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Qisheng Lin
The Ames Laboratory, qslin@ameslab.gov

John D. Corbett
Iowa State University

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Article

Mg$_{35}$Cu$_{24}$Ga$_{53}$: A Three-Dimensional Cubic Network Composed of Interconnected Cu$_6$Ga$_6$ Icosahedra, Mg-Centered Ga$_{16}$ Icosioctahedra, and a Magnesium Lattice

Qisheng Lin and John D. Corbett*

Ames Laboratory[1] and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Single-crystal X-ray structural determinations for the Mg$_{35.12(4)}$Cu$_{24}$Ga$_{53.58(6)}$ and Mg$_{35.6(4)}$Cu$_{24}$Ga$_{52.66(6)}$ refined compositions ($Fd\bar{3}m$, $Z = 4$) reveal empty (Cu,Ga)$_{12}$ icosahedra and centered MgGa$_{16}$ icosioctahedra that are interconnected at every vertex to a compact three-dimensional anion network. A small range of variable occupancy exists on one of three Ga and one of four Mg positions. The clusters are well-bonded and held in different sized cavities, in which they are also directly bonded to a Mg cation network. The two networks thus interpenetrate each other, and there are no spacers. The new phase is isostructural with K$_{39}$In$_{80}$, K$_{17}$In$_{41}$, and the electron-poorer Na$_{35}$Cd$_{24}$Ga$_{56}$, all of which contain clathrate-II-type cation frameworks. Electron counting using the classic (MO-based) cluster assignments indicates that the refined structure is substantially ideal and closed-shell. The symmetry of the present structure does not suggest a ready conversion to an icosahedral quasicrystal or its approximants.

Introduction

Quasicrystal phases are a novel class of solid crystalline intermetallic compounds with rotational symmetries in their diffraction patterns that are incommensurate with translational periodicity.[2] They are generally recognized as electron phases that may be described by Hume-Rothery stabilization rules,[3,4] with restricted ranges of valence electron counts per atom and with band gaps or pseudogaps at or near their Fermi energies.[5] Known quasicrystals and their presumed approximants are extensively employed to generalize experience and to search for new quasicrystals. Approximants are translationally normal crystalline compounds, generally with large unit cells, that contain condensed intrinsically high-symmetry building blocks such as icosahedra and dodecahedra. Their compositions lie close to those of quasicrystals, and they are commonly used as models of quasicrystal structures.

Studies of alkali-metal compounds of the triel elements Ga, In, and Tl have demonstrated that these intermetallics afford a rich collection of isolated, centered, interbridged, and fused icosahedra, among other polyhedra.[6] These compounds evidently exist with relatively flexible structures that enable the alkali-metal countercations to be accommodated in voids, but they also open promising avenues of exploration for new quasicrystals through substitution of better network-forming cations, such as Mg, Ca, Cu, Zn, etc., that also lie among the so-called *icosogen*[7] elements. We have been attempting to synthesize derivatives of Mg$_2$Zn$_{11}$-type structures that contain some amounts of a triel. This primitive cubic parent structure consists of self-centered Zn icosahedra and octahedra that are partly interbridged via covalent Zn–Zn bonds[8] and is a continuous covalently bound lattice that appears to be one necessity for the formation of quasicrystals. Our newly discovered Mg$_2$Cu$_6$Ga$_5$ compound

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* E-mail: jcorbett@iastate.edu.

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occurs in this structure type, in which three formula units, Cu_6 octahedra, and $Ga@Cu_{12}$ icosahedra are interconnected by $Ga_{14}Mg_6$ networks.[9] Furthermore, electronic structure calculations for $Mg_2Cu_6Ga_5$ show that a pseudogap exists just above the Fermi energy and that all pairwise covalent interactions (COOPs) remain bonding to energies above that point. These factors suggest that the compound is hypoelectronic with a four-electron deficiency per unit cell, and such a derivative with Sc substituting for Mg yields the desired body-centered-cubic (bcc) quasicrystal approximant $Sc_3Mg_{0.16}Cu_{10.50}Ga_{7.50}$.[10] This article reports on the result of our alternate attempts to tune the primitive structure of the ternary $Mg_2Cu_6Ga_5$ phase to a quasicrystalline approximant by modifying the ratio of Cu and Ga in order to gain four electrons. Instead, this unexpectedly leads to the title compound with a face-centered-cubic (fcc) structure, for which we here report the synthesis, structure, and bonding analysis.

