Angewandte
Communications

DOI: 10.1002/anie.201203504

Lithium-Rich Compounds

Copper Silicides with the Highest Lithium Content: Li_7CuSi_2 Containing the 16-Electron Group $[CuSi_2]^{7-}$ and $Li_{7.3}CuSi_3$ with Heterographene Nets $^{2}_{\infty}[CuSi]^{3.3-}$**

*Adam Slabon, Serhiy Budnyk, Eduardo Cuervo-Reyes, Michael Wörle, Christian Mensing, and Reinhard Nesper**

Dedicated to Professor Roald Hoffmann on the occasion of his 75th birthday

Binary and ternary lithium compounds have received growing attention owing to their potential as novel electrode materials for lithium-ion batteries. Lithium silicides exhibit highest theoretical lithium capacities (up to 4200 $mAh\,g^{-1}$ in case of $Li_{21}Si_5$),[1] but suffer from chemical instability, which is mostly due to large volume changes during electrochemical cycling processes. Pöttgen et al. recently published a review on lithium transition-metal tetralides with respect to their crystal chemistry and lithium mobility.[2] We reinvestigated the Li-Cu-Si system because higher cycling stability in comparison to the binary lithium silicides and better compatibility with the copper current collector was expected.[3–7] Low-temperature Cu-Si alloying and excellent electronic conductivities[8] make Li-Cu-Si compounds interesting materials for anode application.

It is known that Cu atoms can replace silicon in Zintl anions.[9,10] The first investigations on the Li-Cu-Si system were performed in the late 1960s by Schönemann et al., who characterized the crystal structure of $LiCu_2Si$.[11] Bodak et al. published the structures of $LiCu_3Si_2$, $Li_7Cu_7Si_5$, $Li_{145}Cu_{119}Si_{177}$, and $Li_{113}Cu_{54}Si_{57}$.[12–15] Only recently, Kevorkov reported some new ternary phases in the Li-Cu-Si system, but crystallographic data and compositions were not certain.[16]

Pushing the limits towards lithium-richer ternary phases within the Li-Cu-Si system, we were able to synthesize and characterize the two new compounds Li_7CuSi_2 and $Li_{7.3}CuSi_3$, both of which fulfill the Zintl–Klemm concept in peculiar manners.[17,18] Just like the lithium silicides, the two compounds are extremely sensitive to air and moisture: for example, they would not reach the ground when being dropped in ambient environment.

Up to now, Li_7CuSi_2,[19] which crystallizes as a new structure type, is the lithium-richest phase in the system. According to the Zintl–Klemm concept, the compound contains an anionic linear $[CuSi_2]$ group with a formal charge of −7 being a very peculiar heteronuclear 16-electron species. Figure 1 illustrates the structural motives of Li_7CuSi_2 with the Cu-centered linear $[Si\text{-}Cu\text{-}Si]^{7-}$ Zintl anion, which is isoelectronic and isostructural to carbon dioxide, $[NCN]^{2-}$, $[NBN]^{3-}$, $[CCC]^{4-}$, $[CBN]^{4-}$, and $[CBC]^{5-}$.[20–24] Corbett reported a linear Tl_3^{7-} ion in the ternary Zintl phase $Na_{23}K_9Tl_{15.3}$. However, the central Tl atom was underoccupied by two-thirds, and a possible 16-electron species must thus be disordered.[25]

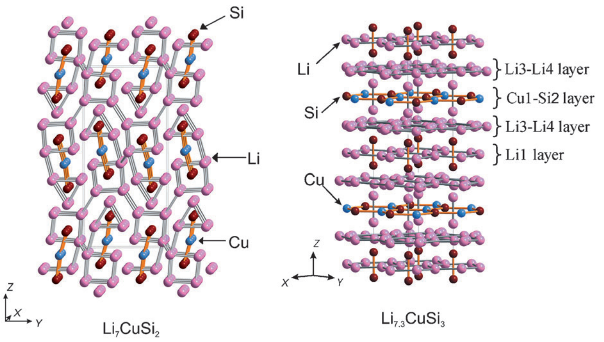

Figure 1. Projections of the crystal structures of Li_7CuSi_2 (left) and of $Li_{7.3}CuSi_3$ (right). Li pink, Cu blue, Si red.

