$Li_{10}Mg_6Zn_{31}Al_3$: A New Intermetallic Phase Containing Building Blocks for Decagonal Quasicrystals**

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Dedicated to Professor Hans Georg von Schnering on the occasion of his 70th birthday

Since the discovery of a quasicrystalline structure in the Mn–Al system,[1] the complete structural characterization of a quasicrystal remains an active and vital segment of quasicrystal research. This problem entails finding both the positional coordinates of the atomic network as well as how the network is decorated by the constituent elements. Most quasicrystalline phases involve ternary and quaternary compositions, which create complex structural problems to solve, and also appear to exist for two different regimes: icosahedral and dodecahedral systems.[2] Many strategies to solve these structures utilize related crystalline phases, called approximants, to provide models of atomic arrangements that may exist in the quasicrystal itself.[3] An important class of approximants for icosahedral quasicrystals is the Bergman-phase structure,[4] which occurs for numerous A–M–X (s–p–d) materials (A = Li, Mg; M = Cu, Zn; X = Al). Our own investigations have included detailed experimental and theoretical studies of the structure, phase width, and site preferences for Bergman phases in the Li-Mg-Zn-Al system.[5–7] Herein we report a new compound discovered during this systematic investigation, $Li_{10}Mg_6Zn_{31}Al_3$, whose structure contains a pseudo-pentagonal unit that could be considered as a possible model of decagonal quasicrystalline structures.

$Li_{10}Mg_6Zn_{31}Al_3$ crystallizes in the space group *Cmcm*, with five independent positions (A1–A5) for Li/Mg atoms and eight positions (M1–M8) for Zn/Al atoms (Figure 1).[8] The Zn/Al atoms form a three-dimensional (3D) network of truncated tetrahedra (one of the Friauf polyhedra) along with two other polyhedra with 12 and 14 vertices that resemble two different ways to fuse an icosahedron and a truncated tetrahedron. All of these polyhedra encapsulate Li/Mg atoms. The shortest M–M distances range between 2.42 and 2.85 Å. Most of the M sites are 100% Zn; only the M6 and M8 sites refine as a mixture of Zn and Al atoms (site occupancies are: M6 = 0.93(1) Zn + 0.07 Al; M8 = 0.39(1) Zn + 0.61 Al). As evident in Figure 1 and emphasized in Figure 2, the important structural kernel is a pseudo-pentagonal unit formed by a ring of five truncated tetrahedra, each sharing two hexagonal faces with adjacent polyhedra (shaded dark gray in Figure 1 and 2).

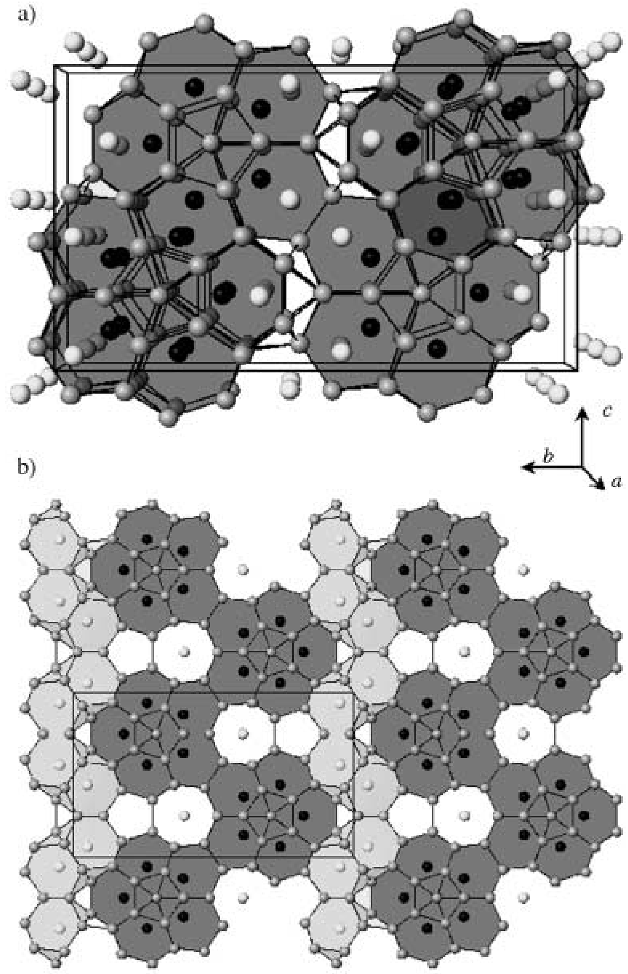

Figure 1. a) The three-dimensional structure of $Li_{10}Mg_6Zn_{31}Al_3$ projected along [100]; black: A1–A3 sites; white: A4, A5 sites; gray: M1–M8 sites; b) projection along [100] emphasizing sheets of two different ribbons of edge-sharing Friauf polyhedra running along [001].

