig. 1. X-ray powder pattern of Li_3NaSi_6 (top), α -Si (centre), and allo-Si (bottom, Cu $K\alpha_1$ radiation).

4. Formation of allo-Si

Protic solvents such as water or alcohol react with Li_3NaSi_6 crystals with evolution of gas parallel to the (100) plane and the crystals decompose into graphite-like flashes of allo-Si. No silanes are formed, as in the reaction of other alkali metal silicides with protic solvents but hydrogen is evolved as in the preparation of allo-Ge from Li_7Ge_{12} [3]. According to the qualitative and quantitative analysis of the products, the following equation is valid:

 $Li_3NaSi_6(s) + 4HX(solv) = 6 allo-Si(s) + 2H_2(g) + 4MX(solv)$

 $(X \equiv OH^-, OR^-; M \equiv Li, Na)$

In a solution of benzophenone in dry tetrahydrofurane (THF), Li_3NaSi_6 reacts slowly (6 - 10 weeks) to allo-Si. Samples prepared in this way show much less fan-out than those which are obtained from reaction with protic solvents.

From the X-ray investigations it is clear that the two-dimensional structural units ${}^{2}_{\alpha}[Si_{6}]^{4-}$ of Li₃NaSi₆ are conserved and linked to each other as in a radical polymerization forming a three-dimensional ${}^{3}_{\omega}[Si]^{0}$ network which is characteristic for allo-Si. Precession photographs show that the reaction can be considered as strongly topotactic. The degree of crystallinity of the products depends on the velocity of the reaction. After a short time, the reaction with H₂O, methanol or ethanol yields a highly disordered allo-Si product. The ramified layer blocks and the ensuing disorder can be recognized by raster electron microscopy photographs. However, allo-Si crystals with a lower degree of disorder are obtained after reacting Li₃NaSi₆ for several days with a mixture of isopropanol and petroleum ether (1:9 by volume) (Fig. 2).

TABLE 1

Crystallographic data fo	or Li ₃ NaSi ₆ and allo-Si
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Li ₃ NaSi ₆						Allo-Si		
h k l	d (pm)	Relative intensity	h kl	d (pm)	Relative intensity	<i>d</i> (pm)	Relative intensity	
200	898.6	100	711	208.1	14	416.0	30	
101	893.6	25	513	207.6	9	351.7	50	
201	677.1	22	214	207.2	3	293.7	5	
301	517.8	49	8.02	205.9	2	281.6	10	
002	514.9	31	703	205.6	8	258.2	30	
102	495.0	4	314	200.6	3	239.7	15	
202	446.8	4	712	196.5	18	225.3	50	
401	411.8	30	901	196.0	5	219.7	35	
302	390.5	15	604	195.3	10	207.8	10	
011	355.5	22	305	194.8	11	193.9	50	
210	349.1	4	613	193.9	20	189.1	50	
111	348.8	13	810	193.2	3	181.3	5	
501	339.4	2	414	192.4	18	162.0	50	
402	338.5	6	811	189.9	30	152.7	5	
103	337.2	49	020	189.4	64	151.0	10	
211	330.6	9	405	187.2	8	141.8	5	
203	320.7	4	220	185.3	2	127.8	15	
311	305.7	78	015	181.0	52	120.2	15	
112	300.8	29	713	180.7	13	115.7	10	
600	299.5	23	321	177.9	4	113.7	5	
303	297.9	20	022	177.8	3	105.8	25	
502	294.7	4	215	177.4	4			
410	289.6	11	1001	177.0	3			
601	287.6	14	911	174.1	10			
411	278.8	10	614	173.6	37			
403	272.8	12	315	173.2	13			
312	271.9	11	421	172.1	4			
602	258.9	37	106	170.9	4			
004	257.5	33	322	170.4	2			
013	254.4	59	605	169.7	4			
511	252.8	3	1002	169.7	8			
412	252.4	80	804	169.3	8			
701	249.1	6	813	168.4	4			
503	248.3	5	123	165.1	11			
304	236.6	7	306	165.0	5			
610	235.0	46	1010	162.4	15			
313	234.1	4	620	160.1	7			
512	232.6	8	323	159.8	6			
611	229.1	27	1003	159.2	3			
404	223.4	11	621	158.2	5			
801	219.5	6	904	157.8	2			
114	211.5	5	1102	155.7	3			
504	209.3	6	423	155.6	4			



