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Interpenetrating Networks of Three-Dimensional Penrose Tiles in $CaAu_3Ga$, the Structurally Simplest Cubic Approximant of an Icosahedral Quasicrystal

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Double-Friauf polyhedra (DFPs) which play important roles in quasicrystal (QC) models are the unique building blocks in the novel 1/0 AC, $CaAu_{3+\Delta}Ga_{1-\Delta}$ ($\Delta \approx$ 0–0.13) [$Pa\bar{3}$; $a =$ 9.0875(3)–9.1107(5) Å]. The packing of DFPs generates interpenetrating networks of condensed three-dimensional Penrose tiles, the geometry of which is close to that assumed for QCs.

Intermetallic phases with valence electron counts per atom (*e*/*a*) near those in Hume–Rothery phases[1] have recently stimulated renewed interest[2–5] because they show close kinships to quasicrystals (QCs) and their corresponding crystalline approximants (ACs).[6] The latter two types generally populate a narrow *e*/*a* region.[7] In contrast to QCs, which exhibit forbidden rotational symmetries (5-, 8-, 12-fold, etc.),[6] ACs are conventional crystalline compounds, yet with special structural characteristics. For example, ACs are assumed to possess local structural motifs the same or similar to those of their corresponding QCs, and they may have chemical compositions and *e*/*a* values close to those of QCs. Therefore, explorations of novel ACs are particularly important because they not only enrich our understanding of polar intermetallic and Hume–Rothery phases but also possibly shed light on the secret structures of QCs.

In six-dimensional crystallography, the lattice parameter of a *q*/*p* cubic AC ($a_{q/p}$) has a fixed numerical relationship to that of the corresponding QC (a_6): $a_{q/p} = 2a_6(p + q\tau)/(2 + \tau)^{1/2}$, in which p and q are any two consecutive Fibonacci numbers and τ is the golden mean, 1.618.[8] Accordingly, a QC represents the highest order cubic AC with an infinitely large lattice constant (p and q are infinite), and a higher order AC is closer in structure to the corresponding QC than are any of lower order. A survey of the literature reveals that 1/1 AC structural data are available for most icosahedral QC systems and 2/1 for some. In contrast, 1/0 AC phases are reported to exist only in Al−Cu−Ru,[9] Al−Rh−Si,[10] Al−Pd−M (M = Fe, Ru, and Os),[11] etc., systems. However, $Al_6Cu_{0.63}Ru_{1.66}$ ($P2_13$)[12] is the only 1/0 AC that has been structurally characterized among these phases, although what appear to be 2 × 2 × 2 superstructures of 1/0 ACs for Al−Pd−Ru ($P23$ and $Fm3$),[13,14] Al−Pd−Fe ($Fm3$),[14] and Al−Cu−Ru−Si ($Fm3$)[15] are available. In addition, $Mg_2Cu_6Al_5$ ($Pm\bar{3}$),[16] a structure reported in 1949, also qualifies as the 1/0 AC of a Mg−Cu−Al icosahedral QC.[17] However, the isostructural $Mg_2Cu_6Ga_5$[18] and Mg_2Zn_{11}[19] are evidently not 1/0 ACs because no corresponding QC can be found in the respective systems even though both are precursors for QC tunings.[3,20] In this work, we report the synthesis and structure of a new 1/0 AC compound, which has a structural motif evidently different from those of Al-based 1/0 ACs mentioned above, and discuss its possible impact on QC modeling and discovery.

