

## **Li<sub>8</sub>MgSi<sub>6</sub>, a Novel Zintl Compound Containing Quasi-aromatic Si<sub>5</sub> Rings**

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Li<sub>8</sub>MgSi<sub>6</sub> is the compound with the highest silicon content in the ternary system Li/Mg/Si. The gray compound forms columnlike crystals with metallic lustre and is very sensitive to moisture. It reacts spontaneously with water to silanes and amorphous silicon. Li<sub>8</sub>MgSi<sub>6</sub> is a diamagnetic semiconductor with  $E_g = 0.72$  eV,  $\rho(292\text{ K}) = 1.3 \times 10^3 \Omega\text{ cm}^{-1}$ . The compound is monoclinic and crystallizes in space group  $P2_1/m$ ,  $a = 12.701$ ,  $b = 4.347$ ,  $c = 10.507$  Å,  $\beta = 107.58^\circ$ ,  $Z = 2$ . The structure of Li<sub>8</sub>MgSi<sub>6</sub> contains isolated silicon atoms and planar five-membered Si<sub>5</sub> rings which form  $^1_2[\text{LiSi}_5]$  sandwich stacks. Semiempirical SCF calculations are in accordance with the physical properties and support a description of the five-membered silicon rings as quasi-aromatic 26 electron systems. A generalization of the electron counting rules of Zintl and Klemm is proposed. A remark on the ambiguous Li<sub>11</sub>Ge<sub>6</sub> is given. © 1986 Academic Press, Inc.

### **1. Introduction**

Recent investigation of the lithium-silicon (1) and lithium-germanium (2, 3) systems reveal apparent similarities between the binary phases, e.g.,  $M_{12}X_7$  (4),  $M_{14}X_6$  (1),  $M_{21}X_5$  (5) with  $M = \text{Li}$ ,  $X = \text{Si}$ ,  $\text{Ge}$ , although there are some germanides to which corresponding silicides do not exist, e.g., Li<sub>7</sub>Ge<sub>12</sub> (3), LiGe (5), Li<sub>15</sub>Ge<sub>4</sub> (6). Especially the semimetal rich compounds are very interesting with respect to their chemical and physical properties and for an understanding of bonding in semimetal clusters and frameworks. Mixed silicide germanides of the type Li<sub>12</sub>(Si,Ge)<sub>7</sub> and Li<sub>14</sub>(Si,Ge)<sub>6</sub> have been prepared and analyzed and will be reported elsewhere (7). The corresponding silicon compounds of Li<sub>7</sub>Ge<sub>12</sub> and LiGe types have not been obtained. We then have focused our interest

on the replacement of lithium by magnesium, expecting a stabilization of other possible structures by the higher charged Mg atoms. The full investigation of the ternary Li-Mg-Si system will be published elsewhere (8). We report here the silicon richest compound Li<sub>8</sub>MgSi<sub>6</sub> which contains the planar quasi-aromatic  $[\text{Si}_5]^{6-}$  ring in the same multidecker- $\pi$ -complex arrangement as in Li<sub>12</sub>Si<sub>7</sub>. Furthermore there is a striking similarity to the structure of Li<sub>11</sub>Ge<sub>6</sub> reported earlier (9).

### **2. Experimental**

The ternary system Li-Mg-Si has been scanned around the pseudobinary sections by chemical synthesis and coulometric titration (8). The preparations have been performed in boron nitride crucibles which were welded in niobium ampoules. The am-

poules were heated in a closed quartz apparatus under argon atmosphere.

$\text{Li}_8\text{MgSi}_6$  is prepared from stoichiometric amounts of the pure elements [3N silicon (Ventron); 3N lithium (Ventron); magnesium 99.5% (Merck)] using a slight excess (5 atom %) of lithium. The sample is heated up to 1320 K for 1 hr, kept at 1270 K for 15–17 hr and cooled down to room temperature within 10 hr.  $\text{Li}_8\text{MgSi}_6$  crystallizes as gray columnlike crystals of metallic luster. The compound reacts spontaneously with water and acids. The reactivity is comparable to that of  $\text{Li}_{12}\text{Si}_7$ , it burns immediately on contact with water and air. A chemical analysis was performed using the atomic emission method (ICP, Appl. Res. Lab) on a sample containing additional silicon. In selected crystals the ratio of Li : Mg was determined to be 8.5(7) : 1.