Experimental Section

Syntheses. Experience shows that Ga intermetallic compounds generally cannot be readily obtained directly from a synthesis with the nominal composition sought; rather, a shift of product stoichiometries is generally observed toward compounds poorer in Ga. This likely has to do with Ga's particularly low melting point and the physical segregation that results. Therefore, we have used a self-flux method to grow crystals and an internal sieve in the container tube to separate crystals from the melts, as has been described elsewhere.[9,11]

Syntheses were performed via reactions of the as-received elements Mg (turnings), Cu (powder), and Ga (chunks) (all 99.9%, Alfa). These were weighed in a glovebox under a nitrogen atmosphere and weld-sealed under an argon atmosphere into ~9-mm-diameter tantalum containers, into which perforated Ta disks had been sealed near the midpoint. These were, in turn, held within an evacuated SiO_2 jacket to avoid air oxidation. The mixtures were heated to 800 °C for 2 h to homogenize them, cooled to 570 °C in 6 min, and then cooled to 400 °C at a rate of 2 °C/h for crystal growth. The assembly was then inverted and rapidly centrifuged to filter the crystalline products from the excess melt.

Exploratory experiments with stoichiometric compositions such as $Mg_2Cu_{4.33}Ga_{6.67}$ ($Mg_{15.4}Cu_{33.3}Ga_{51.3}$) and $Mg_{3.33}Cu_{4.67}Ga_5$ ($Mg_{25.6}Cu_{35.9}Ga_{38.5}$) were first loaded with the aim of synthesizing a compound in which the bonding states would be optimized according to the electronic structure analysis of $Mg_2Cu_6Ga_5$.[9] The reactions instead led to the formation of either other known phases or the new, then-unidentified phase described here, or both. For example, the former gave ~60% $Mg_2Cu_6Ga_5$ and ~30% MgCuGa[12] and a small amount of an unknown phase, according to powder diffraction. To track the unidentified phase, a reaction run with Mg/Cu/Ga proportions near 33.3:16.7:50.0 gave, as filtered products, ~60% MgCuGa and ~40% as the title phase. Further experiments showed that high yields of the title phase (>90%) were obtained by the same method if the Mg/Cu/Ga compositions were

Table 1. Loaded Compositions, Lattice Parameters, and EDS Analyses of the Title Phase Therefrom[a]

loaded composition	a (Å)	V (Å³)	EDS Mg/Cu/Ga (%)
$Mg_{36.4}Cu_{9.1}Ga_{55.5}$[b]	19.8742(8)	7850.0(5)	31.0(3)/21.3(4)/47.7(9)
$Mg_{33.3}Cu_{16.7}Ga_{50}$[b]	19.8646(7)	7838.6(5)	30.7(2)/21.9(3)/47.4(8)
$Mg_{36.5}Cu_{12.5}Ga_{51}$	19.8637(4)	7837.6(3)	30.6(3)/21.2(4)/48.2(9)
$Mg_{37.5}Cu_{12.5}Ga_{50}$	19.8615(9)	7834.9(6)	
$Mg_{30}Cu_{10}Ga_{60}$	19.8590(6)	7832.0(4)	30.2(2)/21.5(3)/48.3(7)
$Mg_{30.8}Cu_{7.7}Ga_{61.5}$	19.8524(9)	7824.2(6)	
		average	30.6(3)/21.5(4)/47.9(9)
		normalized	34.2(3)/24/53.5(10)

[a] Cell parameters were refined from about 50 observed peaks in the 2θ range of 5−80°; $\lambda = 1.540\ 598$ Å, 23 °C. [b] Source of single crystals studied.

kept in the ranges of (30−37):(9−17):(50−60) atom %. Examination of the as-grown crystals under a microscope inside a glovebox revealed a metallic luster and a regular morphology with crystal growth terraces evident, the largest being about $0.4 \times 0.4 \times 0.4$ cm.