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(1) Hume-Rothery, W. *J. Inst. Met.* **1926**, *35*, 295.
(2) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670.
(3) Lin, Q.; Corbett, J. D. *J. Am. Chem. Soc.* **2005**, *127*, 12786.
(4) Lin, Q.; Corbett, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 6789.
(5) Miller, G. J.; Lee, C.-S.; Choe, W. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2002; pp 21−53.
(6) Janot, C. *Quasicrystals: A Primer*, 2nd ed.; Oxford University Press: Oxford, U.K., 1994.
(7) Tsai, A. P. In *Physical Properties of Quasicrystals*; Stadnik, Z. M., Ed.; Springer: New York, 1999; pp 5−50.
(8) Goldman, A. I.; Kelton, K. F. *Rev. Mod. Phys.* **1993**, *65*, 213.
(9) Weseda, A.; Araki, K.; Kimura, K.; Ino, H. *J. Non-Cryst. Solids* **1993**, *153–154*, 635.
(10) Koshikawa, N.; Ohtsuki, M.; Edagawa, K.; Yoda, S.; Tamura, R.; Takeuchi, S. *J. Alloys Compd.* **2002**, *342*, 35.
(11) Shibuya, T.; Asao, T.; Tamura, R.; Takeuchi, S. *Mater. Sci. Eng., A* **2000**, *294–296*, 61.
(12) Kirihara, K.; Kimura, K.; Ino, H.; Dmitrienko, V. E. In Quasicrystals, Proceedings of the 6th International Conference, Tokyo, 1997; Takeuchi, S., Fujiwara, T., Eds.; World Scientific, Singapore, 1998, pp 243–246.
(13) Mahne, S.; Steurer, W. *Z. Kristallogr.* **1996**, *211*, 17.
(14) Sugiyama, K.; Hiraga, K.; Saito, K. *Mater. Sci. Eng., A* **2000**, *294–296*, 345.
(15) Sugiyama, K.; Kato, T.; Saito, K.; Hiraga, K. *Philos. Mag. Lett.* **1998**, *77*, 165.
(16) Samson, S. *Acta Chem. Scand.* **1949**, *3*, 809.
(17) Sastry, G. V. S.; Rao, V. V.; Ramachndrarao, P.; Anantharaman, T. R. *Script. Met.* **1986**, *20*, 191.
(18) Lin, Q.; Corbett, J. D. *Inorg. Chem.* **2003**, *42*, 8762.
(19) Samson, S. *Acta Chem. Scand.* **1949**, *3*, 835.
(20) Lin, Q.; Corbett, J. D. *Philos. Mag.* **2006**, *86*, 607.

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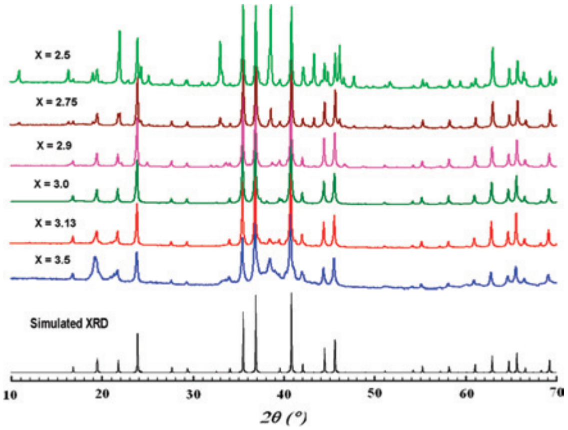

Figure 1. Experimental XRD patterns for nominal $CaAu_xGa_{4-x}$ (x = 2.5–3.5) and a pattern simulated from the single-crystal data of $CaAu_3Ga$. Note that in the $x = 3.0$ pattern there are four very weak unidentified peaks positioning at 37.46°, 38.15°, 38.29°, and 39.81°. (The middle two peaks are not visible at this level.)

The title 1/0 AC was first obtained in ~60% yield in a reaction of "$CaAu_{4.5}Ga_{1.5}$", which was aimed at an exploration of the phase width of the Ca−Au−Ga 2/1 AC.[21] Preliminary single-crystal structure analyses revealed that the cubic crystal had a refined composition of $CaAu_{3.13(1)}Ga_{0.87(1)}$. So, reactions $CaAu_xGa_{4-x}$ (x = 3.5, 3.13, 3.0, 2.9, 2.75, 2.5, and 2.0) were loaded and reacted with the same temperature profile: 800 °C for 24 h, cooled at 2 °C/h to 500 °C, then annealed at this temperature for 3 weeks, and quenched in water. Note that earlier reactions with Ca−Au−In close to 1:3:1 yielded mainly $Ca_4Au_{10}In_3$[22] rather than a "$CaAu_3In$" phase.

