Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ (x = 3.2): a new intermetallic structure type

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The new ternary lithium copper aluminide, Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ (x = 3.2), dodecalithium nonadecacopper tricosaaluminide, crystallizes in a new structure type with space group $P4/mbm$. Among nine independent atomic positions, two Al (one of which is statistically disordered with Cu) and three Li atoms have point symmetry $m.2m$, two statistically disordered Al/Cu atoms are in $m..$ sites, one Al atom is in a $4/m..$ site and one Cu atom occupies a general site. The framework of Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ consists of pseudo-Frank–Kasper polyhedra enclosing channels of hexagonal prisms occupied by Li atoms. The crystallochemical peculiarity of this new structure type is discussed in relation to the derivatives from Laves phases (LiCuAl$_2$ and Li$_8$Cu$_{12+x}$Al$_{6-x}$) and to the well known CaCu$_5$ structure.

## Comment

The Li–Cu–Al ternary system has been the subject of intense scientific scrutiny for many decades. The first report on the crystal structures of intermetallides existing in this system was made by Hardy & Silcock (1955–1956), but the majority of papers dedicated to the investigation of these compounds were published beginning in the late 1980s. Intermetallides in this system adopt highly symmetrical structures: Li$_3$CuAl$_5$ (Audier *et al.*, 1988; Guryan *et al.*, 1988), LiCu$_4$Al$_{7.5}$ (Schneider & von Heimendahl, 1973) and Li$_3$CuAl$_6$ (Dubost *et al.*, 1986; Konno *et al.*, 2002) belong to the cubic system, while LiCuAl$_2$ (Knowles & Stobbs, 1988; Van Smaalen *et al.*, 1990) and Li$_8$Cu$_{12+x}$Al$_{6-x}$ (Pavlyuk *et al.*, 2008) are hexagonal. The family of quasicrystals of nominal composition close to Li$_3$CuAl$_6$, reviewed by Steurer & Deloudi (2008), has attracted the greatest interest among researchers.

Within the framework of our continuing studies of lithium aluminides, we report here the structure of the new com-

pound, Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ (x = 3.2). To our knowledge, it is the first compound with tetragonal symmetry in the Li–Cu–Al system. Moreover, this intermetallide crystallizes in a new structure type with space group $P4/mbm$ (No. 127), Pearson symbol tP54. The structure of Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ contains three Li, one Cu, two Al and three statistically mixed Al/Cu positions in the asymmetric unit. For simplicity, hereinafter the last positions are designated as Al2, Al3 and Al6, because more Al than Cu is located on these sites. The clinographic projection of the unit cell and coordination polyhedra of atoms are shown in Fig. 1.

