

## $\text{Li}_{15}\text{Al}_3\text{Si}_6$ ( $\text{Li}_{14.6}\text{Al}_{3.4}\text{Si}_6$ ), a compound displaying a heterographite-like anionic framework

Laurent Spina, Monique Tillard\* and Claude Belin

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier Cedex 5, France  
Correspondence e-mail: mtillard@univ-montp2.fr

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The title compound, lithium aluminium silicide ( $15/3/6$ ), crystallizes in the hexagonal centrosymmetric space group  $P6_3/m$ . The three-dimensional structure of this ternary compound may be depicted as two interpenetrating lattices, namely a graphite-like  $\text{Li}_3\text{Al}_3\text{Si}_6$  layer and a distorted diamond-like lithium lattice. As is commonly found for LiAl alloys, the Li and Al atoms are found to share some crystallographic sites. The diamond-like lattice is built up of Li cations, and the graphite-like anionic layer is composed of Si, Al and Li atoms in which Si and Al are covalently bonded [ $\text{Si}-\text{Al} = 2.4672$  (4) Å].

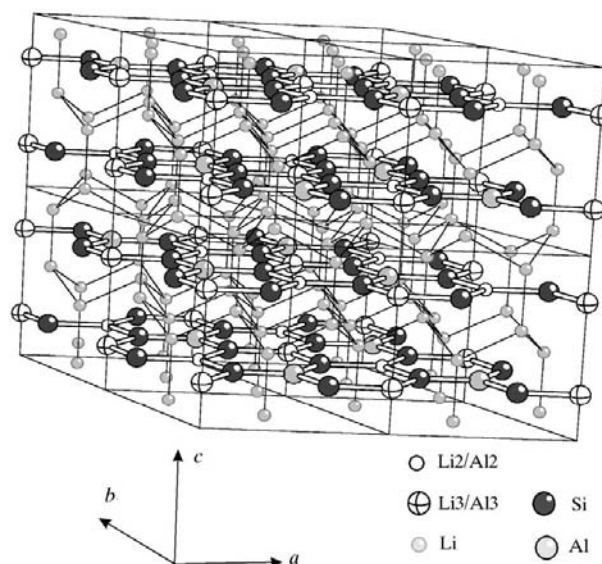
### Comment

Lithium alloys have been the subject of considerable interest in electrochemistry as possible replacements for lithium metal as the negative electrode in lithium batteries (Winter *et al.*, 1998; Winter & Besenhard, 1999; Huggins, 1999). Silicon-based lithium-alloying materials are also particularly interesting. Silicon is, after oxygen, the second most common element on earth. Aluminium and silicon are very cheap compared with other metal candidates, and their electronegativities and low weights would provide batteries with high potential and mass capacities.

With a view to some future electrochemical work, we decided to reinvestigate the ternary LiAlSi system, on the basis of the phase diagram established at 523 K (Kevorkov *et al.*, 2001) using differential thermal analysis and X-ray powder diffractometry. This work led to the discovery of a new ternary compound with the idealized formula  $\text{Li}_{15}\text{Al}_3\text{Si}_6$ , the stoichiometry of which has been confirmed by atomic absorption spectrophotometry of single crystals. Here, we present the structure of  $\text{Li}_{15}\text{Al}_3\text{Si}_6$ .

The atomic packing within the hexagonal unit cell of  $\text{Li}_{15}\text{Al}_3\text{Si}_6$  may be formally described as interpenetrating anionic and cationic lattices, a graphite-like  $\text{Li}_3\text{Al}_3\text{Si}_6$  layer and a distorted diamond-like lithium lattice (Fig. 1). The

diamond-like lattice is built up of Li1 atoms that have a distorted tetrahedral environment, with Li1–Li1 distances ranging from 2.688 (11) to 2.861 (6) Å and angles ranging from 97.3 (3) to 118.4 (4)° (Table 1). Within the graphite-like layer, some covalent Al–Si bonding is observed, with Al1 being linked to three Si atoms [ $\text{Al}-\text{Si} = 2.4672$  (4) Å]. Owing to the Al/Li occupational disorder found at crystallographic sites 2*a* and 2*c* (Table 2), each Si atom is connected to three neighbours, Al1, Al/Li2 and Al/Li3, with interatomic distances of 2.4672 (4), 2.5667 (4) and 2.5162 (4) Å, respectively.



**Figure 1**

A representation of the atomic packing of  $\text{Li}_{15}\text{Al}_3\text{Si}_6$  in the hexagonal cell ( $2 \times 2 \times 2$  unit cells), emphasizing the two-dimensional heterographite-like (Si, Al, Li) and three-dimensional diamond-like (Li) sublattices.