Cu–Si distances of the nearly linear $[CuSi_2]$ unit of 2.31 and 2.32 Å are practically identical and relatively short. In the heterographene net of $Li_{7.3}CuSi_3$, the shortest separation (Cu–Si) is as large as 2.48 Å. An alternative description of two isolated Si anions of formal charge −4 as ($[Si^{4-}]\ Cu^{+}\ [Si^{4-}]$) is less likely for several reasons: 1) the short Cu–Si distance; 2) relatively short Li–Cu separations of 2.62 and 2.67 Å that are similar to the shortest Li–Si distances; 3) the pronounced position of the copper with respect to the other +1 cations; and 4) no disorder of Cu and Li, and frequent observations of Cu introduction into silicon clusters and frameworks. It should be noted that both descriptions fulfill the Zintl–Klemm concept.[26] Similar short Si–Cu distances of 2.32 Å and 2.37 Å, respectively, are found in $LiCu_3Si_2$ and $Li_{145}Cu_{119}Si_{177}$.[12,15]

The density of states (DOS) of Li_7CuSi_2 is shown in Figure 2 (top). The low-energy bands have dominant s character and are mainly combinations of the 3s orbitals of the eight silicon atoms of the unit cell and copper 4s and 4p orbitals. The copper d shell can be considered closed, as the corresponding flat bands are well below the Fermi level E_F. A broad sector of well-dispersed bands from −5 eV up to the

---

[*] A. Slabon, Dr. S. Budnyk, Dr. E. Cuervo-Reyes, Dr. M. Wörle, Dipl.-Ing. C. Mensing, Prof. Dr. R. Nesper
Department of Chemistry, ETH Zürich
Wolfgang-Pauli-Strasse 10, CH-8093 Zürich (Switzerland)
E-mail: nesper@inorg.chem.ethz.ch

[**] This work was financially supported by the SNF under project no. 2-77937-10 and the ETHZ.

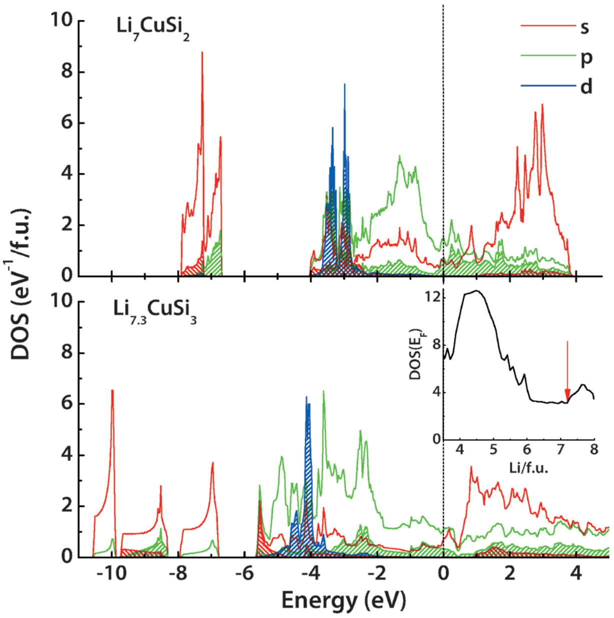

Figure 2. Density of states of $\mathrm{Li_7CuSi_2}$ (top) and $\mathrm{Li_8CuSi_3}$ (bottom). s-DOS in red lines, p-DOS in green lines, and d-DOS in blue lines. The dashed areas indicate the copper contributions. The d states are rescaled by 0.25 to fit the graphical plot. Inset: DOS at the Fermi level as a function of the lithium content. The red arrow corresponds to the lithium content of the title compound.

Fermi level mainly arises from silicon p orbitals mixed with copper states along with a stabilizing contribution by lithium.