### 3. Physical Properties

The electrical conductivity of  $\text{Li}_8\text{MgSi}_6$  was measured by a two-point method from

TABLE I

$\text{Li}_8\text{MgSi}_6$ ; CRYSTAL DATA, DATA COLLECTION, AND STRUCTURE DETERMINATION

Formula, molecular weight	$\text{Li}_8\text{MgSi}_6$ , 248.34 amu
Lattice constants	$a = 12.701(2)$ , $b = 4.347(1)$ , $c = 10.507(2)$ Å, $\beta = 107.58(1)^\circ$
Temperature	296 K
Space group, $Z$	$P2_1/m-C2_2h$ (Nr. 11), $Z = 2$
Volume, $d_c$	$553.0$ Å <sup>3</sup> , $1.491(1)$ g/cm <sup>3</sup>
Crystal dimensions	$0.1 \times 0.1 \times 0.1$ mm
$\lambda$ , $\mu$ (Mo $K\alpha_1$ )	$0.71069$ Å, $8.13$ cm <sup>-1</sup>
Measuring instrument	SYNTEX P1 four-circle diffractometer graphite monochromator, scintillation counter
Measuring range	$3.5^\circ \leq 2\theta \leq 55^\circ$ , $\omega$ scan
Measuring speed	$3.5 \leq \nu \leq 29.3$ deg/min
Reflections $N(hkl)$	1214, unique 1172, 1162 with $I > 3\sigma(I)$
Absorption correction	$\psi$ scan, 11 $hkl$ , $10^\circ$ increment
Structure solution	Direct methods (SHELXTL), 172 $E$ 's. The best solution gave the correct positions of all Si atoms. The Li atoms and the Mg positions were detected in subsequent Fourier synthesis.
Refinement	Full matrix least-squares method, 130 variables
Weighting scheme	$1/\sigma^2$
$R(\text{iso})$ , $R(\text{anis})$	0.035, 0.021
Weighted	0.038, 0.022

TABLE II

$\text{Li}_8\text{MgSi}_6$ ; ATOMIC POSITIONAL PARAMETERS, EQUIISOTROPIC ( $\text{Si1-Li8}$ ) AND ISOTROPIC TEMPERATURE FACTORS [ $\text{pm}^2$ ] ( $\text{Mg11-Mg18}$ ) AND SITE OCCUPATION FACTORS (SOF) (STANDARD DEVIATIONS)

Atom	$x$	$y$	$z$	$U$	SOF
Si1	0.66091(4)	‡	0.00979(5)	157(2)	1
Si2	0.65567(4)	‡	0.23190(5)	148(2)	1
Si3	0.84075(4)	‡	0.37706(5)	153(2)	1
Si4	0.95736(5)	‡	0.23917(5)	149(2)	1
Si5	0.84860(4)	‡	1.01471(5)	152(2)	1
Si6	0.34404(5)	‡	0.38244(5)	169(2)	1
Li1	0.4424(3)	‡	0.9008(4)	228(11)	1
Li2	0.2938(4)	‡	0.6167(4)	317(14)	1
Li3	0.0275(4)	‡	0.6005(4)	287(13)	1
Li4	0.0017(3)	‡	0.8899(4)	232(12)	1
Li5	0.2113(3)	‡	0.8448(4)	249(12)	1
Li6	0.4230(4)	‡	0.1688(5)	418(17)	1
Li7	0.1693(5)	‡	0.1540(5)	464(17)	1
Li8	0.8521(5)	0.616(3)	0.6011(6)	792(46)	0.5
Mg11	0.5669(2)	‡	0.4591(2)	262(7)	0.422(8)
Mg12	0.548(1)	‡	0.525(1)	203(45)	0.06(1)
Mg13	0.512(2)	‡	0.601(3)	437(128)	0.04(2)
Mg14	0.490(1)	0.100(5)	0.634(2)	282(66)	0.04(1)
Mg15	0.643(2)	‡	0.751(1)	345(54)	0.07(1)
Mg16	0.7028(8)	‡	0.7669(7)	317(27)	0.13(1)
Mg17	0.7950(9)	‡	0.609(1)	560(39)	0.11(1)
Mg18	0.686(2)	‡	0.509(2)	205(75)	0.03(1)

295 to 1070 K with a pressed polycrystalline sample. Above 825 K the compound decomposes under loss of lithium. Therefore the bandgap was determined in the range up to 550 K.  $\text{Li}_8\text{MgSi}_6$  is a semiconductor with a band gap of  $E_g = 0.72$  eV which is slightly higher than that of the similar but more electron rich  $\text{Li}_{12}\text{Si}_7$  ( $E_g = 0.67$  eV). The electrical resistivity changes from  $\rho(295 \text{ K}) = 1.3 \cdot 10^3 \text{ } \Omega \text{ cm}^{-1}$  to  $\rho(550 \text{ K}) = 1.1 \cdot 10^5 \text{ } \Omega \text{ cm}^{-1}$ .

