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$Li_8Cu_{12+x}Al_{6-x}$ (x = 1.16): a new structure type related to Laves phases

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The new ternary lithium copper aluminide $Li_8Cu_{12+x}Al_{6-x}$ (x = 1.16) crystallizes in the $P6_3/mmc$ space group with six independent atom positions of site symmetries $\bar{3}m.$ (Al/Cu mixture), $\bar{6}m2$ (Li atoms), $3m.$ (Al/Cu mixture and Li atoms) and $.m.$ (Cu atoms). The compound is a derivative of the K_7Cs_6 binary structure type and is related to the binary $MgZn_2$ Laves phase and the $LiCuAl_2$, $MgCu_{1.07}Al_{0.93}$ and $Mg(Cu_{1-x}Al_x)_2$ (x = 0.465) ternary Laves phases. The coordination polyhedra of the atoms in this structure are icosahedra (Cu atoms), slightly distorted icosahedra and bicapped hexagonal antiprisms (Al/Cu statistical mixture), and Frank–Kasper and distorted Frank–Kasper polyhedra (Li atoms). All interatomic distances indicate metallic type bonding.

Comment

The Li–Cu–Al system has attracted great attention since the middle of the last century, primarily due to the mechanical properties of alloys based on these components. They are widely used in industrial manufacturing of light, super-light and deformation-stable materials. They also show good prospects for taking one of the leading places in energy-saving technologies. Many papers have been dedicated to investigations of the crystal structures of intermetallides which exist in this system (Hardy & Silcock, 1955–1956; Knowles & Stobbs, 1988; van Smaalen *et al.*, 1990; Audier *et al.*, 1988; Guryan *et al.*, 1988; Dubost *et al.*, 1986; Leblanc *et al.*, 1991).

We report here the single-crystal structure determination for the ternary compound $Li_8Cu_{12+x}Al_{6-x}$ (x = 1.16), detected during systematic investigations of the Li–Cu–Al system at 473 K. This compound represents a new structure type, which is derived from the K_7Cs_6 binary type (von Simon *et al.*, 1976) by a redistribution of the occupied Wyckoff sites. The unit-cell volume of $Li_8Cu_{12+x}Al_{6-x}$ is one-sixth of that of K_7Cs_6. The K atom sites (2*a* and 12*k*) are now occupied by a statistical mixture of Al/Cu and Cu atoms, respectively. Two Cs positions (4*f*) are occupied by Li atoms and an Al/Cu statistical mixture (for simplicity, hereinafter referred to as Al1 and Al2, because more Al than Cu is situated on these sites). Another two Cs sites (2*b* and 2*c*) are now exclusively occupied by Li atoms. A clinographic projection of the $Li_8Cu_{12+x}Al_{6-x}$ unit cell and coordination polyhedra of atoms are shown in Fig. 1. The interatomic distances in the first coordination spheres of the atoms (Table 1) are in agreement with typical values for intermetallics. The coordination polyhedra of the Cu3 atoms (Wyckoff site 12*k*) are $[Cu3Cu_4Al_3Li_5]$ icosahedra. Two types of polyhedra are observed for the Al1 and Al2 atoms on Wyckoff sites 4*f* and 2*a*, namely bicapped hexagonal $[Al1AlCu_6Li_7]$ antiprisms and slightly distorted $[Al2Cu_6Li_6]$ icosahedra, respectively. The coordination spheres around the Li1 (2*b*) and Li2 (2*c*) atoms consist of 15 atoms, resulting in 15-vertex $[Li1Cu_6Li_3Al_6]$ and $[Li2Cu_6Li_3Al_6]$ polyhedra. The Li3 atoms (4*f*) are characterized by 16-vertex $[Li3Al_4Cu_9Li_3]$ polyhedra similar to those in Laves phases.

Both the $Li_8Cu_{12+x}Al_{6-x}$ and K_7Cs_6 structures are derivatives of Laves phases. The $MgZn_2$ (Komura & Tokunaga,

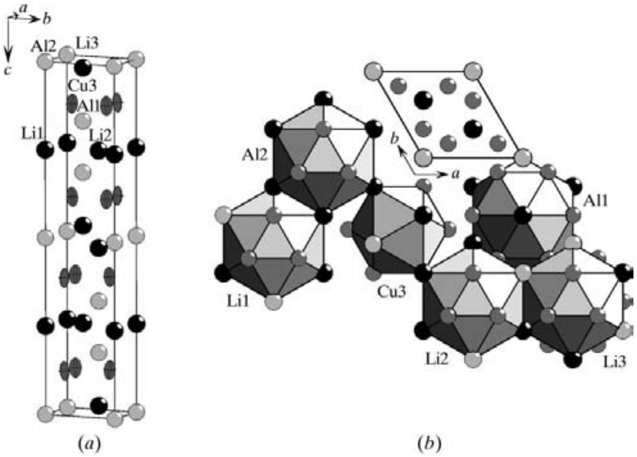

Figure 1
(*a*) Clinographic projection of the $Li_8Cu_{12+x}Al_{6-x}$ unit-cell contents, with displacement ellipsoids drawn at the 95% probability level. (*b*) The unit-cell projection of the $Li_8Cu_{12+x}Al_{6-x}$ compound, on to the (110) plane, and coordination polyhedra of the atoms.