Figure 1 shows the XRD patterns of all products, together with a pattern simulated according to the single-crystal structure for the stoichiometric $CaAu_3Ga$ (bottom). The patterns for x = 3.5 and 3.13 products are dominated by the title 1/0 AC phase plus some $CaAu_5$ (<10 vol %),[23] whereas those from x = 2.9, 2.75, and 2.5 are mainly the title phase and $Ca_3Au_{6.6}Ga_{3.4}$[24] (~5%, 25%, and 50% of the latter, respectively). The stoichiometric reaction (x = 3) gives the highest yield (>95%) of the title gold-rich phase, plus a trace of unidentified phase marked by four very weak (<5% I/I_{max}) diffraction peaks within 2θ = 37–40°. For x = 2.0 (not shown), $CaAu_3Ga$ is not observed but rather the product falls in the phase region of $Ca_3Au_{6.6}Ga_{3.4}$.[24]

The cell parameters, refined from the 20 strongest peaks in 2θ between 10° and 70° by the program *UnitCell*,[25] vary from 9.1107(5) Å for x = 3.5 to 9.0875(3) Å for x = 2.5, with a range of 0.0232(6) Å (0.76% in volume). Such a small variation suggests a very narrow phase width for the 1/0 AC, as confirmed by single-crystal results,[26] ca. $CaAu_{3+\Delta}Ga_{1-\Delta}$ (Δ = 0–0.13; see Tables S1–S3 in the Supporting Information). The variation of the cell parameters is a result of Ga/Au mixing at an 8c Wyckoff position (Table S3). Note that the stoichiometric product can only be obtained via Ga-richer reactions (i.e., x = 2.75), consistent with general observations that pure gallides are obtained only from Ga-richer reactions.[18,27] In the following, structural data for the stoichiometric product are used for discussion.

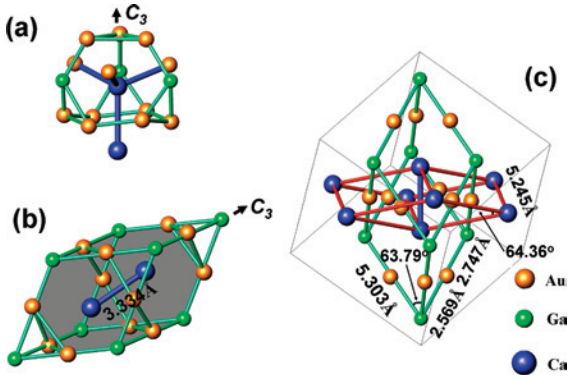

Figure 2. (a) Environment of Ca (blue) in $CaAu_3Ga$ ($Pa\bar{3}$), in which the 12 vertices lying on pseudo-5-fold vertices form a Friauf polyhedron (green bonds). The other four on pseudo-6-fold vertices are tetrahedrally oriented (blue bonds). (b) Ga PR in $CaAu_3Ga$. Each PR contains a DFP, gray shaded, and is centered by a Ca_2 dimer (blue bond). The two Ga atoms on the 3-fold axis complete the truncated tetrahedra in DFP. (c) At the unit cell level, each Ga PR (green lines) interpenetrates a Ca oblate rhombohedron (OR, red lines) by sharing Ca_2 dimers. Some important distances and angles are marked.

Strictly speaking, the structure of $CaAu_3Ga$ ($Pa\bar{3}$; Pearson symbol $cP40$) is the antitype of $NaAu_3Si$ and $NaAu_3Ge$[28] inasmuch as the electropositive Ca atoms occupy the electronegative Si/Ge sites, whereas the electronegative Ga atoms lie on the former Na sites (Table S4 in the Supporting Information). In the QC field, $CaAu_3Ga$ can also be termed as the 1/0 cubic AC of the Ca−Au−Ga QC because its lattice constant strongly correlates with that of higher order ACs and QC (14.69 Å for 1/1, 23.92 Å for 2/1, and 5.33 Å for QC).[21] This is the first 1/0 AC free of Al.

