Li$_{12}$Cu$_{12.60}$Al$_{14.37}$: a new ternary derivative of the binary Laves phases

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New ternary dodecalithium dodecacopper tetradeca-aluminium, Li$_{12}$Cu$_{12.60}$Al$_{14.37}$ (trigonal, $R\bar{3}m$, $hR39$), crystallizes as a new structure type and belongs to the structural family that derives from binary Laves phases. The Li atoms are enclosed in 15- and 16-vertex and the Al3 atom in 14-vertex pseudo-Frank–Kasper polyhedra. The polyhedra around the statistical mixtures of (Cu,Al)1 and (Al,Cu)2 are distorted icosahedra. The electronic structure was calculated by the TB–LMTO–ASA (tight-binding linear muffin-tin orbital atomic spheres approximation) method. The electron localization function, which indicates bond formation, is mostly located at the Al atoms. Thus, Al—Al bonding is much stronger than Li—Al or Cu—Al bonding. This indicates that, besides metallic bonding which is dominant in this compound, weak covalent Al—Al interactions also exist.

Comment

In the search for new electrode materials for lithium batteries, we carried out extensive studies of the interactions of the components in the ternary systems that consist of lithium, transition metals and *p*-elements. Thus, we synthesized and studied the crystal structures of new compounds from the Li–Cu–Si ternary system, such as LiCu$_3$Si$_2$ (Pavlyuk *et al.*, 1995*a*), Li$_7$Cu$_7$Si$_5$ (Pavlyuk *et al.*, 1995*b*), Li$_{113}$Cu$_{54}$Si$_{57}$ (Pavlyuk *et al.*, 1995*c*) and Li$_{119}$Cu$_{145}$Si$_{177}$ (Pavlyuk *et al.*, 1995*d*). The structure of the Li$_5$Cu$_2$Ge$_2$ ternary germanide from the Li–Cu–Ge ternary system was also investigated (Pavlyuk & Bodak, 1992).

In this paper, we present new results for a ternary phase of the Li–Cu–Al system. The first report on the crystal structures of intermetallides of the Li–Cu–Al system was made by Hardy & Silcock (1955–56). Note that the majority of scientific

papers on these compounds were published in the early 1990s. A characteristic feature is that the 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) are cubic, while LiCuAl$_2$ (Knowles & Stobbs, 1988; Van Smaalen *et al.*, 1990) is hexagonal. Stable Li$_3$CuAl$_6$ was initially reported by Hardy & Silcock (1955–56), but was later identified as an icosahedral quasicrystalline phase (Ball & Lloyd, 1985). We synthesized and described the crystal structures of two previously unknown ternary phases, *viz.* Li$_8$Cu$_{12+x}$Al$_{6-x}$ (Pavlyuk *et al.*, 2008*a*) and Li$_{12}$Cu$_{16+x}$Al$_{26-x}$ (Pavlyuk *et al.*, 2008*b*), which crystallize with hexagonal and tetragonal symmetries, respectively.

During the systematic study of ternary alloys of the Li–Cu–Al system in the region between the Li$_{50}$Cu$_{25}$Al$_{25}$ and Li$_{35}$Cu$_{35}$Al$_{30}$ compositions, we detected a new ternary compound. The powder diffraction pattern of this compound is not similar to the powder patterns of the earlier investigated phases from this system. Therefore, a full structure analysis was performed using single-crystal X-ray diffraction.

The obtained single-crystal data show that the title compound crystallizes with a new trigonal structure type (space group $R\bar{3}m$). A projection of the unit cell and the coordination polyhedra of the atoms are shown in Fig. 1. The number of neighbouring atoms correlates well with the sizes of the central atoms.

The coordination polyhedra around the statistical mixtures of (Cu,Al)1 and (Al,Cu)2 (on the 18*h* and 3*a* sites, respectively) are distorted icosahedra of compositions [(Cu,Al)1-(Cu,Al)$_4$(Al,Cu)Al$_2$Li$_2$Li$_3$] and [(Al,Cu)2(Cu,Al)$_6$Li$_6$]. The Al3 atom, with 6*c* site symmetry, is surrounded by 14 adjacent atoms [Al3Al(Cu,Al)$_6$LiLi$_6$] in the form of a pseudo-Frank–Kasper polyhedron. The Li atoms are enclosed in 15- and 16-vertex polyhedra that can be treated as distorted pseudo-Frank–Kasper polyhedra of compositions [Li4(Cu,Al)$_6$Li$_3$Al$_6$] and [Li5Al(Al,Cu)$_3$(Cu,Al)$_6$Li$_3$(Cu,Al)$_3$].