Samples of the new phase were originally handled in the glovebox or in sealed capillaries, but it later turned out that they were quite inert in air at room temperature, so this was discontinued.

Powder X-ray Diffraction. These studies were performed on a Huber 670 Guinier powder camera equipped with an area detector and Cu Kα radiation ($\lambda = 1.540\ 598$ Å). Ground powder was homogeneously dispersed on the flat Mylar support with the aid of petrolatum grease. The step length was set at 0.005°, and the exposure time was 1 h. Data acquisition was controlled via the in situ program. The peak search, indexing, and least-squares refinements were done with the aid of Winplotr and its built-in programs.[13] Some refined cell parameter results for the title phase secured from different reactions are given in Table 1. Some small composition variation of the phase seems to be indicated. Cell parameters for the first two were later used in the calculations of bond distances from the refined structures.

EDS Analyses. The elemental compositions of several single crystals were determined via semiquantitative energy-dispersive X-ray spectroscopy (EDS) on a JEOL 840A scanning electron microscope with an IXRF X-ray analyzer system and a Kevex Quantum light-element detector. A beam of 20 kV and 0.3 mA was used to gain count rates of about 2500 s⁻¹. To increase the accuracies, measurements on flat, clean surfaces of small, crushed single crystals were attempted. Results are also listed in Table 1.

Structure Determinations. Single crystals were selected and inserted into thin-walled glass capillaries for singularity checks with the aid of Laue photographs. Single-crystal data were collected from a crystal taken from the $Mg_{36.4}Cu_{9.1}Ga_{55.5}$ composition at 296 K with the aid of a Bruker APEX Platform CCD diffractometer and graphite-monochromatized Mo Kα radiation. The data were collected over a full sphere of reciprocal space up to 28.21° in Θ. The individual frames were measured with an ω rotation of 0.3° and an acquisition time of 10 s. SMART software was used for the data acquisition, and SAINT was used for the data extraction and reduction. The absorption correction was performed using SADABS. Diffraction data from a second crystal taken from the $Mg_{33.3}Cu_{16.7}Ga_{50}$ reaction were collected at room temperature on a Rigaku AFC6R diffractometer, and the structure was also determined and refined. ψ scans were employed for the absorption correction in this case.

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Structure solutions and refinements for both crystals were performed using the SHELXTL package of crystallographic programs.[14] The assignment of the space group $Fd\bar{3}m$ (setting 2) was made on the basis of the $m\bar{3}m$ Laue symmetry determined by the diffractometer, the systematic absences, and the Wilson statistics, and it was confirmed by the subsequent successful solution and refinement of the structure. The structures of the two samples were both solved by direct methods. For the first crystal, the first four heavy-atom positions were initially assigned to Ga atoms and two light ones to Mg on the basis of both peak heights and bond distances. Subsequent least-squares refinements and difference Fourier syntheses quickly gave two more Mg positions. Refinements with isotropic thermal parameters proceeded smoothly to R1 = 5.90%, wR2 = 16.91%, and GOF = 1.151, but Ga3 on the 32e (x, x, x; $3m$) and Mg4 on 8a ($^1/_8$,$^1/_8$,$^1/_8$; $\bar{4}3m$) exhibited anomalously large thermal parameters. This suggested, tentatively, that these Mg and Ga positions might be partially occupied, and refinements of both of their occupancies gave values in the neighborhood of ~60% (see below). The refinements converged to R1 = 4.21% and wR2 = 9.99%, and the thermal parameters were then reasonable. Because mixing of Cu and Ga on the same site occurs in other compounds (e.g., Mg$_2$Cu$_3$Ga[12] and Cu$_9$Ga$_4$[15]), the Ga/Cu proportions in each of the three 96g positions initially assigned as pure Cu or Ga were allowed to vary separately (with the total occupancies fixed at 100%) along with a single isotropic displacement parameter. This gave a 6:94(10) proportion for Ga/Cu for the first position and R ~ 3.89%, indicating that a Cu assignment was probably correct, whereas allowance of Cu mixing at the two Ga 96g sites yielded either negative Cu occupancies or unstable refinements. In the final stage, uncertainties in the B_{eq} values for the fractional Mg4 sites at $x = ^1/_8$ were relatively large [17(5) and 6(6)] in the two refinements; therefore, these occupancies were then refined with $B_{eq} = 11$, which is the average of the values for the other three Mg positions, and then fixed. The final refinement, with anisotropic displacement parameters and an extinction parameter, converged at R1 = 2.44%, wR2 = 5.71%, and GOF = 1.429 for 35 variables and 512 independent reflections in the APEX dataset and the composition Mg$_{35.12(4)}$Cu$_{24}$Ga$_{53.58(6)}$. The Ga3 atom in the 32e site was concluded to be substantially free of Cu, in view of the agreement of the X-ray refinements with EDS analyses (see below). The maximum and minimum peaks in the final difference Fourier map were 0.71 e/Å^3 (0.62 Å from Ga1) and −1.14 e/Å^3 (0.89 Å from Ga1). The only faint indication of any problem with the structure might be a slightly larger thermal parameter for the Ga3 atom, but this is plausible because the position is ~70% occupied and lies in a large hexagonal channel with the longest Ga−Ga neighbor separations in the structure (Figure S1, Supporting Information). The principal anisotropic components are generally quite uniform for each atom type for which variation is allowed.