The distance of 4.47 Å between the anionic units in $\mathrm{Li_7CuSi_2}$ along the ecliptic stacking direction b is in a typical range of σ interactions of π states of adjacent triatomic anions and also determines the mutual packing of Li cations. Such peculiar stacking arrangements are frequently found in many tetralide Zintl phases and induce metallic conductivity.[27]

$\mathrm{Li_{7.3}CuSi_3}$ exhibits a new two-dimensional heterographene net consisting of infinite $^{2}_{\infty}[\mathrm{Cu_3Si_3}]$ layers (Figure 1). Just as for $\mathrm{Li_7CuSi_2}$, the sites are clearly distinct for different atoms. Two of the lithium positions have an underoccupancy. The crystal structure of $\mathrm{Li_{7.3}CuSi_3}$ consists of three different types of six-ring layers: layer A is solely made up by lithium, which is penetrated in perpendicular manner by silicon dumbbells, B has a heterographene structure $^{2}_{\infty}[\mathrm{Cu_3Si_3}]$ which is penetrated similarly by Li dumbbells with a fairly short distance d(Li–Li) = 2.42 Å, and C denotes the slightly distorted six-ring net formed by the underoccupied Li3 and Li4 sites which can be understood as two trigonal planar subnets slightly shifted against each other in z direction. It is likely that each of these C subnets is ordered in itself but their stacking sequence is random or at least so disordered that it cannot be resolved by XRD. According to the structure analysis, two Li sites are split and partially occupied with occupancies of 2.67 (Li3), 1.33 (Li4a), and 2.67 (Li4b) hinting at some triplication of periodicity.

Based on the stoichiometric amount of Li3 versus Li4a and Li4b, the occurrence ratio of the subnets is 2:1. Thus, we suppose that occupancy of both sites, Li3 and Li4a, in one layer is quite unlikely. Comparing the layer-forming Li1, Li3, and Li4, it appears that the Li–Li separations in these layers are roughly the same at about 2.48 Å, which is fairly short for positively polarized lithium atoms. For Li1, this seems to be counterbalanced by six relatively close negatively charged Si neighbors at an average distance of 2.71 Å. Li3 has only four close Si contacts at 2.77 Å, and Li4a only three at 2.83 Å average distance. Clearly, Si dumbbells and B layers are of anionic character whereas A and C layers are electron-donating. The direct distance between the Cu and Si atoms d(Cu–Si2) is 2.48 Å. Ternary rare-earth copper silicides with $\mathrm{AlB_2}$ structure, such as CeCuSi, LaCuSi, and PrCuSi,[28] contain similar Cu–Si heterographene layers with distances in the range of 2.38 Å, being shorter than those in $\mathrm{Li_{7.3}CuSi_3}$. This difference may be due to large Li–Li repulsion in the cation-richer title compound. The Si dumbbell of Si1 atoms has a separation of 2.33 Å, which is seemingly shorter than expected for a single-bonded $[\mathrm{Si_2}]^{6-}$ unit.

As calculations of band structures require periodic systems, we built ordered models close to the observed stoichiometry $\mathrm{Li}_x\mathrm{CuSi_3}$ with $x = 7.3$; that is, $x = 6$ and $x = 8$. In both cases, only the underoccupied Li sites are concerned: for $x = 6$ the split position Li4 was moved to its center of gravity and fully occupied, while Li3 remains empty; for $x = 8$ both positions have been moved to their centers of gravity and are fully occupied. The neglected disorder or the occurrence of an ordered supercell should add a small smearing to the bands and may reduce the total energy, but should not change the overall electronic distribution. This was confirmed by the practically indistinguishable band structures of the two models, which allowed us to assume a rigid band picture and to draw the DOS for the title compound performing a linear interpolation. The DOS of $\mathrm{Li_{7.3}CuSi_3}$ is shown in Figure 2 (bottom) and the total DOS at the Fermi level, as a function of the lithium content, isin the inset of Figure 2.The Fermi level of $\mathrm{Li_{7.3}CuSi_3}$ falls in the region with the lowest DOS (cf. red arrow).

The lower-energy sector contains bands of dominant s character arising from the silicon atoms. The middle block has a significant contribution from Cu s and Cu p states, as it would be expected for a center in a heterographene layer. The Cu d shell is closed, in this compound as well. From −5 eV to $E_{\mathrm{F,}}$ Si p, Cu s and p, and Li s are found. The significant stabilization of Cu p orbitals supports our view of Cu–Si interactions having polar covalent character, and our interpretation of the CuSi layer as a heterographene sheet. The stabilization of the heterographene substructure requires at least 3.5 electrons per atom. This number represents the minimal value of the valence electron concentration (VEC) for each atom of the heterographene net. With four valence electrons from silicon and one from copper, at least two electrons should be contributed by lithium. Furthermore, should be discussed whether the Si dumbbells carry double- or single-bonded character,respectively, as it is well-known that both Zintl anions exist.[18] For $x = 6$, it is logical to assume a $[\mathrm{Si_2}]^{4-}$ (double bonded) configuration and VEC = 3.5 for the [CuSi] net. There are a few heterographene compounds with a VEC lower than 4, such as BaLiSi (VEC = 3.5)[29] and LiAuSn (VEC = 3).[30] The contribution of copper p states below the Fermi level indicates that, on increasing x from 6 to