A detailed crystal chemical analysis shows (Fig. 2) that the title structure is a derivative of the binary Laves phases, such as MgZn$_2$ and MgNi$_2$ (Villars, 1997). As a result of the unit-cell deformation of the initial MgZn$_2$ and MgNi$_2$ Laves phases, the structure types of W$_6$Fe$_7$ (Arnfelt & Westgren, 1935) and
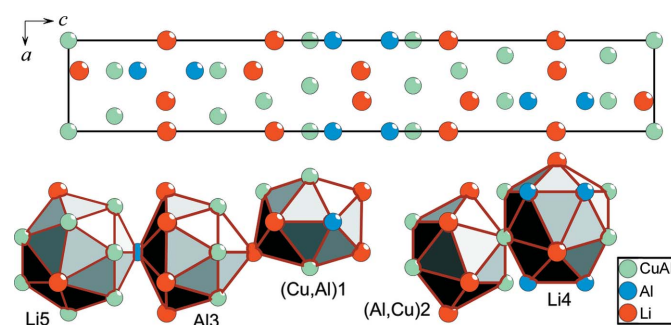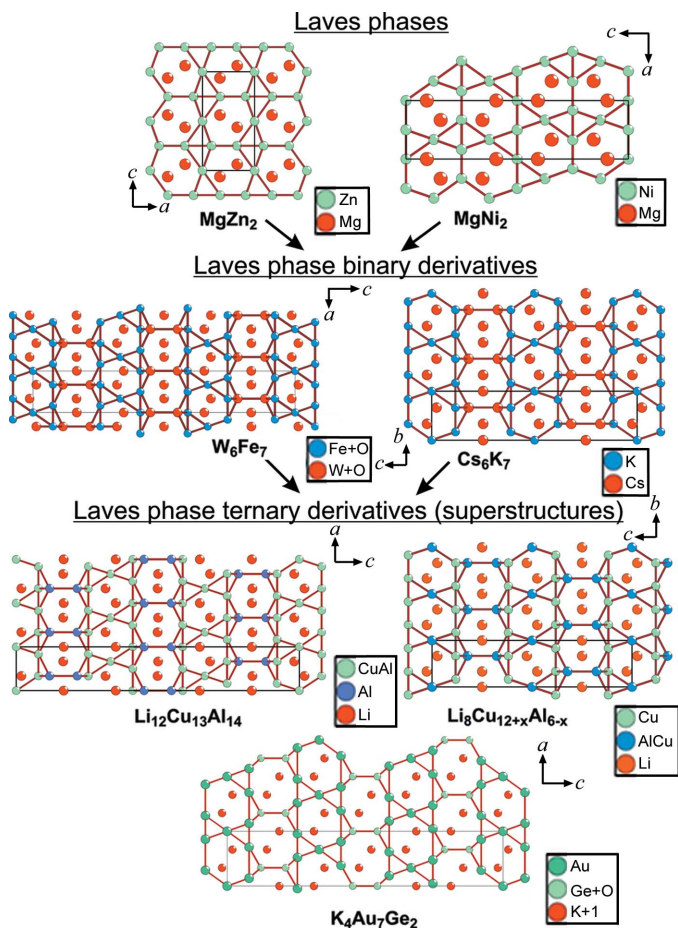

Figure 1
The clinographic projection of the Li$_{12}$Cu$_{12.60}$Al$_{14.37}$ unit-cell contents and the coordination polyhedra of the atoms.

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Figure 2
The relationship between the structures of $MgZn_2$, $MgNi_2$, W_6Fe_7, Cs_6K_7, $Li_{12}Cu_{13}Al_{14}$ ($Li_{12}Cu_{12.60}Al_{14.37}$), $Li_8Cu_{12+x}Al_{6-x}$ and $K_4Au_7Ge_2$.