Very similar situations were encountered during refinement of the dataset from the second crystal for the composition Mg$_{35.02(1)}$Cu$_{24}$Ga$_{52.66(6)}$. Complete data collection parameters and details of the two structure solutions and refinements for the two compounds are given in Table S1 of the Supporting Information, and a summary is listed in Table 2. The refined positional parameters and isotropic-equivalent displacement ellipsoids are listed in Table 3, and the important atom separations, according to the first APEX dataset, are given in Table 4. The remainder are given in the Supporting Information.

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Table 2. Some Data Collection and Refinement Parameters of the Title Compounds

refined comp.	Mg$_{35.12}$Cu$_{24}$Ga$_{53.58}$	Mg$_{35.06}$Cu$_{24}$Ga$_{52.66}$
space group, Z	$Fd\bar{3}m$ (No. 227), 4	$Fd\bar{3}m$ (No. 227), 4
lattice parameters		
a (Å)	19.8742(8)	19.8646(7)
V (Å^3)	7850.0(5)	7838.6(5)
d_{calcd} (g/cm^3)	5.175	5.125
μ(Mo Kα) (mm^{-1})	24.648	24.376
residuals R1, wR2^a (%)	2.44, 5.71	2.61, 4.65

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)]^{1/2}$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/\sigma_F^4$.

Table 3. Positional ($\times 10^4$) and Displacement ($\times 10^3$) Parameters for Mg$_{35.12(4)}$Cu$_{24}$Ga$_{53.58(6)}$ and Mg$_{35.06(4)}$Cu$_{24}$Ga$_{52.66(6)}^a$

atom	Wyckoff symbol	site symmetry	x	z	B_{eq}^b	occupancy ≠ 1 (%)
Cu	96g	..m	399(1)	3781(1)	8(1)	
			398(1)	3783(1)	11(1)	
Ga1	96g	..m	786(1)	2673(1)	12(1)	
			785(1)	2676(1)	14(1)	
Ga2	96g	..m	801(1)	4873(1)	8(1)	
			801(1)	4872(1)	10(1)	
Ga3	32e	.3m	389(1)		26(1)	69.6(7)
			393(1)		29(1)	58.4(8)
Mg1	96g	..m	3159(1)	1300(1)	12(1)	
			3157(1)	1300(2)	14(1)	
Mg2	32e	.3m	2809(1)		10(1)	
			2808(2)		12(1)	
Mg3	8b	−43m	$^3/_8$	$^3/_8$	10(1)	
			$^3/_8$	$^3/_8$	11	
Mg4	8a	−43m	$^1/_8$	$^1/_8$	11	56(2)
			$^1/_8$	$^1/_8$	11	53(2)