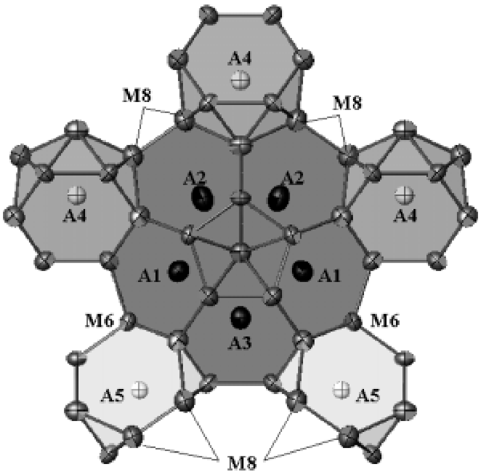

Figure 2. The pseudo-pentagonal motif of shared truncated tetrahedra (dark gray) plus coordination polyhedra around A4 (medium gray) and A5 sites (light gray). A sites and mixed-metal M sites are labeled; sites with no labels are Zn.

This condensation of truncated tetrahedra creates two pentagonal pyramids of Zn/Al atoms (M–M distances range between 2.64 and 2.68 Å) connected by a short distance

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(2.42 Å) between apical atoms. The A1–A3 sites (Figure 2) coordinated by the truncated tetrahedra involve different mixtures of Li and Mg atoms (site occupancies: A1 = 0.48(2) Li + 0.52 Mg; A2 = 0.38(2) Li + 0.62 Mg; A3 = 0.24(2) Li + 0.76 Mg). The next shell of polyhedra for this motif consists of two Li-centered $(A5)M_{12}$ (light gray) and three Li-centered $(A4)M_{14}$ cages (medium gray). These pseudo-pentagonal units form zigzag chains along the *c* direction by sharing two 14-vertex cages and the M8–M8 edges (2.63 Å) that connect them (see Figure 1 b). The resulting chains are stitched together in the *b* direction to form layers by sharing hexagonal faces of the Li-centered $(A5)M_{12}$ cages, which also creates chains of these polyhedra along the *c* direction (note: there is a short Li–Li distance of 2.86(5) Å through the shared hexagonal face. This distance lies between the covalent diameter, 2.46 Å, and van der Waals diameter, 3.10 Å of Li). The subsequent layers in the *bc* plane (emphasized in Figure 1) are stacked along the *a* axis with a shift of *b*/2 from one layer to the next. Therefore, the ribbons of pseudo-pentagonal units alternate with the zigzag chains of LiM_{12} cages in each layer.

The site symmetry of the pseudo-pentagonal unit in $Li_{10}Mg_6Zn_{31}Al_3$ is C_{2v} with pseudo-fivefold symmetry along the *a* axis at the M4 sites. The deviations from pentagonal symmetry are slight: all M–M distances and M-M-M angles in the bases of the pentagonal pyramids are 2.67(2) Å and 108.0(5)°, respectively; all A–A distances and A-A-A angles between the truncated tetrahedra are 3.22(2) Å and 108.0(4)°, respectively. A similar pseudo-pentagonal construct is found in the icosahedral approximants, the Bergman phases $Li_{16}Mg_{10}(Zn_xAl_{1-x})_{54}$ $(0.36 \leq x \leq 0.73)$,[6] with a site symmetry C_s, but these motifs are fused to form the 84-atom Samson cluster, and show substantial deviations from pentagonal symmetry: in the bases of the pentagonal pyramids, three M–M distances are 2.65(1) Å, while two are 2.80(1) Å. The truncated tetrahedra encapsulate slightly different mixtures of Li and Mg atoms, which may influence the observed metrics: among the five A sites, in $Li_{10}Mg_6Zn_{31}Al_3$ there are 2 × 48(2), 2 × 38(2). and 1 × 24(2) % Li; whereas in the quaternary Bergman phases there are 2 × 75(2) and 3 × 34(2) % Li.[6]