Fig. 2. Raster electron microscopy photographs of allo-Si. Samples prepared from: (a) $Li_3NaSi_6 + H_2O$; (b) $Li_3NaSi_6 + isopropanol petroleum ether (1:9 by volume)$. The layers are parallel (100). The magnification ranges from 20 to 200 μ m and is indicated by the length of the black bar.

To be certain that allo-Si is a new modification of silicon, various anallyses were performed. Li_3NaSi_6 reacts with protic solvents with the evolution of gas. The evolved gas consists exclusively of hydrogen and does not contain silanes as shown by a mass spectroscopic analysis. The evolving hydrogen is caught in a pneumatic tank and the volume determined. Three measurements yielded an average conversion of 97% relative to allo-Si. Atomic absorption spectroscopy gave the composition $Li_{0.02}Na_{0.03}Si$ (silicon content, 95%) for a product from the reaction with H₂O. The residual alkali 302

metal results from the absorption of the alkali metal hydroxide, which can reach considerable amounts in the reaction with H_2O (see Fig. 2).

The analysis of the characteristic X-ray emission only shows the wellknown silicon radiation for allo-Si. However, this information is only partly useful because elements with Z < 10 cannot be detected in our apparatus.

5. Properties of allo-Si

Allo-Si is a dim grey substance and strongly resembles α -Si. It differs from other known silicon modifications (α -Si, amorphous silicon (a-Si)) in the morphology: allo-Si forms lamellar crystals which are similar to graphite (Fig. 2) and in fact, allo-Si can be smeared out. Allo-Si is as inert as α -Si towards protic solvents, acids and bases. Further experiments are needed to show whether allo-Si possesses a reactivity different from that of α -Si.

Allo-Si is diamagnetic with $\chi_{mol} = -37.8 \times 10^{-6}$ emu mol⁻¹. This is a considerable rise in the molar susceptibility compared with that of α -Si (-3.8×10^{-6} emu mol⁻¹). The electrical conductivity has not yet been determined. Figure 1 shows the X-ray powder pattern of allo-Si which shows only a few lines compared with that of Li₃NaSi₆ and these are remarkably sharp. The additional strong lines are due to α -Si crystallites, which apparently are formed during the topotactical reaction.

If heated under an inert gas $(10^{\circ} \text{ min}^{-1})$, allo-Si shows a smeared-out exothermal effect at 498 K and a somewhat sharper exothermal effect at 788 K. These effects occur neither during the cooling nor for other heating periods. They are clearly due to irreversible processes. After such treatment the product is pure α -Si. For the investigation of the thermal effects, a powder sample of allo-Si was measured on an automatic powder diffractometer with a heating facility. It turned out that the exothermal effect at 498 K is due to an order-disorder transition. The strongly disordered allo-Si crystals recrystallize with a diminution of the quasi-amorphous regions. This is reflected by the very sharp lines in a corresponding Guinier-Simon X-ray photograph.

The thermal effect at 788 K corresponds to the irreversible transformation of allo-Si to α -Si. The transformation of the metastable modification takes place so slowly under normal condition that, although α -Si is the only thermodynamically stable modification, allo-Si exists also at room temperature and normal pressure.

The quantitative transformation of allo-Si to α -Si is good proof that allo-Si is in fact a new silicon modification. After heating allo-Si under inert conditions to 1275 K, the X-ray powder pattern shows exclusively the lines of α -Si. There are no other lines, especially not those of silicon oxides.