### 4. Crystal Structure Determination

Crystal data and details of the structure determination are listed in Table I. Tables II and III contain the atomic positional parameters, equisotropic, isotropic, and anisotropic temperature factors together with the site occupation factors. The interatomic distances are collected in Table IV.

The Mg atom is found to be distributed on split positions in a circular area around

TABLE III  
Li<sub>8</sub>MgSi<sub>6</sub>; ANISOTROPIC TEMPERATURES TENSOR  
COEFFICIENTS [PM<sup>2</sup>] FOR SILICON AND LITHIUM  
ATOMS (STANDARD DEVIATIONS)

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Si1	147(3)	163(3)	156(3)	0	38(2)	0
Si2	146(3)	130(3)	173(3)	0	55(2)	0
Si3	148(3)	178(3)	143(3)	0	57(2)	0
Si4	160(3)	135(3)	168(3)	0	73(2)	0
Si5	166(3)	157(3)	152(3)	0	79(2)	0
Si6	192(3)	178(3)	159(3)	0	87(2)	0
Li1	224(18)	164(18)	278(18)	0	50(15)	0
Li2	480(26)	250(21)	260(19)	0	171(18)	0
Li3	372(22)	178(19)	271(18)	0	39(17)	0
Li4	268(19)	196(19)	280(18)	0	157(16)	0
Li5	204(18)	221(19)	344(20)	0	117(16)	0
Li6	613(32)	363(26)	387(23)	0	316(23)	0
Li7	564(30)	368(26)	326(22)	0	-67(21)	0
Li8	271(28)	1635(128)	395(31)	332(46)	-10(24)	-423(49)

Note. The coefficients are defined for  $\exp[-2\pi^2(U_{11}h \cdot a^{*2} + \dots + 2U_{12}h \cdot ka^*b^* + \dots)]$ .

$x, \frac{1}{4}, z$  ( $x = 0.66; z = 0.62$ ) with a radius of  $R = 160$  pm (Table II). The main electron density is concentrated at the position Mg11 and corresponds to 0.42 Mg. This cannot be attributed to lithium (1.70 Li). The SOFs of the positions Mg11 to Mg18 sum up to unity within the standard deviations and confirm together with the analytical results and theoretical considerations the composition Li<sub>8</sub>MgSi<sub>6</sub> (Section 6).

The anisotropic temperature factors (Table II) for the silicon and lithium atoms do not show extraordinary coefficients except for Li8. This atom is obviously affected by the local distribution of the magnesium atoms in the mirror plane ( $x, \frac{1}{4}, z$ ). Li8 occupies a pair of split positions with respect to the mirror plane and shows in addition a high coefficient  $U_{22}$  (Table II). In the Fourier synthesis (Fig. 1) small residual electron density maxima between the silicon atoms in the five-membered ring can possibly be attributed to valence electron densities along the Si-Si bonds. We will not discuss these effects here, because the data set does not include high angular data and does therefore not allow for an profound  $X$ - $X$  electron density investigation.

## 5. Description of the Structure

The crystal structure contains planar Si<sub>5</sub> rings and isolated Si atoms Si6 (Figs. 2 and 3). The Si<sub>5</sub> rings are ecliptically stacked along [010] having Li atoms (Li1) inserted between adjacent rings. This is in fact an infinite sandwich complex  $\frac{1}{2}[\text{LiSi}_5]$  which had been found already in Li<sub>12</sub>Si<sub>7</sub> (4) and in Li<sub>11</sub>Ge<sub>6</sub> (9). The five-membered Si<sub>5</sub> rings of the piles are coordinated by six further Li atoms (Li1-Li7) which are located in the plane of the sandwiched Li atoms (Li5) and form a large distorted six-membered ring (Figs. 2 and 3). The isolated Si atom Si6 lies in the plane of the five-membered Si<sub>5</sub> rings and is coordinated by Mg and Li atoms (Table IV, Fig. 2). Si6 separates the  $\frac{1}{2}[\text{LiSi}_5]$  piles and is coordinated by the outer Li atoms of the piles and the Mg atoms. From the structures with  $\frac{1}{2}[\text{LiSi}_5]$  piles known so far, there is an indication that additional