Atoms Li1 and Li2 occupy $4g$ and $4h$ Wyckoff sites and are surrounded by 15 neighbouring atoms in the form of tricapped distorted icosahedra, *viz.* [(Li1)Li$_2$Cu$_4$Al$_4$LiAl$_4$] and [(Li2)Li$_3$Cu$_4$Al$_8$]. The coordination around atom Li3 ($4h$ site) consists of 14 atoms, resulting in a deformed icosahedron with two additional vertices, *viz.* [(Li3)LiAl$_3$Cu$_4$Al$_6$]. The bonding distances for the Li atoms cover the range 2.49 (5)–3.24 (2) Å. The coordination polyhedra around the Cu atoms (in the $16l$ position) are distorted icosahedra of composition [(Cu1)Al$_2$-Cu$_2$Al$_4$Li$_3$Al] with distances to the nearest and farthest atoms of 2.453 (2) and 3.324 (1) Å. Atom Al5 ($2a$ site) is surrounded by 20 adjacent atoms [(Al5)Al$_{12}$Cu$_8$] in the form of a pseudo-Frank–Kasper polyhedron. Atoms Al4 and Al6 (Wyckoff sites $4h$ and $8i$, respectively) are characterized by irregular icosahedra with two extra vertices, *viz.* [(Al4)LiAlCu$_4$Al$_2$Li$_6$] and [(Al6)Cu$_2$Al$_2$Cu$_2$Al$_2$Li$_3$AlLi$_2$], similar to the Li3 atoms. The coordination environments of atoms Al2 ($4g$) and Al3 ($8j$) are distorted (to different degrees) icosahedra, *viz.* [(Al2)Cu$_4$Al$_4$-Li$_4$] and [(Al3)Cu$_4$Al$_2$LiAl$_2$LiAl$_2$]. The shortest and longest contacts for Al atoms in the structure are 2.453 (2) and 3.324 (1) Å. The interatomic distances of the first coordination spheres of the atoms (Table 1) are in good agreement with the
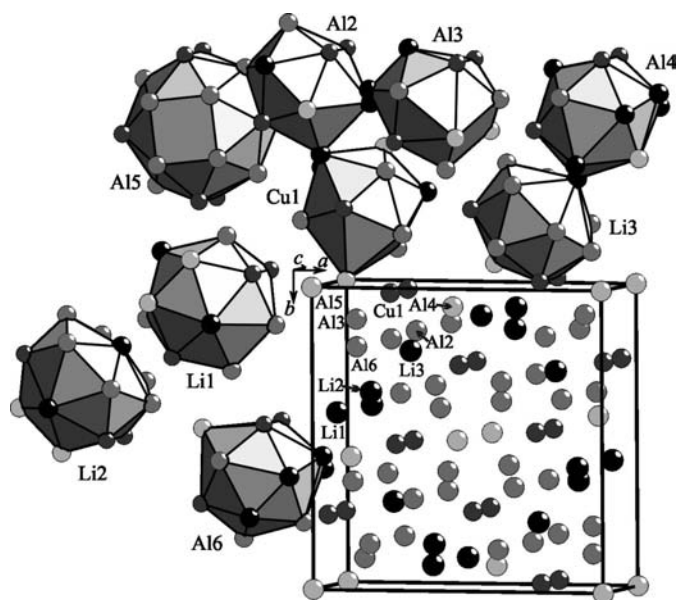
Figure 1
The clinographic projection of the Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ (x = 3.2) unit-cell contents and the coordination polyhedra of atoms. The labels of the central atoms are displaced outside the limits of their corresponding polyhedra.

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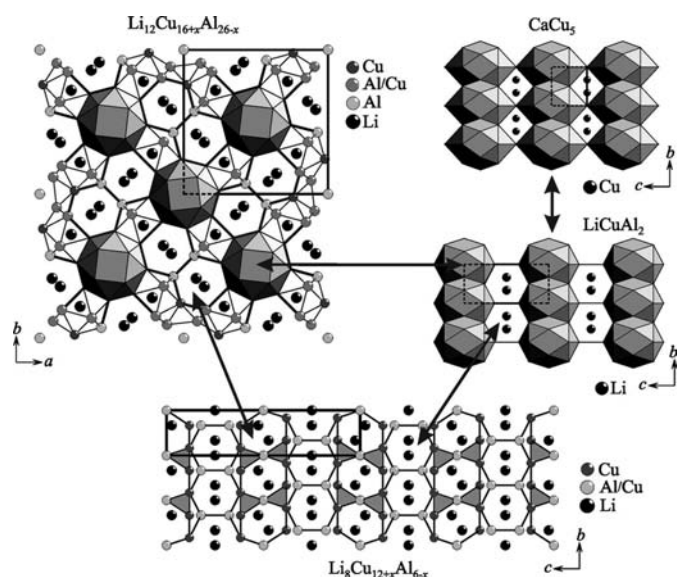
Figure 2
The relationship between the $Li_{12}Cu_{16+x}Al_{26-x}$, $Li_8Cu_{12+x}Al_{6-x}$, $LiCuAl_2$ and $CaCu_5$ structures.

atomic radii of constituent elements (Emsley, 1991) and indicate metallic type bonding [the shortest Cu—Al distance, 2.453 (2) Å, is 90.6% of the sum of single-bond radii].