6. Electrochemical reactions

Another way of preparing allo-Si is the coulometric titration of Li_3NaSi_6 . The anode was pure lithium metal and the cathode consisted of exactly 200 mg of powdered Li_3NaSi_6 in a molybdenum crucible. The experimental set-up was used in the standard way (lithium metal|LiCl/KCl, eutectic melt (melting point, 630 K)|Li_3NaSi_6, powder) [21].

The electrode reactions are as follows:

anode: $Li_3NaSi_6 \longrightarrow allo-Si + 3Li^+ + Na^+ + 4e$

cathode: $3Li^+ + Na^+ + 4e \longrightarrow 3Li + Na$

The overall reaction is

 $Li_3NaSi_6 \longrightarrow allo-Si + 3Li + Na$

Measurements of the potential difference ΔE vs. Li concentration, and of the charge transfer, allow the exact determination of the composition of the reaction product. The change in the potential difference as a function of time and composition gives further information about the rate of the reaction and the possible existence of intermediate phases [21].

Generated by the coulometric titration of Li_3NaSi_6 , in comparison with the lithium cathode, allo-Si has an infinitely small lithium activity, just like any other phase without lithium metal. Consequently the end of the titration is characterized by a sharp rise in the potential curve. This observation provided reliable evidence for the composition of the product. The samples have been identified by X-ray methods. During the titration, there is a progressive change in the potential difference, which indicates the slow transformation of Li_3NaSi_6 into allo-Si. No stable intermediate product occurs during the reaction.

For the electrochemical reaction of Li_3NaSi_6 (200 mg; 0.9 mmol) to allo-Si, a charge of Q = 361 C is necessary to extract the whole of the alkali metal. During the procedure a constant current of I = 20 mA was used so that the final potential of allo-Si, *i.e.* the end of the titration, should have been reached after exactly 5 h. Actually, the titration was already finished after 4 h 50 min; in other words, only 348 C were needed, which corresponds to 96% of allo-Si. Therefore, the product has the formal composition $M_{0.03}$ Si (M = Li, Na) with a small alkali metal residue of about 4%. The complete course of the reaction cannot be doubted, because the very small deficit in the charge transferred ($\Delta Q = 13$ C) could be due to inaccuracies in the method.

Both the results of the analysis and the titration experiments with Li_3NaSi_6 show that allo-Si is a new metastable modification of silicon.

7. Crystal structure of Li₃NaSi₆

The crystal structure was determined from single-crystal data. Crystallographic data, positional and thermal parameters and bond distances are compiled in Tables 2 - 5.

 Li_3NaSi_6 represents a novel structure type which is characterized by a two-dimensional infinite complex layer substructure of covalently bonded

TABLE 2

Crystal data, data collection and structure determination for Li₃NaSi₆

Formula, molar mass Crystal size Lattice constants Temperature Space group Z Volume, molar volume d _x	Li ₃ NaSi ₆ , 212.32 a.m.u. Platelet, 0.4 mm × 0.1 mm × 0.2 mm a = 1797.2(4) pm, $b = 378.8(1)$ pm, $c = 1029.9(3)$ pm 296 K Pnma-D ¹⁶ _{2h} (no. 62), $Z = 4$ 701.13 Å ³ , 105.56 cm ³ mol ⁻¹ , 2.011 g cm ⁻³
Measurement	Syntex PI four-circle diffractometer, graphite mono- chromator, scintillation counter, Mo K α radiation, ω scan, $3.5^{\circ} \le 2\theta \le 55.0^{\circ}$, $829 \ hkl$ measured, $809 \ hkl$ with $I > 3\sigma(I)$. 396 unique reflections with $I > 3\sigma(I)$
Absorption correction	ψ scan, 11 <i>hkl</i> , 10° increment, μ (Mo K α) = 10.49 cm ⁻¹
Structure determination and refinement	Direct methods (SHELXTL), 127 E's, subsequent Fourier synthesis, full-matrix least-squares method, 62 variables, $1/\sigma^2$ weighting
R(iso), R(aniso) R (weighted)	0.090, 0.025 0.090, 0.025