^{a} Data for Mg$_{35.12}$Cu$_{24}$Ga$_{53.58}$ are listed first for each parameter; $y = x$ for all atoms. ^{b} B_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond Distances (Å) in Mg$_{35.12}$Cu$_{24}$Ga$_{53.58}$

Ga1−Cu		2.455(1)	Cu−Cu	2×	2.7978(9)	
Ga1−Ga1		2.610(1)	Cu−Ga1		2.455(1)	
Ga1−Ga1	2×	2.696(1)	Cu−Ga2		2.446(1)	
Ga1−Ga3		2.967(1)	Cu−Ga2	2×	2.5831(7)	
Ga1−Mg1	2×	3.079(2)	Cu−Mg1	4×	2.912(1)	
Ga1−Mg1	2×	3.139(2)	Cu−Mg2		2.774(1)	
Ga1−Mg2		3.089(3)				
Ga1−Mg4		3.1153(7)	Mg1−Cu	2×	2.912(1)	
			Mg1−Ga1	2×	3.079(2)	
Ga2−Cu	2×	2.5831(7)	Mg1−Ga1	2×	3.139(2)	
Ga2−Cu		2.446(1)	Mg1−Ga2	2×	2.983(2)	
Ga2−Ga2		2.525(1)	Mg1−Mg1		3.180(2)	
Ga2−Ga2	2×	2.608(1)	Mg1−Mg1		3.322(2)	
Ga2−Mg1	2×	2.983(2)	Mg1−Mg2		3.156(2)	
Ga2−Mg2	2×	3.056(2)				
Ga2−Mg3		3.0139(7)	Mg2−Cu	3×	2.774(1)	
			Mg2−Ga1	3×	3.089(3)	
Ga3−Ga1	6×	2.967(1)	Mg2−Ga2	6×	3.056(2)	
Ga3−Ga3		2.680(4)	Mg2−Mg1	3×	3.156(2)	
Ga3−Mg4		2.963(2)				
			Mg3−Ga2	12×	3.0139(7)	
			Mg3−Mg3	4×	3.235(1)	
			Mg4−Ga1	12×	3.1153(2)	
			Mg4−Ga3	4×	2.963(2)	

Syntheses and Composition. The filtration-at-temperature technique was utilized to isolate six apparently single-phase samples of this cubic phase, Mg$_{\sim 35}$Cu$_{24}$Ga$_{\sim 53.5}$, from a variety of compositions at 400 °C. Data in Table 1 show that the six reactions studied covered a range of Mg, generally in excess, and an excess of Ga flux, whereas Cu was limiting. A range of cubic lattice parameters of ≤0.022(1) Å was evident largely because of the superior precision of the results from the Huber Guinier camera, with
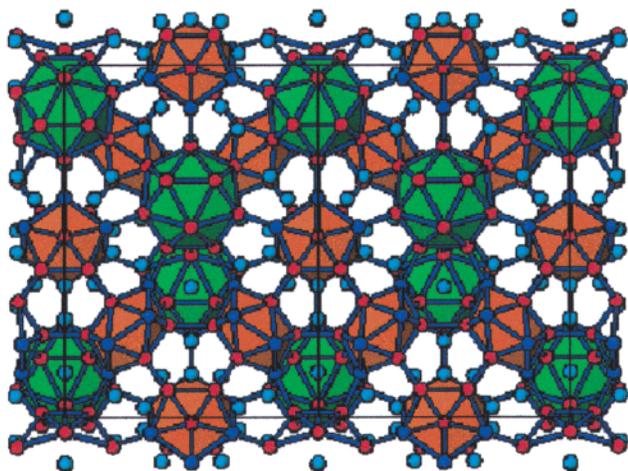
**Figure 1.** [110] section of the structure of Mg$_{35}$Cu$_{24}$Ga$_{53}$, which is built of Cu$_6$Ga$_6$ icosahedra (orange) and Mg-centered icosioctahedra (green). The flattened icosahedra lie behind and are seen from the side. All bonds to Mg (light blue) are omitted for clarity.