The pseudo-Frank–Kasper polyhedra around atoms Al5 are slightly distorted compared with the analogous polyhedra in the $CaCu_5$ structure for the Ca atoms (Haucke, 1940). These 20-vertex polyhedra, sharing their rhombohedral faces in $CaCu_5$ and $LiCuAl_2$ (Van Smaalen *et al.*, 1990), form layers with rhombohedral and hexagonal channels between them, respectively. In $Li_{12}Cu_{16+x}Al_{26-x}$, the same constructive elements, namely pseudo-Frank–Kasper polyhedra connected along the [001] direction and hexagonal channels, can also be recognized (Fig. 2). For all the lithium-containing compounds in this family, including $Li_8Cu_{12+x}Al_{6-x}$ (Pavlyuk *et al.*, 2008), a special feature is that the Li atoms are located inside these hexagonal channels, which are connected by sharing edges and faces or faces only.

Experimental

The title compound was prepared from elemental lithium (rod, 99.9 at.%), copper (ingots, 99.999 at.%) and aluminium (ingots, 99.999 at.%) in the slightly off-stoichiometric 25:35:40 ratio. The reaction mixture was sealed under an argon atmosphere in a pure iron crucible and heated to 1370 K, with intensive shaking started at approximately 1270 K. After holding for 10 min at the maximum temperature, the product was cooled rapidly by removing the crucible from the furnace into ambient conditions. In the crushed sample, metallic dark-grey plate-shaped crystals were found using a conventional light microscope. On the basis of previous studies with successive detailed chemical analyses of similar systems (Pauly, 1966; Pauly *et al.*, 1968), a loss of Li of up to 1 at.% in nominal composition during sample preparation in hermetically closed crucibles can be expected. A single crystal was protected from air during X-ray data collection in a sealed thin-walled glass capillary (Heidelberg, No. 10).

Crystal data

$Li_{12}Cu_{19.21}Al_{22.84}$	$Z = 1$
$M_r = 1920.43$	Mo $K\alpha$ radiation
Tetragonal, $P4/mbm$	$\mu = 13.05$ mm^{-1}
$a = 12.696$ (2) Å	$T = 295$ (2) K
$c = 4.982$ (1) Å	$0.1 \times 0.08 \times 0.04$ mm
$V = 803.0$ (2) Å^3	

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	2572 measured reflections
	490 independent reflections
Absorption correction: empirical (using intensity measurements) (*CrysAlis RED*; Oxford Diffraction, 2005)	281 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.091$
$T_{min} = 0.29$, $T_{max} = 0.60$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	36 parameters
$wR(F^2) = 0.098$	$\Delta\rho_{max} = 0.98$ e Å^{-3}
$S = 0.99$	$\Delta\rho_{min} = -1.03$ e Å^{-3}
490 reflections	

Table 1
Selected bond lengths (Å).

Cu1—Al2	2.4532 (15)	Al6—Cu1[i]	2.624 (4)
Al3—Cu1[i]	2.494 (3)	Li1—Li2	2.688 (18)
Al4—Li3	2.63 (3)	Li2—Li3	2.49 (5)

Symmetry code: (i) $-y, x, z$.

A statistical test of the distribution of the E values using the program *E-STATS* from the *WinGX* system (Farrugia, 1999) suggested with a probability of 60.9% that the structure is centrosymmetric. The analysis of systematic extinctions yielded the space group $P4/mbm$ (No. 127), which was confirmed by the following structure refinement. The structure was solved after an empirical absorption correction. In the first stage of the refinement, the positions of the Cu and Al atoms were obtained correctly by direct methods. The remaining Li atoms were located in subsequent difference Fourier syntheses. The Al2, Al3 and Al6 positions (Wyckoff sites $4g$, $8j$ and $8i$, respectively) showed displacement parameters considerably smaller than those of other Al sites, suggesting that these positions are partially occupied by the heavier Cu atom. The attempts to refine all atoms, except for lithium, with anisotropic displacement parameters and Al/Cu statistical distribution for three sites failed because of a very small content of copper in the Al6 site. Assuming this position to be occupied only by aluminium led to unreasonable displacement parameters. The Al:Cu ratio of the Al6 site was varied with fixed displacement parameters and eventually was fixed at 95:5 on the basis of R factor values. In the final refinement cycles, isotropic and common isotropic displacement parameters for the Al6 position and all Li sites, respectively, were refined. All other atoms were successfully refined with anisotropic displacement parameters without any constraints. The maximum and minimum electron-density features in the final difference map are 1.37 and 0.90 Å, respectively, from the Cu1 site.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3156). Services for accessing these data are described at the back of the journal.

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