### Experimental

Initially, our goal was to synthesize the known compound  $\text{Li}_{12}\text{Al}_3\text{Si}_4$ , so melts of the elements were prepared in this stoichiometry. Silicon was used as a very pure powder, and the surfaces of the pure aluminium and lithium metals were scraped before use to remove any oxide film. The alloy was prepared in a tantalum tube weld-sealed under an argon atmosphere. This tube was protected from air by a silica jacket sealed under vacuum. The mixture was heated for 10 h at 1223 K in a vertical furnace and shaken several times for homogenization. It was then cooled at a rate of 6 K h<sup>-1</sup> for crystal growth. The product of the reaction appeared to be not quite homogeneous, but contained predominantly black and well-crystallized material. A few black crystals were selected and analysed by atomic absorption flame spectrometry to establish their composition. Analysis led to an Li/Al/Si ratio of 1:0.223 (2):0.41 (1), corresponding to a mean formula of  $\text{Li}_{14.63}\text{Al}_{3.26}\text{Si}_6$ . The compound could then be re-prepared following this stoichiometry and obtained in practically 100% yield, as confirmed by the X-ray powder pattern (m.p. 1097 K). Crystals were selected using a microscope inside a glove box filled with purified argon and were then inserted into Lindemann glass capillaries, avoiding any contact with air and moisture, and checked for singularity by preliminary oscillation and Weissenberg X-ray photographs. The best diffracting crystal was used for the intensity measurements.

## Crystal data

Li<sub>14.6</sub>Al<sub>3.4</sub>Si<sub>6</sub>  
*M<sub>r</sub>* = 361.32  
 Hexagonal, *P*6<sub>3</sub>/*m*  
*a* = 7.549 (1) Å  
*c* = 8.097 (1) Å  
*V* = 399.61 (9) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 1.501 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 451 reflections  
 $\theta = 0\text{--}31^\circ$   
 $\mu = 0.67\text{ mm}^{-1}$   
*T* = 293 (2) K  
 Plate, black  
 0.32 × 0.20 × 0.12 mm

## Data collection

Oxford Xcalibur CCD area-detector diffractometer  
 $\omega$  scans  
 3693 measured reflections  
 451 independent reflections  
 274 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.049  
 $\theta_{\text{max}} = 31.2^\circ$   
*h* = −10 → 7  
*k* = −10 → 10  
*l* = −11 → 11

## Refinement

Refinement on *F*  
*R* = 0.036  
*wR* = 0.049  
*S* = 1.10  
 274 reflections  
 24 parameters

Weighting scheme: Chebyshev polynomial with 3 parameters (Carruthers & Watkin, 1979), 0.0509, 7.70 and −1.98  
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.62\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.01\text{ e \AA}^{-3}$

The highest residual density and the deepest hole in the final difference Fourier map were located near the Si and Al1 sites, respectively.

**Table 1**

Selected geometric parameters (Å, °).

Si—Al1	2.4672 (4)	Al1—Li1 <sup>i</sup>	2.885 (4)
Si—Al/Li2	2.5162 (4)	Li1—Li1 <sup>iv</sup>	2.688 (11)
Si—Al/Li3	2.5667 (4)	Li1—Li1 <sup>v</sup>	2.861 (6)
Si—Li1	2.704 (5)	Li1—Li1 <sup>i</sup>	2.862 (8)
Si—Li1 <sup>i</sup>	2.855 (4)	Li1—Li2 <sup>vi</sup>	2.853 (4)
Si—Li1 <sup>ii</sup>	2.865 (4)	Li1—Li3 <sup>i</sup>	2.821 (4)
Si—Li1 <sup>iii</sup>	2.841 (4)		
Al1—Si—Al2	121.993 (17)	Li1 <sup>i</sup> —Li1—Li1 <sup>v</sup>	97.3 (3)
Al1—Si—Al3	119.941 (15)	Li1 <sup>iii</sup> —Li1—Li1 <sup>v</sup>	99.3 (2)
Al2—Si—Al3	118.066 (15)	Li1 <sup>i</sup> —Li1—Li1 <sup>iv</sup>	118.4 (4)
Li1 <sup>i</sup> —Li1—Li1 <sup>iii</sup>	101.2 (3)		

Symmetry codes: (i)  $-x, 1 - y, -z$ ; (ii)  $1 + x - y, 1 + x, \frac{1}{2} + z$ ; (iii)  $y - 1, -x + y, -z$ ; (iv)  $x, y, -\frac{1}{2} - z$ ; (v)  $1 + x - y, 1 + x, -z$ ; (vi)  $-x, 2 - y, -z$ .

**Table 2**

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>).

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$$

	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Si	1.0	−0.00879 (7)	0.66238 (6)	1/4	0.0099
Al1	1.0	−1/3	1/3	1/4	0.0211
Li1	1.0	−0.0064 (3)	0.6635 (3)	−0.0840 (5)	0.0211
Al2	0.545 (9)	0	1	1/4	0.0219
Li2	0.455 (9)	0	1	1/4	0.0219
Al3	0.148 (13)	1/3	2/3	1/4	0.0265
Li3	0.852 (13)	1/3	2/3	1/4	0.0265

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2002); molecular graphics: *DIAMOND* (Brandenburg, 2001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1397). Services for accessing these data are described at the back of the journal.

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