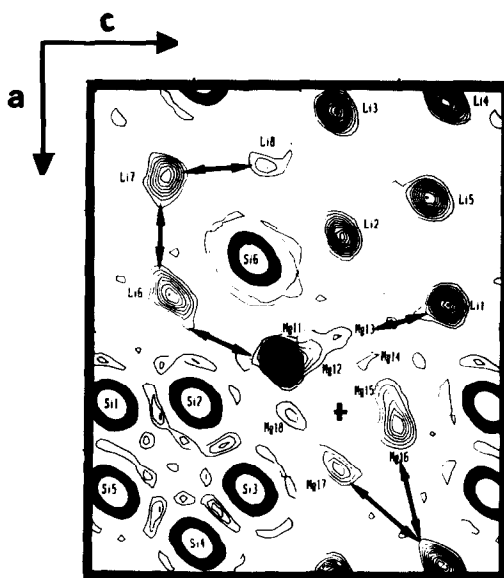


FIG. 1. Li<sub>8</sub>MgSi<sub>6</sub>; Fourier map of the ( $x, \frac{1}{4}, z$ ) plane (distorted). The magnesium atom is distributed statistically over several positions in a nearly circular area centered at + with a pronounced maximum at the Mg11 site. Probable repulsive contacts Li-Li and Li-Mg are indicated by arrows.

TABLE IV  
 $\text{Li}_8\text{MgSi}_6$ ; SELECTED INTERATOMIC DISTANCES [pm] AND ANGLES [degrees] (STANDARD DEVIATIONS)

S11	- S12 235.47 (9)	S16	- Mg18 253.7 (13)	L13	- S13 270.9 (3)	L18	- L18 116.6 (23)
	- S15 236.87 (8)		- Mg18 253.7 (13)		- S13 270.9 (3)		- MG17 176.1 (12)
	- Mg15 266.3 (15)		- Mg12 257.1 (11)		- S14 272.1 (3)		- L12 253.9 (7)
	- L11 266.3 (4)		- Mg12 259.7 (6)		- S14 272.1 (3)		- S14 256.2 (6)
	- Mg16 275.9 (9)		- Mg12 259.7 (6)		- L18 274.0 (9)		- Mg18 258.8 (19)
	- L11 284.2 (3)		- L18 261.4 (7)		- L18 274.0 (9)		- S16 261.4 (7)
	- L11 284.2 (3)		- L18 261.4 (7)		- S13 278.8 (4)		- L17 273.1 (9)
	- L16 285.9 (3)		- Mg15 261.7 (9)		- L15 290.1 (5)		- L13 274.0 (9)
	- L16 285.9 (3)		- Mg15 261.7 (9)		- L13 296.3 (5)		- S13 280.8 (9)
	- L15 286.3 (2)		- Mg13 261.9 (27)		- L13 296.3 (5)		- MG17 285.8 (12)
	- L15 286.3 (2)		- Mg16 264.1 (4)		- MG17 298.2 (13)		
			- Mg16 264.1 (4)				
S12	- S11 235.47 (9)		- Mg14 265.2 (20)	L14	- S15 265.3 (5)	Mg11	- S16 269.9 (2)
	- S13 238.46 (7)		- Mg14 265.2 (20)		- S14 269.5 (3)		- S16 276.3 (1)
	- L12 265.5 (2)		- Mg11 269.9 (2)		- S14 269.5 (3)		- S12 293.2 (3)
	- L12 265.5 (2)		- L16 272.1 (6)		- L15 284.2 (6)		
	- L11 267.8 (2)		- L12 272.3 (5)		- S15 286.2 (2)	Mg12	- S16 257.1 (11)
	- L11 267.8 (2)		- L17 273.3 (4)		- S15 286.2 (2)		- S16 259.7 (6)
	- Mg18 281.6 (23)		- Mg11 276.3 (1)		- L17 294.3 (5)		- S16 259.7 (6)
	- L16 282.7 (5)		- Mg11 276.3 (1)				
	- Mg11 293.2 (3)		- Mg14 280.5 (15)	L15	- L11 281.5 (6)	Mg13	- S16 261.9 (27)
			- Mg14 280.5 (15)		- L14 284.2 (6)		- S16 281.3 (20)
S13	- S14 236.42 (9)		- Mg13 281.3 (20)		- S15 285.7 (3)		- S16 281.3 (20)
	- S12 238.46 (7)		- Mg13 281.3 (20)		- S15 285.7 (3)		
	- MG17 267.1 (12)		- MG17 281.9 (7)		- S11 286.3 (2)	Mg14	- S16 265.2 (20)
	- L13 270.9 (3)		- MG17 281.9 (7)		- S11 286.3 (2)		- S16 280.5 (15)
	- L13 270.9 (3)				- L12 289.1 (7)		- S12 304.8 (21)
	- Mg18 272.7 (27)	L11	- S11 266.3 (4)		- L13 290.1 (5)	Mg15	- S16 261.7 (9)
	- L12 277.8 (3)		- S12 267.8 (2)		- S14 299.1 (3)		- S16 261.7 (9)
	- L12 277.8 (3)		- S12 267.8 (2)		- S14 299.1 (3)		- S11 266.3 (15)
	- L13 278.8 (4)		- L15 281.5 (6)				- S15 318.6 (15)
	- L18 280.8 (9)		- S11 284.2 (3)	L16	- Mg14 254.2 (19)	Mg16	- S16 264.1 (4)
	- L18 280.8 (9)		- S11 284.2 (3)		- Mg14 254.2 (19)		- S16 264.1 (4)
			- L16 290.0 (7)		- Mg15 256.2 (11)		- S15 270.1 (7)
S14	- S15 234.57 (8)		- L16 298.9 (5)		- Mg15 256.2 (11)		- S11 275.9 (9)
	- S13 236.42 (9)		- L16 298.9 (5)		- S16 272.1 (6)		
	- L18 256.2 (6)	L12	- Mg14 252.4 (19)		- S12 282.7 (5)		
	- L18 256.2 (6)		- Mg14 252.4 (19)		- S11 285.9 (3)		
	- L14 269.5 (3)		- Mg14 252.4 (19)		- S11 285.9 (3)	MG17	- S13 267.1 (12)
	- L14 269.5 (3)		- L18 253.9 (7)		- Mg16 289.5 (8)		- S16 281.9 (7)
	- L13 272.1 (3)		- L18 253.9 (7)		- Mg16 289.5 (8)		- S16 281.9 (7)
	- L13 272.1 (3)		- Mg18 259.5 (14)		- L11 290.0 (7)		
	- L15 299.1 (3)		- Mg18 259.5 (14)		- L11 298.9 (5)	Mg18	- S16 253.7 (13)
	- L15 299.1 (3)		- S12 265.5 (2)		- L11 298.9 (5)		- S16 253.7 (13)
			- S12 265.5 (2)				- S13 272.7 (27)
S15	- S14 234.57 (8)		- S16 272.3 (5)	L17	- Mg16 269.1 (6)		
	- S11 236.87 (8)		- S13 277.8 (3)		- Mg16 269.1 (6)		
	- L14 265.3 (5)		- S13 277.8 (3)		- L18 273.1 (9)		
	- Mg16 270.1 (7)		- Mg13 282.4 (34)		- L18 273.1 (9)		
	- L17 277.0 (3)		- L15 289.1 (7)		- S16 273.3 (4)		
	- L17 277.0 (3)				- S15 277.0 (3)		
	- L15 285.7 (3)				- S15 277.0 (3)		
	- L15 285.7 (3)				- L14 294.3 (5)		
	- L14 286.2 (2)						
	- L14 286.2 (2)						