TABLE 3

Positional and thermal parameters U_{ij} (pm²) for Li₃NaSi₆ (standard deviations in parentheses). The thermal parameters U_{ij} are defined for exp $\{-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}-klb^*c^*)\}$, $U_{12} = U_{13} = 0$. All atoms occupy the special position 4c (x1/4z)

Atom	x	У	z	U _{iso/equi}	<i>U</i> ₁₁	U ₂₂	U ₃₃	U23
Li1	-0.0677(4)	1/4	0.0157(6)	233(20)	175(32)	236(34)	288(38)	10(26)
Li2	0.0278(4)	1/4	0.4089(7)	256(20)	249(34)	263(35)	256(37)	-36(29)
Li3	-0.1876(4)	3/4	-0.0607(8)	296(22)	435(43)	143(30)	310(40)	42(30)
Na	0.42455(8)	3/4	0.2494(2)	270(5)	336(9)	201(8)	274(9)	-45(7)
Si1	0.19666(5)	1/4	0.52254(9)	104(3)	101(4)	106(4)	105(4)	-7(3)
Si2	0.05518(5)	1/4	0.16682(9)	113(3)	121(4)	116(4)	102(4)	-12(3)
Si3	0.29478(5)	1/4	0.35753(9)	109(3)	119(4)	101(4)	107(5)	0(3)
Si4	0.11866(5)	3/4	0.49598(9)	111(3)	132(4)	101(4)	100(5)	-4(4)
Si5	0.11762(5)	3/4	0.25881(9)	99(2)	110(4)	92(4)	96(4)	-3(4)
Si6	0.24901(5)	1/4	0.74099(9)	100(2)	109(4)	90(4)	101(4)	2(3)

silicon atoms and intercalated alkali metal atoms (Fig. 3). The silicon framework contains homoatomic twofold, threefold and fourfold bonded silicon atoms, which can be described as $(2b)Si^{2-}$, $(3b)Si^{-}$ and $(4b)Si^{0}$ [22] respectively, forming the polyanion \hat{z}^{2} [Si₆⁴⁻]. The structural functions of the six crystallographically independent silicon atoms are as follows: Si2 is $(2b)Si^{2-}$; Si3, Si4 are $(3b)Si^{-}$; Si1, Si5, Si6 are $(4b)Si^{0}$. The catenation of the silicon atoms results in a system of fivefold tubes (tube axis [010]) interconnected along [001] to the characteristic corrugated two-dimensional substructure, shown in Fig. 3, which is responsible for the distinct mechanical cleavage of

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TABLE 4

Atom pair	d (pm)	n	A tom pair	d (pm)	n	Atom pair	d (pm)	n	Atom pair	d (pm)	n
Li1-Si2	267.8(4)	2 ×	Na-Li1	307.6(5)	2 ×	Si3-Si6	237.6(1)	2×	Si5-Si2	239.7(1)	2×
-Si2	270.2(7)		-Li2	311.3(6)	2×	-Si1	244.9(1)		-Si6	240.4(1)	
- S i3	279.5(7)		-Si6	312.0(2)		–Li1	279.5(7)		–Si4	244.3(1)	
-Si5	296.6(6)		-Si2	313.7(1)	$2 \times$	-Li3	284.0(6)	28	-Li2	293.0(6)	2 imes
-Li3	297.5(8)	$2 \times$	-Si1	319.4(2)		-Na	320.4(2)	$2 \times$	-Li1	296.6(6)	
	. ,		- S i3	320.4(2)	$2 \times$				-Li3	305.5(6)	2 imes
Li2-Si2	254.1(7)		-Si4	331.7(2)	$2 \times$	Si4-Si1	237.2(1)	$2 \times$	-Na	347.1(2)	
-Si4	265.7(5)	$2 \times$	-Si5	347.1(2)		-Si5	244.3(1)				
-Si4	280.9(7)					- Li2	265.7(5)	$2 \times$	Si6-Si3	237.6(1)	$2 \times$
-Li2	284.7(11)	2x				–Li2	280.9(7)		-Si5	240.4(1)	
- S i5	293.0(6)	$2 \times$	Si1-Si4	237.2(1)	2x	–Na	331.7(2)	$2 \times$	-Si1	243.9(1)	
			- Si6	243.9(1)			. ,		–Li3	288.7(6)	$2 \times$
Li3-Si2	261.9(7)		-Si3	244.9(1)							
-Si3	284.0(6)	2×	–Li3	284.0(5)	2×						
-Si1	284.0(5)	$2 \times$	–Na	319.4(2)							
-Si6	288.7(6)	2×		()							
-Li1	297.5(8)	$2 \times$	Si2-Si5	239.67(9)	2x						
			-Li2	254.1(7)							
			–Li3	261.9(7)							
			–Li1	267.8(4)	2x						
			-Li1	270.2(7)							
	_	_	-Na	313.7(1)	2×	_					