Tight-binding, linear muffin-tin orbital atomic sphere approximation (TB-LMTO-ASA) calculations were performed on "$Li_{10}Mg_6Zn_{30}Al_4$" as a model for the observed structure to understand the composition and bonding characteristics of $Li_{10}Mg_6Zn_{31}Al_3$.[11, 12] The total density of states (DOS) curve (Figure 3) shows no band gap at the Fermi level ($E_F = -1.7$ eV) at the valence electron count per atom (vec) of 1.86 e^- per atom for $Li_{10}Mg_6Zn_{31}Al_3$. In fact, it lies just below a distinct minimum in the DOS curve. The crystal orbital Hamilton population (COHP) curves for M–M, M–A, and A–A interactions indicate that none of their orbital populations (i.e., bond orders) are optimized at 1.86 e^- per atom.[13] The COHP for all M–M contacts is optimized at vec = 1.96 e^- per atom (Figure 3), which locates the minimum in the DOS curve and corresponds to the possible compositions $Li_{16-x}Mg_xZn_{34-y}Al_y$ $(x + y = 14)$. The M–A COHP optimizes at an even higher vec value of 2.11 e^- per atom. Attempts to synthesize "$Li_{10}Mg_6Zn_{26}Al_8$" (vec = 1.96 e^- per atom) produced the Bergman phase structure: $x = 0.71$ for $Li_{16}Mg_{10}(Zn_xAl_{1-x})_{54}$. The overall compositions of these two phases, $Li_{10}Mg_6Zn_{31}Al_3 \equiv A_{16}M_{34}$ and the Bergman phases $Li_{16}Mg_{10}(Zn_xAl_{1-x})_{54} \equiv A_{26}M_{54} \approx A_{16}M_{33.2}$ are very similar. Since the Li-Mg-Zn-Al Bergman phases are observed for a vec value in the range 2.00–2.28 e^- per atom,[5–7] this new quaternary compound prefers to form at lower vec values, that is Zn-rich compositions, when compared to the Bergman phases. Although the TB-LMTO-ASA calculations identify that M–M and M–A interactions are strongest at low vec values, further analysis of interatomic potentials may be needed to elucidate the driving forces for forming this structure.

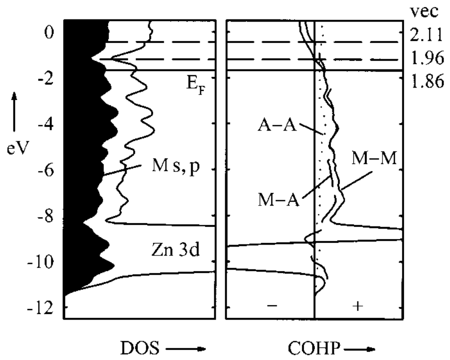

Figure 3. TB-LMTO-ASA DOS and COHP curves for $Li_{10}Mg_6Zn_{30}Al_4$. The contribution from M (Zn, Al) valence s and p orbitals is shaded. The solid line at −1.7 eV denotes the Fermi energy for the observed vec = 1.86 e^- per atom; the two dashed lines at −1.2 and −0.4 eV, respectively, are Fermi levels for optimized M–M (vec = 1.96 e^- per atom) and M–A (vec = 2.11 e^- per atom) contacts.

To understand the elemental site preferences in this intermetallic phase, extended Hückel calculations were performed on a model of $Li_{10}Mg_6Zn_{31}Al_3$ in which all atomic sites were given the same atomic potential.[14, 15] The site preferences for the different elements among the crystallographic sites are compared by their relative Mulliken populations (Figure 4).[6] This method involves placing the same atomic potential at each site and calculating the Mulliken populations relative to the average value for a range of electron counts. It has proved to be very useful in the characterization of site preferences between electropositive and electronegative elements in intermetallic systems such as

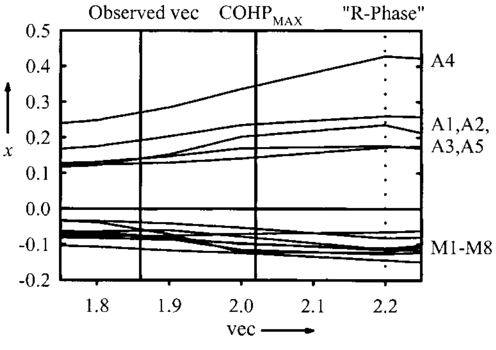

Figure 4. Relative Mulliken populations (x) of the A1–A5 and M1–M8 sites versus the vec range from 1.75 to 2.25 e^- per atom. The two solid lines indicate the observed vec (1.86 e^- per atom) and vec for optimized bonding for M–M and M–A contacts together (2.2 e^- per atom; $COHP_{MAX}$). The optimum vec for the Li-Mg-Zn-Al R-phases is shown as a dotted line.

the Bergman phases, ternary α-Mn structures, and complex Ca-Li-Al systems.[6, 7, 16] The computational result indicates that all A sites are positively polarized and all M sites are negatively polarized for the vec range between 1.8 and 2.2 e^- per atom, which are consistent with the relative electronegativities between Li/Mg and Zn/Al.