### Angles

S11	- S12	- S13	108.44 (3)
S14	- S13	- S12	106.68 (3)
S15	- S14	- S13	109.17 (3)
S14	- S15	- S11	107.77 (3)
S12	- S11	- S15	107.93 (3)

Note. The distances are displayed up to 300 pm (Si and Li: all neighbors, Mg: silicon coordination). The angles are listed only for the  $\text{Si}_5$  ring.

units as  $\text{Si}^{4-}$  or  $\text{Si}_4^{12-}$  are necessary to provide for a suitable packing of the fivefold piles. This may be the reason that com-

pounds like  $\text{Li}_6\text{Si}_5$  and  $\text{Li}_6\text{Ge}_5$  have not been observed.

The Si-Si bond distances in  $\text{Li}_8\text{MgSi}_6$

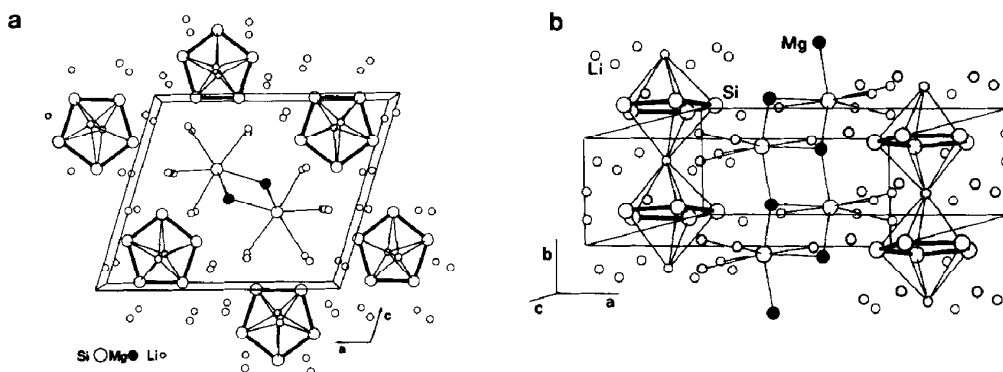


FIG. 2. Perspective view of the Li<sub>8</sub>MgSi<sub>6</sub> structure (a) along [010] and (b) perpendicular to (100) (Si: big, Mg: black, Li: small circles).