Interatomic distances in Li₃NaSi₆ (standard deviations in parentheses)

TABLE 5 Bond angles Si-Si-Si in $Li_3NaSi_6 (\sigma = 0.03 \cdot 0.10^\circ)$

Si atoms	Bond angle (deg)	n	Si atoms	Bond angle (deg)	n	Si atoms	Bond angle (deg)	n
3-1-4	110.2	2×	2-5-4	113.5	2×	1-6-3	109.8	2×
3-1-6	110.4		2-5-2'	104.4		1 - 6 - 5	117.1	
4-1-4'	106.0		2 - 5 - 6	115.9	$2 \times$	3-6-3'	105.7	
4-1-6	109.5	$2 \times$	4-5-6	93.9		3-6-5	107.0	2×
1-3-6	96.4	2×	1 - 4 - 5	96.9	2×	5 - 2 - 5'	104.4	
6-3-6'	105.7		1-4-1'	106.0				

the crystals parallel to (100). With a simple structure model it can be shown that an isolated fivefold tube of this kind, formed by tetrahedrally bonded atoms, would bend along the tube axis [23]. The curvature of this unit is compensated by the present E connection (trans) of tubes via a glide-plane symmetry operation, comparable with the equivalent arrangement in the BaP₁₀ and K₄P₂₁I structures [23 - 25]. The fivefold tubes of the ${}^{2}_{\omega}$ [Si₆⁴⁻] polyanion (Fig. 3) are identical with the subunits of the GeAs₂ structure [26] and are similar to the building units of Hittorf's phosphorus and their derivatives [23]. Very recently Hurng *et al.* found the ternary KSi₃As₃ phase [27]



Fig. 3. (a) Li_3NaSi_6 structure: view down [010] showing the separation of the $a^2[Si_6^{4-}]$ polyanions and the region of intercalated alkali nonasila-tricyclononane unit (d) of the fivefold tubes with the central unit of the α -Si (diamond) structure (for atomic labelling, cf. Tables 3 - 5). metal cations. (b) Fivefold tubes of the polyanions compared with (c) the units of Hittorf's phosphorus. Relation of the condensed

with an almost identical ${}^{2}_{\omega}[Si_{3}As_{3}^{-}]$ polyanion. The isoelectronic 28-electron polyanions ${}^{2}_{\omega}[Si_{6}^{4-}]$ and ${}^{2}_{\omega}[Si_{3}As_{3}^{-}]$ differ only in the arrangement of the intertube bonds, just like stereoisomers. Moreover, Fig. 3 illustrates the relation to the diamond structure and shows the system of condensed fivemembered and six-membered rings (chair and boat) typical of these structures. The two-dimensional layer structure of polymerized fivefold tubes is quite different from other ternary I–I–IV phase structures (Li₅NaSn₄ [28], Li₅Na₂Sn₄ [29]) because of the much lower valence electron concentration (VEC) per anionic atom, namely, VEC equals 4.67 but is less than five.