Cs_6K_7 (Simon *et al.*, 1976) can be obtained, respectively. By the systematic replacement of some atoms by atoms of a third component in the deformed binary derivatives, the ternary phases $Li_{12}Cu_{12.60}Al_{14.37}$ and $Li_8Cu_{12+x}Al_{6-x}$ are obtained. The main features of both these compounds are channels of hexagonal prisms with Li atoms inside. Further displacement of some atoms, as a result of internal deformation, leads to a structure similar to the $K_4Au_7Ge_2$ type (Zachwieja, 1995). As a result, in this structure, half of the above-mentioned hexagonal prisms are transformed into octagonal prisms (Fig. 2).

The electronic structure of the title compound was calculated using the tight-binding linear muffin-tin orbital (TB–LMTO) method in the atomic spheres approximation (TB–LMTO–ASA; Andersen, 1975; Andersen & Jepsen, 1984; Andersen *et al.*, 1985, 1986), using the experimental crystallographic data which are presented here. The exchange and correlation were interpreted in the local density approximation (von Barth & Hedin, 1972).

The TB–LMTO–ASA calculations were performed on an ordered $Li_{12}Cu_{13}Al_{14}$ model of the title compound with the statistical mixture on the (Cu,Al)1 site approximated by a pure Cu occupation and on the (Cu,Al)2 site by a pure Al occupation, taking into account the refined proportions of
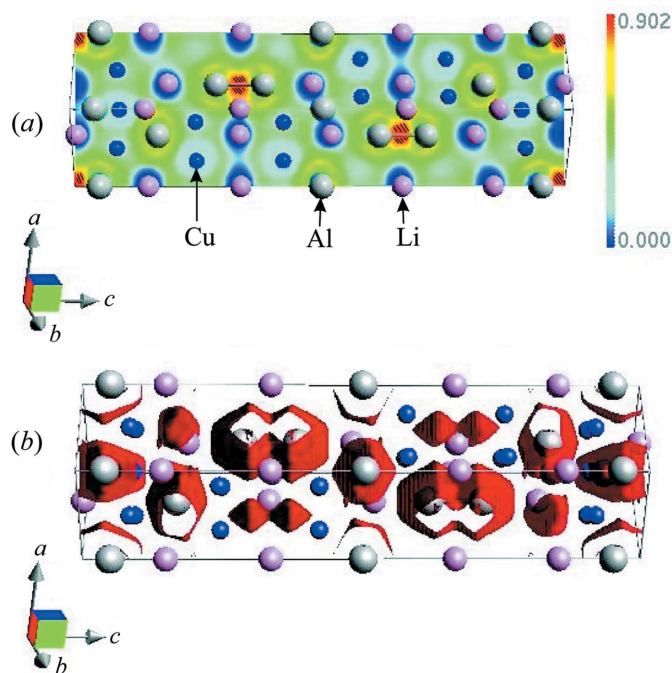
Figure 3
(*a*) The electron localization function (ELF) mapping and (*b*) isosurfaces of the electron localization function around the atoms for $Li_{12}Cu_{13}Al_{14}$.