range from 234.6 to 238.5 pm with a mean value of 236.4 pm and are very similar to those observed in the corresponding Si<sub>5</sub> cluster in Li<sub>12</sub>Si<sub>7</sub> (235.6, 237.9, 236.7 pm). However, the comparison of the two equivalent ring systems shows differences which are probably due to packing effects in the crystal structures. This seems especially true for the longer distance of about 238–239 pm which occurs in the region of closest approach of the piles. Similar arguments hold for the angles in the Si<sub>5</sub> ring which do not differ very much and show values around the ideal angle of  $3\pi/5 = 108^\circ$  for a planar five-membered ring. The local coordination of the Si atoms in the Si<sub>5</sub> ring is completed either by 6 or 7 metal atoms giving rise to slightly different mean distances so that a comparable overall coordination results for all ring atoms (Fig. 3).

The isolated silicon Si6 is surrounded by 3 Mg and 4 Li atoms with very similar overall coordination number. Nevertheless Si6 and Mg form a building unit, which has the shape of a puckered ladder expanding along [010].

The Li atoms as well as the main Mg position (Mg11) are coordinated by 5 Si atoms except Li5 which is “sandwiched” between two Si<sub>5</sub> rings having 10 neighboring Si atoms. The Mg atom is distributed around a circular area which is perpendicular to and centered at the line Si6–Si6' along [010] (Fig. 1). The central position in 0.66,  $\frac{1}{4}$ , 0.62 (Fig. 1) has too short distances to the Si6 atoms (217 pm) and, therefore, cannot be occupied. On a circle with a radius of about  $R = 160$  pm around that point, a suitable Mg–Si distance is reached allowing for additional contacts to the silicon at-

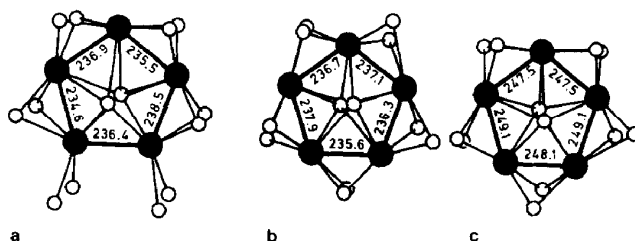


FIG. 3. One-dimensional  $\frac{1}{2}$ [LiSi<sub>5</sub>] piles (a) in Li<sub>8</sub>MgSi<sub>6</sub>, (b) in Li<sub>12</sub>Si<sub>7</sub>, and (c) in “Li<sub>11</sub>Ge<sub>6</sub>” perpendicular to the mean plane, including the outer metal coordination. The geometry of the central part does not change significantly while the outer coordination changes slightly. Bond length Si–Si and Ge–Ge, respectively, in pm.

oms of the five-membered ring. The other surrounding Si atoms, however, favor certain positions on that circle which gives rise to 3 pronounced maxima in that region with decreasing electron density, e.g., Mg11, Mg16, and Mg17. The other Mg positions occur in the difference Fourier map and have been used to collect the total electron density as far as possible. We interpret these small density regions as possible positions of moving or statistically distributed Mg atoms, which are, however, most probably found at the Mg11 site. All these positions have digestible distances to other atoms and are well coordinated by silicon atoms. This was found to be consistent with very similar coordination spheres for the different positions determined by the effective coordination number ECON (10) and bond order method (18) calculations.

The distribution of Li8 and its high  $U_{22}$  coefficient are due to a relaxation along the  $b$  axis with respect to the local Mg disorder. Li8 does not change its coordination considerably in this way, but avoids the Mg atom. Similar but weaker interactions occur between Li7–Li8, Li7–Li6–Mg11, and Li2–Mg13 and give rise to slightly higher temperature factor components along corresponding directions (see arrows in Fig. 1).

## 6. Discussion

The structure of  $\text{Li}_8\text{MgSi}_6$  gives once more the opportunity to demonstrate the validity of the *generalized* Zintl–Klemm concept. This means that multicenter bonds, multiple bonds, and aromatic bonding as well as the occupancy of antibonding states can well be considered for the analysis of the correlation between electron count and structure. It is furthermore not important whether this is applied to isolated clusters, one-, two-, and three-dimensional structures (or partial structures) or to localized and delocalized electronic states

(bands). In general this is quite common for the elements of the first and second period, but hardly taken into account for the higher ones up to now. We think that there is a strong indication to consider these effects for the higher elements, too, on a much broader basis now.