The Ca neighbors in $CaAu_3Ga$ consist of 12 Au, 3 Ga, and 1 Ca, as shown in Figure 2a; 12 of these 16 atoms (9 Au + 3 Ga) lie on pseudo-5-fold axes, and the other four (3 Au + Ca), on pseudo-6-fold axes. The former group atoms define a truncated tetrahedron or a Friauf polyhedron (green bonds). Friauf polyhedra are common structural motifs in Frank−Kasper,[29] Laves, and related phases[30] (see also references cited therein) and appear to have connections with QCs.[31] The two neighboring Friauf polyhedra shaded gray in Figure 2b share a common hexagonal face and form a double-Friauf polyhedron (DFP). DFPs are the interstitial clusters among rhombic triacontahedra in both Bergman- and

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(21) Lin, Q. Corbett, J. D., manuscript in preparation.

(22) Lin, Q.; Corbett, J. D. *Inorg. Chem.* **2007**, *46*, 8722.

(23) Raub, C. J.; Hamilton, D. C. *J. Less-Common Met.* **1964**, *6*, 486.

(24) Cordier, R.; Roehr, C.; Kussmann, D.; Hoffmann, R. D.; Poettgen, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2053.

(25) Holland, T. J. B.; Redfer, S. A. T. *Miner. Mag.* **1997**, *61*, 65.

(26) Single-crystal data for products of "$CaAu_{4.5}Ga_{1.5}$" and x = 3.5, 3.0, and 2.75 in $CaAu_xGa_{4-x}$ were collected on a Bruker APEX CCD diffractometer. The refined compositions vary from $CaAu_3Ga$ to $CaAu_{3.13(1)}Ga_{0.87(1)}$; see Tables S1–S3 in the Supporting Information.

(27) Lin, Q.; Corbett, J. D. *Inorg. Chem.* **2005**, *44*, 512.

(28) Doering, W.; Schuster, H. U. *Z. Naturforsch. B* **1980**, *35*, 1482.

(29) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1958**, *11*, 184; **1959**, *12*, 483.

(30) Fredrickson, D. C.; Lee, S.; Hoffmann, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1958.

(31) Shoemaker, D. P.; Shoemaker, C. B. In *Introduction to Quasicrystals*; Jarić, M. V., Ed.; Academic Press, Inc.: New York, 1988; pp 1–52.

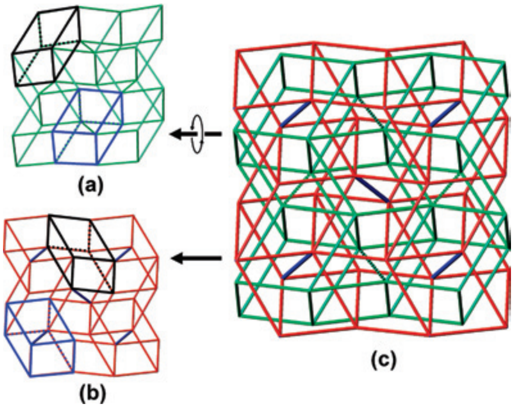

Figure 3. (a) Extended network of Au and Ga. The packing of Ga PR automatically generates its dual, Ga OR and vice versa. A PR and OR pair is highlighted in black and blue, respectively. The same scheme is used for b. (b) Extended network of Ca. (c) The sum of parts a and b. For clarity, all atoms in parts a–c are deemphasized to render the geometry.

Tsai-type 2/1 ACs,[32,33] but they are absent in the corresponding 1/1 ACs. Noteworthy is the fact that the building blocks in the known 1/0 ACs, i.e., $Al_6Cu_{0.63}Ru_{1.66}$[12] ($P2_13$) and $Mg_2Cu_6Al_5$[16] ($Pm\bar{3}$), are quite different, and both lack DFP clusters. In the present structure, DFPs appear as the only building block and yield a new structural motif for a 1/0 AC.

The three-dimensional packing of DFPs in the present 1/0 AC cannot seamlessly fill all space but rather they leave tetrahedral vacancies, each of which is defined by three Au and one Ga. Actually, these Au_3Ga vacancies are exactly the parts truncated along the unique 3-fold axis of a Friauf polyhedron (i.e., the unshaded parts in Figure 2b). As a result, each DFP is bounded by two Au_3Ga tetrahedra to form a complex structural unit termed a prolate rhombohedron (PR, a cube elongated along a 3-fold axis). In this PR, Ga atoms occupy all six vertices (thus referred to below as a Ga PR), whereas Au atoms locate close to the midpoints of PR edges. All PR edges are equal in length, 5.303 (2) Å, and are close to the sum [5.316 (3) Å] of the two independent Au−Ga bonds (Table S3 in the Supporting Information).