atoms in these mixtures. The chemical bonding in the $Li_{12}Cu_{13}Al_{14}$ intermetallic compound is visualized by means of the electron localization function (ELF) mapping, which is shown in Fig. 3(*a*), where the dark regions (blue in the electronic version of the paper) indicate zero electron localization around Li atoms, indicating that they are positively polarized. The electron concentration is higher around Cu atoms (light shading; light-blue regions) and the maximum ELFs are observed between Al atoms (dark hatched; red regions). This indicates that, besides metallic bonding which is dominant in this compound, a weak covalent Al—Al interaction also exists. This is also highlighted by the isosurfaces of the ELF around the cited atom types (Fig. 3*b*). The rest of the crystal space has free electron-like behaviour (light background; green region). The total and partial densities of states (DOS) of $Li_{12}Cu_{13}Al_{14}$ calculated by the TB–LMTO–ASA method are shown in Fig. 4(*a*). The Fermi level (*EF*) lies in a continuous DOS region indicating a metallic character for the title compound. The DOS is low over the entire energy range near the Fermi level and confirms its relative stability. The DOS values indicate that for the title compound the Cu atoms mainly contribute to the valence band. The chemical bonding (iCOHP, integrated crystal orbital Hamilton populations, curve) exhibits strong Al—Al interactions between -3 and -2 eV (Fig. 4*b*). These interactions are Al3—Al3($-x$, $-y$, $-z$) [2.678 (6) Å and iCOHP = 0.1717 Ry cell^{-1}] (Ry = Rydberg, 1 Ry = 13.60 eV). An almost twice weaker interaction is observed between Al and Cu atoms, for example, for Al3—Cu1($x-1$, $y-1$, z) [2.6963 (13) Å and iCOHP = 0.0857 Ry cell^{-1}]. The interaction between the closest Cu atoms [Cu1—Cu1($-x+y$, $-x+1$, z)] is 2.4606 (13) Å and
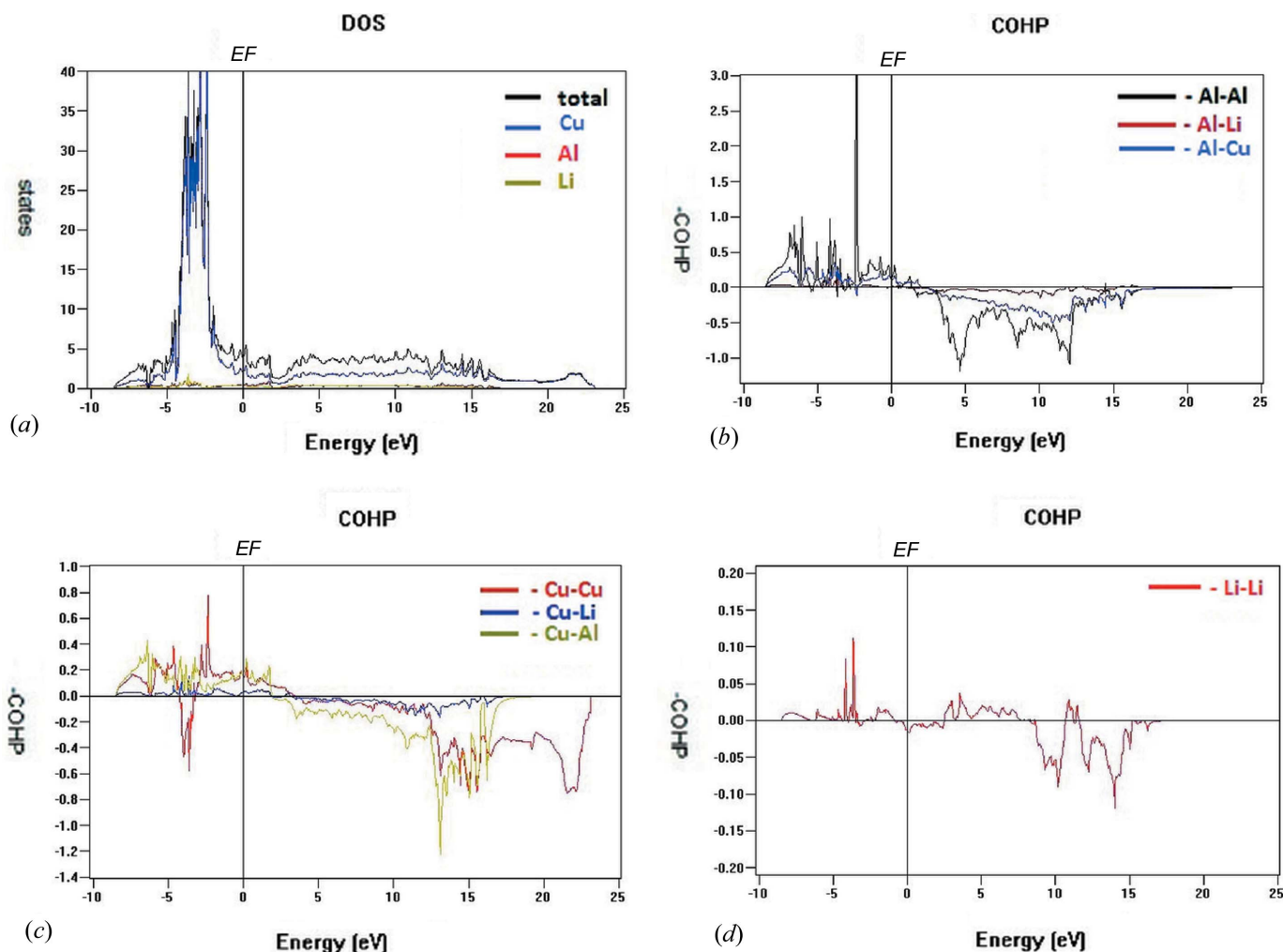
Figure 4
(a) Total and partial DOS (densities of states), and (b), (c) and (d) iCOHP curves for $Li_{12}Cu_{13}Al_{14}$ from TB–LMTO–ASA calculations.