A transfer of electrons into antibonding states does not necessarily lead to bond breaks, if the antibonding state can be stabilized by perturbation arising from the environment of the cluster. The electronic state in question should fulfill the requirements of a so-called frontier orbital (20). This was shown, e.g., for the  $28e$   $\text{Si}_4$  star in  $\text{Li}_{12}\text{Si}_7$  (13).  $\text{Li}_8\text{MgSi}_6$  fulfills the electronic rules of Zintl and Klemm (11) and Mooser and Pearson (12) indeed only if the planar  $\text{Si}_5$  ring is assumed to be a quasi-aromatic  $26e$  system. The formal electron distribution can be rationalized as  $(\text{Li}^+)_8\text{Mg}^{2+}[\text{Si}_5]^{6-}\text{Si}^{4-}$ . *These formal charges are only used to count the correct number of valence electrons being in crystal orbital states with dominant character of the corresponding atom or cluster.* This description is in complete agreement with the physical properties and is supported by recent band structure calculations for  $\text{Li}_{12}\text{Si}_7$  (13) and  $\text{Li}_8\text{MgSi}_6$  (14) on the basis of a one-dimensional crystal orbital SCF calculation scheme (15, 16). These investigations confirm that in both compounds the  ${}^1_2[\text{LiSi}_5]$  piles represent  $26e$  systems per repeat unit independent of variations of the outer Li coordination ( ${}^1_2[\text{Li}_4\text{LiSi}_5]^-$ ,  ${}^1_2[\text{Li}_5\text{LiSi}_5]^0$ , and  ${}^1_2[\text{Li}_6\text{LiSi}_5]^+$ ). It should be emphasized that the  $\text{Si}_5^{6-}$  units present here are the first proved (deprotonized) pentasilacyclopentadienyl systems. The occurrence of an isolated Si atom of the formal charge 4 fits the normal description in terms of the electronic counting rules without any difficulty.

The comparison of the structures of  $\text{Li}_{12}\text{Si}_7$  and  $\text{Li}_8\text{MgSi}_6$  shows that the translation period along the  ${}^1_2[\text{LiSi}_5]$  piles is nearly

unaffected by the composition. In the case of Li<sub>8</sub>MgSi<sub>6</sub> this gives rise to the unacceptable short distance between the Si6 position and the "ideal" position of Mg at 0.66,  $\frac{1}{4}$ , 0.62. Therefore, the splitting of the Mg over several positions around 0.66,  $\frac{1}{4}$ , 0.62 follows from the fixed length of the LiSi<sub>5</sub> piles. This displacement of the Mg atoms affects of course the adjacent Li8 sites.

Compounds like Li<sub>6</sub>Si<sub>5</sub> and Li<sub>6</sub>Ge<sub>5</sub> with the pure sandwich pile have not been observed. The reason may be that a dense packing of such piles might be unfavorable. In Li<sub>12</sub>Si<sub>7</sub> and Li<sub>8</sub>MgSi<sub>6</sub> the piles are separated from each other by different structural units like the Si<sub>4</sub> star and the  $\frac{1}{\infty}$ [MgSi] ladder, respectively. It should be pointed out that in both cases the additional units contain the higher charged atoms (Li<sub>12</sub><sup>2+</sup>Si<sub>4</sub><sup>2-</sup> in Li<sub>12</sub>Si<sub>7</sub> and Li<sub>2</sub><sup>2+</sup>Mg<sup>2+</sup>Si<sub>4</sub><sup>4-</sup> in Li<sub>8</sub>MgSi<sub>6</sub>), a picture which is strongly supported by the SCF INDO results (13, 14). Although the separation of the Li<sub>12</sub>Si<sub>7</sub> structure into the quoted units might seem somewhat arbitrary, the division of the Li<sub>8</sub>MgSi<sub>6</sub> structure is obvious and justifies the description of Li<sub>12</sub>Si<sub>7</sub> (13).

The comparison of the molar volumes (MV) of Li<sub>12</sub>Si<sub>7</sub>, Li<sub>8</sub>MgSi<sub>6</sub>, "Li<sub>11</sub>Ge<sub>6</sub>," Li<sub>14</sub>Si<sub>6</sub>, Li<sub>13</sub>Si<sub>4</sub>, and Li<sub>21</sub>Si<sub>5</sub> gives a further interesting result. From the MV's for charged Si<sup>x-</sup> anions can be calculated by assuming MV (Li<sup>+</sup>) = 2 cm<sup>3</sup> mole<sup>-1</sup> and MV (Mg<sup>2+</sup>) = 2 cm<sup>3</sup> mole<sup>-1</sup> (19). The corresponding volumes for the uncharged Si atoms are yielded by subtraction of the atomic volumes of lithium (8.5 cm<sup>3</sup> mole<sup>-1</sup>) and magnesium (14 cm<sup>3</sup> mole<sup>-1</sup>) from the molar volumes of the corresponding compounds. There is a general trend of increasing volume with the amount of charge on silicon, as expected in the ionic description: MV (Si<sup>1.71-</sup>) = 22.8, MV (Si<sup>1.67-</sup>) = 24.8, MV (Ge<sup>1.67-</sup>) = 25.7 MV (Si<sup>2.33-</sup>) = 26.3, MV (Si<sup>3.25-</sup>) = 34.0, MV (Si<sup>4.2-</sup>) = 40.9 cm<sup>3</sup> mole<sup>-1</sup> calculated from Li<sub>12</sub>Si<sub>7</sub>, Li<sub>8</sub>MgSi<sub>6</sub>, "Li<sub>8</sub>MgGe<sub>6</sub>" (see below), Li<sub>14</sub>Si<sub>6</sub>, Li<sub>13</sub>Si<sub>4</sub>,