standard deviations of only 1 part in $(2.0-4.5) \times 10^{-5}$. According to EDS data, these samples yielded a rather narrow range of single-phase compositions for the four samples analyzed. The average of these compositions has been normalized to 24 Cu atoms per formula unit because the Cu content appears to be determined fairly unambiguously by crystallography. The normalized average for Mg/Cu/Ga of 34.2(3):24:53.5(10) for all samples compares quite well with the crystallographic results from the APEX and Rigaku diffractometer datasets for the first two of the samples, Mg$_{35.12(4)}$Cu$_{24}$Ga$_{53.58(6)}$ and Mg$_{35.06(4)}$Cu$_{24}$Ga$_{52.66(6)}$, respectively. The normalized average of the EDS analyses for the data-crystal samples is a little closer, Mg$_{34.3(4)}$Cu$_{24}$Ga$_{52.8(8)}$. The quality of these agreements led us to the conclusion that the partial Ga content refined for the 32*e* position could not reflect a significant amount of Cu. The functionality of this site supports this notion. Hereafter, we will generally cite data only from the somewhat more precise refinement of Mg$_{35.1}$Cu$_{24}$Ga$_{53.6}$ from the APEX data.

Results and Discussion

Structure Description. A convenient way to describe the structure of intermetallic compounds of this variety is to identify the unique structural building blocks and then to describe the assembly of the three-dimensional (3-D) structure in terms of these fundamental units. The main building blocks in the Mg$_{35}$Cu$_{24}$Ga$_{54}$ structure are the more anionic Mg4-centered Ga$_{16}$ icosioctahedra and the empty Cu$_6$Ga$_6$ icosahedra, both somewhat distorted from the ideal figures, which are bonded to and encased within a continuous 3-D network of Mg atoms. The present arrangement is unusually compact in that all Ga and Cu atoms in the clusters are exo-bonded directly to an atom in another cluster (Figures 1 and 2) and there are no isolated or spacer Ga or Cu atoms. This is an evidently important basis for the formation of quasi-crystals as well.

The Mg@Ga$_{16}$ icosioctahedra (Figure 2a) are regular deltahedra ($\bar{4}3m$) generated from 12 Ga1, a truncated tetrahedron, on which 4 Ga3 atoms cap the four large hexagonal faces. The internal angles on the triangular faces vary between 52 and 64°. As noted by Brown and Lip-
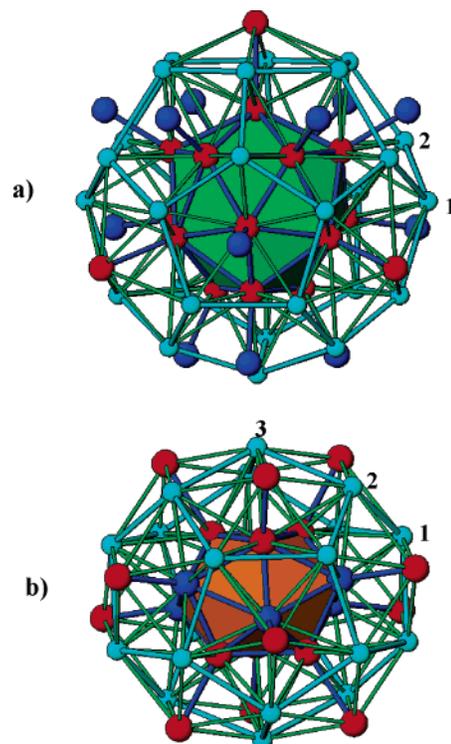
Figure 2. (a) Icosioctahedral Mg@Ga$_{16}$ (green) and (b) Cu$_6$Ga$_6$ icosahedron (orange), shown with exo bonding and the respective surrounding Mg$_{28}$ and Mg$_{20}$ polyhedra. A few of the Mg atoms are numbered. Cu, dark blue; Ga, orange-red; Mg, light blue.

scomb,[16] the overlap between radial orbitals on cluster atoms naturally becomes less as the diameter of the cluster increases, and this may be alleviated somewhat by the encapsulation of another atom in the center of the cavity, which in this case is Mg4, but only at about 56% occupancy. Centered deltahedra are also found in Li$_{38}$(Zn$_{0.337}$Ga$_{0.663}$)$_{101}$[17] and Na$_{35}$Cd$_{24}$Ga$_{56}$[18] and in some In and Tl cluster phases,[19,20] but this is apparently the first triel example in which the centered position is clearly not fully occupied. The Na$_{35}$Cd$_{24}$Ga$_{56}$ isotype is remarkably similar in composition to the present compound, but that compound is about five electrons poorer per formula unit. It shows large Cd-Ga mixing on one 96*g* and one 32*e* site and contains sodium cations, which are less likely participants in general network bonding.