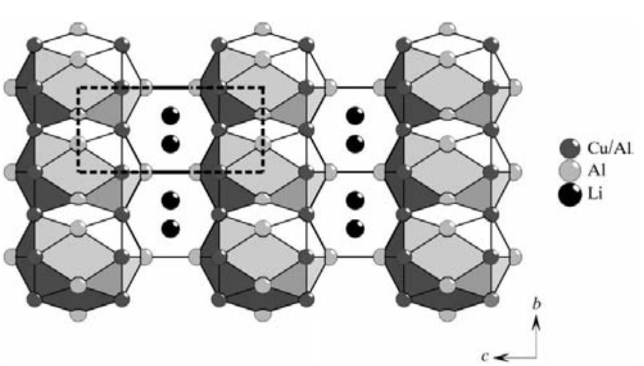

Figure 2
The pseudo-Frank–Kasper polyhedral layers in the $LiCuAl_2$ structure.

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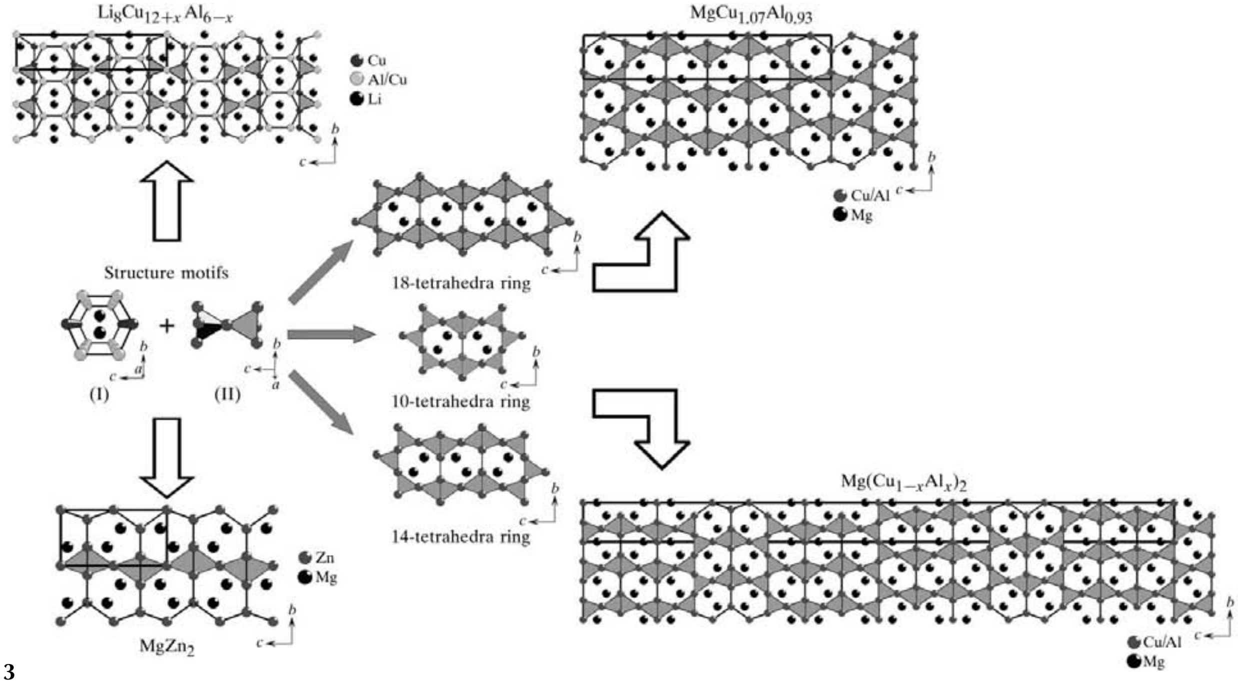

Figure 3
Crystallographic relations between the $Li_8Cu_{12+x}Al_{6-x}$, $MgZn_2$, $MgCu_{1.07}Al_{0.93}$ and $Mg(Cu_{1-x}Al_x)_2$ compounds.