Li<sub>21</sub>Si<sub>5</sub>, respectively. Even in the intermetallic type description, the MV (Si<sup>0</sup>, Ge<sup>0</sup>) values do increase slightly in this series: 11.6, 14.1, 15.0 (Li<sub>11</sub>Ge<sub>6</sub>), 11.2, 12.9, 13.6 cm<sup>3</sup> mole<sup>-1</sup>. In both cases the volume for Li<sub>8</sub>MgSi<sub>6</sub> is apparently higher as expected, but the magnitude of these variations is not extraordinary in the family of silicides and germanides of alkali and earth alkaline metals. Variations are obviously correlated to special cluster types and the arrangement of these units in the solid state. The higher volume of Li<sub>8</sub>MgSi<sub>8</sub> relative to Li<sub>12</sub>Si<sub>7</sub> reflects the observed disorder of magnesium and the corresponding volume requirements of the local vacancies.

## 7. Remark on the Existence of Li<sub>11</sub>Ge<sub>6</sub>

The germanide Li<sub>11</sub>Ge<sub>6</sub> was published some years ago (9). Our recent reinvestigation of the Li-Ge system did not give any indication for a binary compound of this composition (2). The striking similarity with the structure of Li<sub>8</sub>MgSi<sub>6</sub> (planar Ge<sub>5</sub> rings, ecliptical  $\frac{1}{\infty}$ [LiGe<sub>5</sub>] piles, isolated Ge atoms, group-subgroup relationship: "Li<sub>11</sub>Ge<sub>6</sub>"-Cmcm, Li<sub>8</sub>MgSi<sub>6</sub>-P2<sub>1</sub>/m) supports the suspicion that this germanide is in fact a ternary compound. There is evidence even from the crystallographic data of the authors (17) that the real composition is Li<sub>8</sub>MgGe<sub>6</sub> with a disordered Mg atom like in Li<sub>8</sub>MgSi<sub>6</sub>. The temperature factor of Li1 in "Li<sub>11</sub>Ge<sub>6</sub>" (17) is vanishingly small ( $U_{iso} = 0.002 \text{ \AA}^2$ ) while the other atoms show normal values. The coordination of Li1 is outstanding, it has only two Ge neighbors (253 pm) while the other Li atoms are coordinated by 4, 5, or 10 (Li5) Ge atoms. To fit the Zintl-Klemm rule, Li1 has to be partly occupied by Mg (~80%) and one Li atom has to be replaced by Mg with ~20% probability (3/14). There is no other position which shows extraordinary properties so that with the reported X-ray data (17) one can only guess where the rest (20%) of the

magnesium may be distributed. From the comparison of the outer metal coordination of the three known  $\frac{1}{2}[\text{LiX}_5]$  piles ( $X = \text{Si}, \text{Ge}$ ) one would guess that in " $\text{Li}_{11}\text{Ge}_6$ " the positions Li3, Li4, Li5, and Li6 are probably occupied by Li atoms while one Mg and two Li per formula unit might be distributed over the position Li1, Li2, and Li7. The molar volumes of " $\text{Li}_{11}\text{Ge}_6$ " ( $172.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) and  $\text{Li}_8\text{MgSi}_6$  ( $166.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) differ only by  $5.7 \text{ cm}^3 \cdot \text{mol}^{-1}$  which is only 63% of the difference of the atomic volumes for 6 Ge and 6 Si ( $9 \text{ cm}^3 \cdot \text{mol}^{-1}$ ). It is not very probable that " $\text{Li}_{11}\text{Ge}_6$ " should have two more atoms per formula unit. On the basis of these arguments, we believe that its real composition is  $\text{Li}_8\text{MgGe}_6$ . It is interesting to note that the short stacking axis does not change as much (0.8%) as expected from the volume change (1.2%) for the two compounds.

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