The pseudo-pentagonal units in the new intermetallic phase $Li_{10}Mg_6Zn_{31}Al_3$ link together to form layers rather than icosahedral-like cages as in the Bergman phases (Figure 5). If we attempt to build layered models with this building block using the principle of self-similarity to form a framework for a decagonal quasicrystalline phase,[17] two aspects of structural frustration arise: 1) too short M–M distances in polyhedra surrounding A sites; and 2) large void spaces. Nevertheless, the occurrence of five face-sharing truncated tetrahedra in both Bergman-type crystalline approximants as well as the structure of $Li_{10}Mg_6Zn_{31}Al_3$ identifies this motif as an important kernel from which to build models of decagonal and icosahedral quasicrystalline structures.

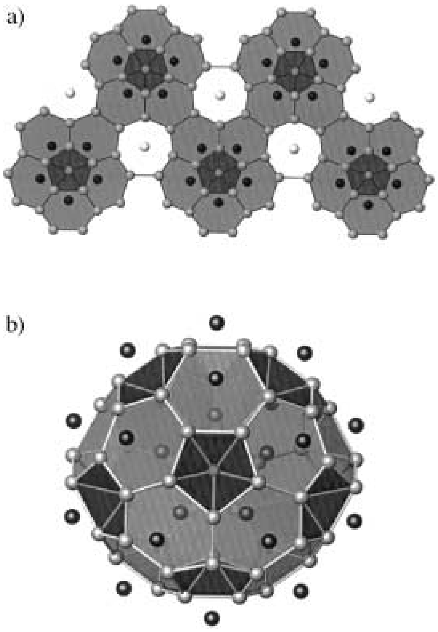

Figure 5. Two observed ways of condensing five face-sharing truncated tetrahedra: a) into ribbons as seen in $Li_{10}Mg_6Zn_{31}Al_3$; and b) into cages as seen in the Bergman phases found in Li-Mg-Zn-Al systems.[5–7] The truncated tetrahedra are shaded light gray and the pentagonal pyramids created by the condensation of these polyhedra are shaded dark gray.

Experimental Section

$Li_{10}Mg_6Zn_{31}Al_3$ was first obtained from a reaction of the elements in the molar ratio Li:Mg:Zn:Al = 32:20:85:23 to study Bergman-type compounds. The reactants were heated in a sealed Ta tube under dynamic vacuum (ca. 10^{-4} atm) at 1070 K for 2 days, then cooled to room temperature in the furnace. The product contained a mixture of the title compound (major), $MgZn_2$ (minor), and a trace amount of Al. The characteristic silvery rods of $Li_{10}Mg_6Zn_{31}Al_3$ could be manually separated from the product. Single-phase $Li_{10}Mg_6Zn_{31}Al_3$ (> 90% according to Guinier X-ray powder diffraction) could be synthesized by mixing the elements in the molar ratio, 10:6:30.75 ± 0.25:3.25 ± 0.25 using the same reaction conditions mentioned above. Several reactions at different (Li/Mg) and (Zn/Al) ratios were performed to study the phase width (Li:Mg:Zn:Al = 10:6:14:20, 10:6:20:14, 10:6:30.5:3.5, 10:6:31:3, and 10:6:34:0). The title phase only occurred for the initial mixture, Li:Mg:Zn:Al = 10:6:31:3. The other reactions yielded mixtures of elements, $MgZn_2$, a Bergman phase, and the title compound, depending on the relative compositions of Li:Mg:Zn:Al. The product is stable in the air for at least two weeks, but decomposes readily in 0.1 M HNO_3(aq). Single crystals suitable for X-ray diffraction analysis were selected from crushed products. At least two independent single-crystal data sets were collected for each sample. 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 number CSD-411919.

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[1] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, *Phys. Rev. Lett.* **1984**, *53*, 1951.