7.3, extra electrons are mostly distributed into the heterographene. This results in a VEC > 4, as found for the majority of heterographene systems reported in the literature.[29] In summary, $Li_{7.3}CuSi_3$ contains two anionic building units, which are most likely $[Si_2]^{4-}$ dumbbells and 2D heterographene $[CuSi]^{3.3-}$.

In summary, the ternary silicides Li_7CuSi_2 and $Li_{7.3}CuSi_3$ are the lithium-richest compounds in the Li-Cu-Si system, with theoretical capacities of 1563 and 1324 $Ah\,kg^{-1}$, respectively. Assuming a full charge transfer from lithium to the anionic species according to the Zintl–Klemm concept, Li_7CuSi_2 would contain a 16-electron Zintl anion carrying the formal charge 7−. Up to now the Zintl–Klemm concept offers the best interpretation of the electronic structure. Hume–Rothery and Wade cluster rules have been tested but do not apply. A check for dense packing also does not provide similarity to either bcc or to fcc arrangements.[31]

Experimental Section

The pure elements (lithium granules: 99.9 wt %, Aldrich; copper powder: 99.5 wt. %, Aldrich; silicon lumps: 99.9999 wt %, Aldrich) were mixed and preheated in a niobium crucible at 300 °C. The porous bulk was ground, pressed into a pellet, sealed in a niobium ampoule and annealed at 600 °C for 7 days with subsequent quenching. For crystal growth, pellets of the ground bulk (for Li_7CuSi_2 with a small excess of lithium) were annealed at 650–700 °C for two hours and cooled to 500 °C at 20 $°C\,h^{-1}$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-424705 (Li_7CuSi_2) and CSD-424704 ($Li_{7.3}CuSi_3$). Interatomic distances, magnetic susceptibility measurements, and band structures of both compounds are provided in the Supporting Information.

Received: May 7, 2012
Revised: September 19, 2012

Keywords: electronic structure · lithium · silicides · solid-state structures · Zintl phases