The Si-Si bond length ranges between 237.2 and 244.9 pm with a mean value of about 241.1 pm, which is close to the bond lengths in Si₄⁴⁻ tetrahedrane anions. The increase, with respect to α -Si (235.1 pm), is effected by the formal charges and corresponds to that in Li₇Ge₁₂ [3]. The mean bond distances become smaller with increasing polarity of the bond: $\bar{d}(\text{Si}^0-\text{Si}^0) = 242.2 \text{ pm}, \bar{d}(\text{Si}^0-\text{Si}^{1-}) = 241.0 \text{ pm}, \bar{d}(\text{Si}^0-\text{Si}^{2-}) = 239.6 \text{ pm}$. The same effects are valid for P-P bond distances in polyanionic phosphides [23]. The ${}^{\circ}_{2}[\text{Si}_{6}^{4-}]$ blocks are 427 pm apart and shifted along [001] (Fig. 3).

The coordination of the alkali metal atoms is quite different and the mean bond distances vary with the coordination number, namely, $\bar{d}(\text{Li1-Si}) = 276.4 \text{ pm}$ (CN 5), $\bar{d}(\text{Li2-Si}) = 275.4 \text{ pm}$ (CN 6), $\bar{d}(\text{Li3-Si}) = 282.2 \text{ pm}$ (CN 7) and 287.4 pm (CN 7 + 2) and $\bar{d}(\text{Na-Si}) = 323.4 \text{ pm}$ (CN 9) respectively. The closest metal-to-metal contacts, with 285.0 pm (Li2-Li2), 297.5 pm (Li1-Li3) and 307.6 pm (Li1-Na) are considerably larger than in the lithium-richer silicides and are obviously influenced by the unusual distribution of anions and cations (Fig. 3).

8. The structure of allo-Si

Completely transformed "crystals" always appear in X-ray photographs, such as that in Fig. 4(d). More than 20 crystals from the reaction with benzophenone (reaction time, 8 weeks) have been investigated. The intensive study of all these X-ray patterns shows clearly that the smeared-out reflections as well as the Debye rings are due to epitaxially grown α -Si crystals. There is a strong relationship between the crystallographic directions [110] in α -Si and [010] in Li₃NaSi₆, which can be seen in Fig. 3(d) as well, comparing the nonasila-tricyclononane (Li₃NaSi₆) and the decasila-adamantane (α -Si). This corresponds to the strong α -Si lines in the powder pattern of such samples (Fig. 1). All efforts to grow suitable single crystals for quantitative measurements failed.

To collect more information about the allo-Si structure, the X-ray diagrams were studied in the course of the chemical reaction of Li_3NaSi_6 with protic solvents forming allo-Si. Figure 4 shows progressive changes in the reflections hk0 and 0kl. In the first stage, disorder occurs in the hk0 zone, *e.g.* between the polyanionic layers, but the positions of the silicon atoms, with respect to y and z (cf. (0kl)) are hardly influenced by the alkali





Fig. 4. Buerger precession photographs (Mo K α radiation) of the (*hk*0) and (*0kl*) zones: (a) Li₃NaSi₆; (b) and (c) partly transformed crystals; (d) allo-Si (scale in millimetres). The reaction was carried out with isopropanol-petroleum ether.

metal deintercalation. The degree of disorder in (hk0) increases continuously during the reaction (Fig. 4). However, it seems to be important that the diffuse smearing-out of the (0kl) reflections still starts at the end of the chemical reaction, just at the topochemical connection of the two-dimensional silicon layers to the three-dimensional network of allo-Si. Figure 4(c) shows the largest amount of disorder. After further reaction time, partly oriented α -Si crystals grow, which give rise to the pattern in Fig. 4(d).

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