Remarkably, interconnection of the eight Ca atoms in the unit cell generates an oblate rhombohedron (OR). (An OR is a cube compressed along a 3-fold axis.) This OR interweaves with the Ga PR (above) through shared Ca_2 dimers (blue) on the unique 3-fold axis, as shown in Figure 2c. The edge length of the Ca OR, 5.245 (4) Å, is slightly shorter than that of the Ga PR. Notably, there are no additional atoms near the midpoints of the Ca OR edges.

Figure 3 shows the two interpenetrating three-dimensional networks of (a) the electronegative Au and Ga, (b) the positive Ca elements in $CaAu_3Ga$, and (c) their combination. The condensation of PRs in each network automatically generates their duals: ORs and vice versa. Significantly, PR and OR units are the two basic three-dimensional Penrose tiles (3DPTs)[34] that have been mathematically proven to allow construction of QC models.[6] The acute ∠Ga−Ga−Ga angle in Ga PR (and Ga OR) here is 63.79(3)°, close to the characteristic angle (63.43°) of ideal 3DPTs (and also the angle between two neighboring 5-fold axes of an icosahedron).[35] Likewise, the acute ∠Ca−Ca−Ca angle is 64.36(5)°. In addition, the edge lengths of PRs or ORs (5.245–5.303 Å) in the two networks approximate the quasilattice constant (5.33 Å).[21] Therefore, this structure represents a new type of *slightly distorted*, *periodic* arrangement of 3DPTs; notably, all edges of the PRs and ORs lie on pseudo-5-fold axes, meaning each vertex has pseudoicosahedral symmetry. However, the composition of the 1/0 AC is far from that of the corresponding QC, $\sim CaAu_3Ga_3$,[21] suggesting that QC modeling via simple decoration of basic Penrose tiles may be endless work.

The attainment of the title phase also indicates that searching for 1/0 AC examples in databases or by exploratory synthesis might greatly aid the discovery of novel quasicrystals, in addition to the pseudogap tuning route.[3] [$CaAu_3Ga$ does not, however, exhibit an obvious pseudogap (Figure S1 in the Supporting Information) even though higher order ACs do.[21]] On the one hand, some conventional crystals might be suitable candidates for 1/0 ACs, but they have not been considered to this point because they have such small lattice parameters and simple structures, in contrast to higher order ACs. On the other hand, synthetic efforts in past years have been focused on developing higher rather than lower order ACs, and 1/0 AC phases may not have received enough attention. We have started the chemical tunings of possible ACs and QCs in M−Au−Si and M−Au−Ge systems in consideration of the existence of the isoelectronic $NaAu_3Si$ and $NaAu_3Ge$.[28] The latter two compounds have already been assigned as 1/0 AC candidates on the basis of a dodecahedral local ordering assumption.[36]

In summary, explorations in the Ca−Au−Ga system have resulted in the discovery of a novel 1/0 AC that features interwoven networks of three-dimensional Penrose tiles close to those assumed for QCs. The discovery of this phase may shed some important light on QC modeling and searching.

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Supporting Information Available: Tables S1–S4 of detailed synthetic information and crystallographic data, Figure S1 of DOS and COHP data for $CaAu_3Ga$, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Lin, Q.; Corbett, J. D. *J. Am. Chem. Soc.* **2006**, *128*, 13268.
(33) Lin, Q.; Corbett, J. D. *Proc. Natl. Acad. Sci.* **2006**, *103*, 13589.
(34) Penrose, B. *Bull. Inst. Math. Appl.* **1974**, *10*, 266.
(35) Hahn, T.; Klapper, H. In *International Tables for Crystallography*, 5th ed.; Hahn, T. , Ed.; Kluwer Academic Publishers: Dordrecht/Boston/London, 2002; Vol. *A*, pp 761–803.
(36) Dmitrienko, V. E. *Acta Crystallogr., Sect. A* **1994**, *50*, 515.