1980), $Mg(Cu_{1-x}Al_x)_2$ (x = 0.468) and $MgCu_{1.07}Al_{0.93}$ (Kitano *et al.*, 1977), and $LiCuAl_2$ (van Smaalen *et al.*, 1990) structures are similar to the title compound. The main features of all of them are channels of hexagonal prisms with Li atoms inside, hereinafter referred to as I. These channels share edges and faces with neighbouring channels, except in $LiCuAl_2$, where only shared faces are realized by pseudo-Frank–Kasper polyhedra (coordination number 20) sharing their rhombohedral faces to form layers, which are separated by I motifs (Fig. 2). All the other structures consist of two different fragments, namely the same motif, I, and another motif, II, consisting of a pair of empty tetrahedra connected by the vertex and rotated with respect to each other through an angle of 30° (Fig. 3). Moreover, in the $MgZn_2$ compound, each II fragment is linked with two neighbouring fragments by face-forming corrugated slabs. The II motifs build up larger ring units of ten and 14 tetrahedra in $Mg(Cu_{1-x}Al_x)_2$ and ten and 18 tetrahedra in $MgCu_{1.07}Al_{0.93}$ around the hexagonal prisms I. In contrast, all II fragments are isolated from each other in the title compound, so that no rings of tetrahedra are formed. This is reflected in the shorter c-axis parameter, corresponding to four I motifs, but six in $MgCu_{1.07}Al_{0.93}$ and even 16 for $Mg(Cu_{1-x}Al_x)_2$.

Experimental

Crystals of $Li_8Cu_{12+x}Al_{6-x}$ (x = 1.16) were obtained from an alloy which was prepared by the solid-state reaction of lithium (rod, 99.9 at.%), copper (ingots, 99.999 at.%) and aluminium (ingots, 99.999 at.%) sealed under argon in a pure iron crucible and heated at 1370 K for 10 min with intensive shaking. The product was then cooled rapidly to room temperature. When the crucible was opened in an Ar-filled glove-box, metallic dark-grey plate-shaped crystals of the title compound were found in the product. The amount of Li lost during sample preparation in hermetically closed crucibles can be estimated (<1 at.%), based on previous studies with successive detailed chemical analyses of similar systems (Pauly, 1966; Pauly *et al.*, 1968).

Crystal data

$Li_8Cu_{13.16}Al_{4.84}$
M_r = 1022.27
Hexagonal, $P6_3/mmc$
a = 4.9351 (10) Å
c = 18.380 (4) Å
V = 387.68 (14) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 17.87 mm^{-1}
T = 295 (2) K
0.09 × 0.05 × 0.01 mm

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer
Absorption correction: empirical (using intensity measurements) (*CrysAlis RED*; Oxford Diffraction, 2005)
T_{min} = 0.35, T_{max} = 0.83
1046 measured reflections
188 independent reflections
133 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.058
S = 0.99
188 reflections
14 parameters
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

Table 1
Selected bond lengths (Å).

Al1—Al1^{i}	2.674 (5)	Cu3—Cu3^{ii}	2.4584 (15)
Al1—Li3	2.775 (18)	Cu3—Li2	2.8107 (9)
Al2—Cu3	2.5980 (8)	Cu3—Li1	2.8160 (9)

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

Analyses of the systematic absences for single-crystal data using the program *ABSEN* (McArdle, 1996) led to the possible space groups $P\overline{3}1c$ (No. 163), $P31c$ (No. 159), $P6_3/mmc$ (No. 194), $P6_3mc$ (No. 186) and $P\overline{6}2c$ (No. 190). A statistical test of the distribution of the *E* values using the program *E-STATS* from the *WinGX* system (Farrugia, 1999) suggested that the structure is centrosymmetric (probability 61.56%). Initial positions of heavier atoms were taken from direct methods. Later, the largest remaining peaks in the difference Fourier syntheses were assumed to correspond to the Li atoms. A decrease of residual *R* factors and an absence of other substantial peaks in the Fourier syntheses clearly indicated that the model was correct. Taking into consideration a significant divergence of the isotropic displacement parameters, it became evident that the 2*a* and 4*f* Wyckoff sites are occupied by mixtures of atoms. The best results were obtained by refining the model with Li1, Li2, Li3 and Cu3 fully occupying the 2*b*, 2*c*, 4*f* and 12*k* positions, respectively, while statistical Al/Cu mixtures were placed in the 2*a* and 4*f* sites. Because of their relatively low atomic number, an overall displacement parameter was refined for the Li atoms. In the final refinement cycles, the anisotropic displacement parameters were refined only for Cu3. The atomic coordinates were standardized using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The final difference Fourier syntheses revealed no significant residual peaks; the highest maximum residual electron density is 0.88 Å from atom Li1 and the deepest hole is 0.84 Å from Li1.

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3108). Services for accessing these data are described at the back of the journal.

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