The Ga-Ga bond distances within the icosioctahedral cluster are typical of those in delocalized systems, all in the range of 2.610(1)-2.967(1) Å, with the longer distance being associated with the fractional Ga3 atoms. The distance from the central (fractional) Mg4 atom to 12 Ga1 [3.115(1) Å] is ∼0.15 Å greater than the distance to the four fractional Ga3 atoms [2.963(2) Å] that cap the larger hexagonal faces. Each of the Ga3 atoms nominally has six more-distant (2.967 Å) Ga1 neighbors within the faces of the cluster and a 2.680 Å bond to a Ga3 atom in an adjacent cluster, whereas each Ga1 atom has five Ga neighbors (3 Ga1 and 2 Ga3) within

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the cluster and a shorter bond to a Cu atom in an adjacent Cu_6Ga_6 icosahedron (2.455 Å).

The empty icosahedra with $\bar{3}m$ (D_{3d}) symmetry are generated by equal numbers of Cu and Ga2 atoms (Figure 2b). The distortion from the ideal I_h symmetry to a symmetry of $\bar{3}m$ differentiates the two kinds and sizes of atoms, or vice versa, with a compression along the 3-fold axis of the Ga2 antiprism, which lies roughly vertical in Figure 2b. This places Ga2 0.40 Å closer to the centroid than Cu. Each atom of the icosahedra naturally has five neighbors within the cluster in addition to an exo bond; the Cu atoms are bonded to Ga1 in an adjacent $MgGa_{16}$ polyhedron at 2.456 Å, and the Ga2 atoms are bonded to a like atom in an adjacent icosahedron with, by 0.09 Å, the shortest Ga–Ga separation in the structure (2.525 Å). These intercluster distances agree fairly well with about the only general reference values one has, the sums of Pauling's single bond metallic radii: 2.42 Å (vs 2.46 Å observed) for Cu–Ga and 2.49 Å (vs 2.52 Å) for Ga–Ga.[21] Only in the mixed icosahedron do the homoatomic bond lengths follow the generality that the intercluster connections appear to be more nearly normal two-center–two-electron bonds and that they are shorter than the intracluster bonds in electron-deficient clusters, as seen in $RbGa_3$[22] and $Na_{22}Ga_{39}$.[23] The normal intracluster bonds in the present situation are generally 0.1–0.2 Å longer, but more surprisingly, the Cu–Cu intracluster lengths of 2.80 Å are 0.45 Å longer. The reason for this is not clear, but it may be related to the compressive distortion of the Ga antiprism. Overall, the distortions may not be very unusual considering the complex intercluster bonding achieved in this structure without any spacers or interbridging atoms (Figure 1).