[2] A. P. Tsai, in *Physical Properties of Quasicrystals* (Ed.: Z. M. Stadnik), Springer, Berlin, **1999**, pp. 1–50.

[3] W. Steurer, T. Haibach, in *Physical Properties of Quasicrystals* (Ed.: Z. M. Stadnik), Springer, Berlin, **1999**, pp. 51–89.

[4] G. Bergman, J. L. T. Waugh, L. Pauling, *Acta Crystallogr.* **1957**, *10*, 254.

[5] C.-S. Lee, G. J. Miller, *J. Am. Chem. Soc.* **2000**, *122*, 4937.

[6] C.-S. Lee, G. J. Miller, *Inorg. Chem.* **2001**, *40,* 338.

[7] G. J. Miller, C.-S. Lee, W.-J. Tsai, *Mat. Res. Soc. Proc.* **2001**, in press.

[8] Crystal data of $Li_{10}Mg_6Zn_{31}Al_3$: $0.07 \times 0.07 \times 0.04$ mm^3; orthorhombic, *Cmcm* ($Z = 2$); $a = 5.1020(19)$, $b = 23.477(9)$, $c = 13.691(5)$ Å; $V = 1639.8(11)$ Å^3; $\rho_{calcd} = 4.704$ g cm^{-3}; $2\theta_{max} = 58.66°$; $Mo_{K\alpha}$, $\lambda = 0.71073$ Å; Smart CCD, three sets of frames with 0.3° scans in ω for an exposure time of 60 s per frame; $T = 298(2)$ K; $N_{meas} = 3015$, $N_{ind} = 1028$ ($I > 2\sigma(I)$); corrections for Lorentz and polarization effects; absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements,[9] $\mu = 22.29$ mm^{-1}; solved by direct methods (SHELXTL-V5.12)[10] and subsequently refined by full-matrix, least-squares calculations based on F^2; all independent atomic sites are assumed to be 100% occupied by (Li/Mg) or (Zn/Al) atoms; thermal parameters for A4 and A5 sites were only refined isotropically due to the unreasonable ellipsoid parameter at U_{11} (A5 only); $\Delta\rho = 1.259$ and -1.388 e$^-$ Å^{-3}, $R_1/wR_2 = 0.0522/0.0884$, GOF = 1.091; detailed results are deposited at the Fachinformationszentrum, Karlsruhe, Germany.

[9] SAINT, Version 4, Siemens Analytical X-ray Instruments, Madison, WI, **1995**.

[10] SHELXTL, Version 5.12, Reference Manual, Siemens Analytical X-ray Systems, Madison, WI, **1996**.

[11] a) O. K. Andersen, *Phys. Rev. B* **1975**, *12*, 3060; b) G. Krier, O. Jepsen, A. Burkhardt, O. K. Andersen, TB-LMTO-ASA Version 47.

[12] "$Li_{10}Mg_6Zn_{30}Al_4$" TB-LMTO-ASA computational parameters: Al at M8 site, Mg at A2, A3 and 50% A1 sites; Wigner–Seitz radii: Li (1.65 Å); Mg (1.80–1.90 Å); Zn (1.40–1.50 Å); Al (1.50 Å); no empty spheres needed to satisfy the overlap criteria; 26 *k* points for Brillouin zone integrations.

[13] a) R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617; b) T. Hughbanks, R. Hoffmann, *J. Am. Chem. Soc.* **1983**, *105*, 3528.

[14] a) R. Hoffmann, W. N. Lipscomb, *J. Chem. Phys.* **1962**, *36*, 2179; b) R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397; c) J. H. Ammeter, H. B. Bürgi, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 3686; d) M.-H. Whangbo, R. Hoffmann, R. B. Woodward, *Proc. R. Soc. London Ser. A* **1979**, *366*, 23.

[15] Atomic orbital parameters (all single-ζ STO functions) for Al: $H_{ii}(3s) = -12.3$ eV, $H_{ii}(3p) = -6.5$ eV, ζ (3s) = 1.37, ζ (3p) = 1.36; 100 *k* points in the first Brillouin zone with overlaps included through second nearest neighbor unit cells.

[16] a) G. J. Miller, *Eur. J. Inorg. Chem.* **1998**, 523; b) C.-S. Lee, PhD thesis, Iowa State University (USA), **2000**.

[17] C. Janot, *Quasicrystals: A Primer*, Clarendon Press, Oxford, **1994**.