iCOHP = 0.0691 Ry cell^{-1} (Fig. 4c). The weakest is the Li1—Li1($-x + \frac{2}{3}$, $-y + \frac{1}{3}$, $-z + \frac{1}{3}$) interaction [2.848 (2) Å and iCOHP = 0.0037 Ry cell^{-1}] (Fig. 4d).

Experimental

The samples from the $Li_{50}Cu_{25}Al_{25}$–$Li_{35}Cu_{35}Al_{30}$ compositional range were prepared from the following reactants: lithium (rod, 99.9 at.%), copper (ingots, 99.999 at.%) and aluminium (ingots, 99.999 at.%). Appropriate amounts were mixed according to the aimed stoichiometry of the product and placed into tantalum crucibles in the glove-box under an argon atmosphere. These crucibles were sealed by arc melting under a dry argon atmosphere. The reaction between the metals was carried out in an induction furnace at 1373 K. After 15 min, the samples were rapidly cooled to room temperature by removing the crucibles from the furnace into ambient conditions. The reaction product was powdered in an agate mortar, placed into a capillary of 0.3 mm diameter and sealed for X-ray diffraction (XRD) on a Stoe Stadi P (Mo $K\alpha_1$ radiation) in Debye–Scherrer mode (2θ from 3 to 59° in 2θ steps of 0.02°, linear position-sensitive detector with 6° aperture). A laminar-like single crystal, exhibiting metallic lustre, was isolated from the alloy by mechanical fragmentation. A single crystal was protected from air during X-ray data collection in a sealed thin-walled glass capillary (Hilgenberg, No. 10).

Crystal data

$Li_{12}Cu_{12.60}Al_{14.37}$	$Z = 1$
$M_r = 1271.71$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}m$	$\mu = 11.82$ mm^{-1}
$a = 4.9301$ (8) Å	$T = 293$ K
$c = 27.561$ (6) Å	$0.16 \times 0.09 \times 0.03$ mm
$V = 580.2$ (3) Å^3	

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	863 measured reflections
	182 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005)	173 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.072$
$T_{min} = 0.291$, $T_{max} = 0.698$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	19 parameters
$wR(F^2) = 0.158$	$\Delta\rho_{max} = 1.67$ e Å^{-3}
$S = 1.25$	$\Delta\rho_{min} = -1.71$ e Å^{-3}
182 reflections	

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The analysis of systematic extinctions yielded the space group $R\bar{3}m$ which was confirmed by the subsequent structure refinement. Also a statistical test of the distribution of the E values using the program E-STATS in the WinGX system (Farrugia, 1999) suggested that the structure is centrosymmetric. The structure was solved after the analytical 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. Initial refinement of atomic parameters showed that the $18h$ and $3a$ positions were occupied by statistical mixtures of Al and Cu atoms and the occupancy ratios of these mixed sites are approximately 1:2 (in the $18h$ site) and 7:1 (in the $3a$ site). In this structure, Al atoms fully occupy only one $6c$ site. The other two crystallographic $6c$ sites are occupied by Li atoms.

In the final refinement cycles, all atoms were successfully refined with anisotropic (Li atoms with isotropic) displacement parameters. The atomic coordinates were standardized using the STRUCTURE TIDY program (Gelato & Parthé, 1987).

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: KU3057). Services for accessing these data are described at the back of the journal.

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