---

[1] C. J. Wen, R. A. Huggins, *J. Solid State Chem.* **1981**, *37*, 271.
[2] R. Pöttgen, T. Dinges, H. Eckert, P. Sreeraj, H. D. Wiemhofer, *Z. Phys. Chem.* **2010**, *224*, 1475–1504.
[3] R. Nesper, *Prog. Solid State Chem.* **1990**, *20*, 1–45.
[4] Y. M. Kang, M. S. Park, J. Y. Lee, H. K. Liu, *Carbon* **2007**, *45*, 1928–1933.
[5] B. C. Kim, H. Uono, T. Satou, T. Fuse, T. Ishihara, M. Senna, *J. Electrochem. Soc.* **2005**, *152*, A523–A526.
[6] S. Yoon, S. I. Lee, H. Kim, H. J. Sohn, *J. Power Sources* **2006**, *161*, 1319–1323.
[7] J. H. Kim, H. Kim, H. J. Sohn, *Electrochem. Commun.* **2005**, *7*, 557–561.
[8] C. Cabral Jr., C. Lavoie, J. M. E. Harper, J. Jordan-Sweet, *Thin Solid Films* **2001**, *397*, 194–202.
[9] L. Yang, Y. Wanga, T. Liu, T. D. Hu, B. X. Li, K. Stahl, S. Y. Chen, M. Y. Li, P. Shen, G. L. Lu, Y. W. Wang, J. Z. Jiang, *J. Solid State Chem.* **2005**, *178*, 1773–1777.
[10] X. Yan, G. Giester, E. Bauer, P. Rogl, S. Paschen, *J. Electron. Mater.* **2010**, *39*, 1634–1639.
[11] H. U. Schuster, D. Thiedemann, H. Schönemann, *Z. Anorg. Allg. Chem.* **1969**, *370*, 160–169.
[12] V. V. Pavlyuk, D. G. Kevorkov, O. I. Bodak, V. K. Pecharskii, *Kristallografiya* **1995**, *40*, 178–179.
[13] V. V. Pavlyuk, D. G. Kevorkov, O. I. Bodak, V. K. Pecharskii, *Kristallografiya* **1995**, *40*, 180–182.
[14] V. V. Pavlyuk, D. G. Kevorkov, O. I. Bodak, V. K. Pecharskii, *Kristallografiya* **1995**, *40*, 188–189.
[15] V. V. Pavlyuk, D. G. Kevorkov, O. I. Bodak, V. K. Pecharskii, *Kristallografiya* **1995**, *40*, 195–187.
[16] D. G. Kevorkov, Ph.D. Thesis, Lviv State University, **1999**.
[17] R. Nesper, H. G. von Schnering, *J. Solid State Chem.* **1987**, *70*, 48–57.
[18] R. Nesper, A. Currao, S. Wengert, *Chem. Eur. J.* **1998**, *4*, 2251–2257.
[19] Crystal structure data for Li_7CuSi_2: *Pnma* (No. 62), $a = 7.9693(16)$, $b = 4.4495(9)$, $c = 17.244\ (3)$ Å, $V = 611.5(2)$ Å^3, $\rho = 1.83\ g\,cm^{-3}$, $Z = 4$, $\theta_{max} = 25.31°$, 40 parameters refined, 5582 measured reflections, 637 unique reflections, $\mu = 3.805$, $R1 = 0.0291$, $wR2 = 0.0722$, max./min. residual electron density: $+0.718/-0.670\ e\,Å^{-3}$. $Li_{7.3}CuSi_3$: $P6_3/mmc$ (No. 194), $a = 4.2877(5)$, $c = 20.582(3)$, $V = 327.69(7)$ Å^3, $\rho = 2.01\ g\,cm^{-3}$, $Z = 2$. $\theta_{max} = 33.64°$, 22 parameters refined, 5157 measured reflections, 302 unique reflections, $\mu = 3.739$, $R1 = 0.0225$, $wR2 = 0.0485$, max./min. residual electron density: $+0.363/-0.377\ e\,Å^{-3}$. Diffractometer: Bruker SMART Platform, monochromated MoK_α radiation. The data were integrated with the SAINT program[32] and corrected for Lorentz factor, polarization, air absorption, and absorption due to the path length through the detector face plate. Both structures were solved by direct methods.[33]
[20] H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1991**, *594*, 113–118.
[21] U. Berger, W. Schnick, *J. Alloys Compd.* **1994**, *206*, 179–184.
[22] J. Goubeau, W. Anselment, *Z. Anorg. Allg. Chem.* **1961**, *310*, 248.
[23] H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1991**, *593*, 185–192.
[24] H. Hillebrecht, F. D. Meyer, *Angew. Chem.* **1996**, *108*, 2655–2657; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2499–2500.
[25] Z.-C. Dong, J. D. Corbett, *Inorg. Chem.* **1996**, *35*, 3107–3112.
[26] W. Klemm, *Proc. Chem. Soc. London* **1959**, 329.
[27] R. Nesper, A. Currao, S. Wengert in *Organosilicon Chemistry II, From Molecules to Materials* (Eds.: N. Auner, J. Weiss), VCH, Weinheim, **1995**, pp. 143–166.
[28] M. L. Fornasini, A. Iandelli, M. Pani, *J. Alloys Compd.* **1992**, *187*, 243–247.
[29] A. Savin, A. Becke, J. Flad, R. Nesper, H. Preuss, H. G. von Schnering, *Angew. Chem.* **1991**, *103*, 421–424; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 409–412.
[30] R.-D. Hoffmann, D. Johrendt, W. Zhiyun Wu, R. Pöttgen, *J. Mater. Chem.* **2002**, *12*, 676–680.
[31] XRD powder patterns were calculated for models in which all atoms were replaced by Li. These theoretical patterns were compared with Li bcc and Li fcc patterns for gross relationships, but no significant similarity was found.
[32] SAINT Version 4.05. Siemens Analtyical X-Ray Instruments, Madison, WI, **1996**.
[33] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.