The Mg1, Mg2, and Mg3 atoms generate a characteristic counternetwork structure in this assembly; one of each type is marked in Figure 2. Each Mg1 simultaneously caps a Cu–Cu–Ga2 face on a $(Cu,Ga)_{12}$ icosahedron and bridges a Ga1–Ga1 edge on $(Mg)Ga_{16}$, and Mg2 caps both a Cu–Ga2–Ga2 face on the icosahedron and a Ga1–Ga1–Ga1 trigonal face on the $(Mg)Ga_{16}$ polyhedron. The Mg3 atoms cap four Ga2–Ga2–Ga2 trigonal faces on the icosahedra. (Drawings of the Mg environments are given in Figure S2 of the Supporting Information.) These Mg atoms are also directly bonded to three or four other Mg atoms at 3.16–3.24 Å (the d_{12} distance in the metal is 3.20 Å[21]), which generates a framework featuring pentagonal and hexagonal faces. A [110] projection of the resulting Mg network is shown in Figure 3. This contains two types of polyhedral cavities, with the smaller defined by a regular Mg_{20} pentagonal dodecahedron built of 12 Mg1, 6 Mg2, and 2 Mg3 atoms and the larger defined by a Mg_{28} framework of 24 Mg1 and 4 Mg2 atoms. These encapsulate the icosahedra and icosioctahedra, the centers of which are marked by orange and green circles, respectively. Further similarities to Figure 1 are clear. Overall, this rather remarkable structure
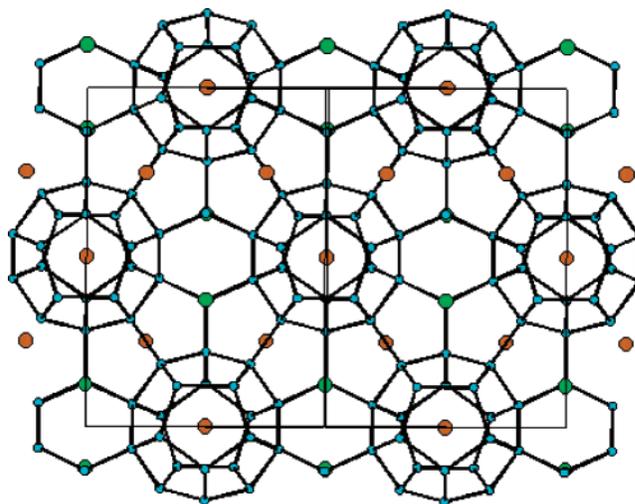
Figure 3. [110] section of the Mg network (light blue), with small orange and green circles marking the centers of the icosahedral and icosioctahedral clusters, respectively. The framework is that of the clathrate-II structures (compare to Figure 1).

thus consists of strongly and directly interlinked $(Cu,Ga)_{12}$ icosahedra and $(Mg)Ga_{16}$ isosioctahedra that are also bonded (mostly through face capping) within dual interlinked Mg_{20} and Mg_{28} polyhedra, respectively. The present phase is also isostructural with cubic $Na_{17}Ga_{29}In_{12}$, $K_{17}In_{41}$,[24] and $Na_{35}Cd_{24}Ga_{56}$,[18] in which differences in stoichiometry arise from different mixed and fractional occupancies. The [110] view of the present cation structure (Figure 3) can be recognized as the clathrate-II-type framework as well.[25] Also to be included in this family are $K_{39}In_{80}$ and two neighboring binary phases in which three different kinds of clusters are accommodated within the same cation network.[26] In this case, the [111] view of the present Mg framework may be more familiar (Figure S3, Supporting Information). The breadth of the clathrate-II organization among diverse compounds has now been found to extend to a total of nearly two dozen examples of the foregoing types of triel cluster compounds.[27]

We will consider a possible derivation of a quasicrystal and its approximants from this complex network after electronic and bonding considerations.

Electron and Bonding Requirements. There are four $(Cu,Ga)_{12}$ icosahedra and two $(Mg)Ga_{16}$ icosioctahedra in one formula unit of the title compound. Extended Hückel molecular orbital calculation results[28] for the isolated stoichiometric $Cu_6Ga_6H_{12}{}^{2-}$ and $Mg@Ga_{16}H_{16}{}^{2-}$ clusters are given in the Supporting Information (Figures S4 and S5). (Ga 4s energies were employed for the terminating H-like atoms.) In agreement with Wade's $2n + 2$ skeletal rule[29] for closo polyhedra, the isolated icosahedron, even with the mixed composition and the compression along the 3-fold axis, still requires 26 skeleton electrons below a gap of ca.

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Table 5. Electron-Counting Scheme for the Intermetallic Phases $Mg_{35.12}Cu_{24}Ga_{53.58}$ and $Mg_{35.06}Cu_{24}Ga_{52.660}$, per Formula Unit (fu)

	$Mg_{35.12}Cu_{24}Ga_{53.58}$		$Mg_{35.06}Cu_{24}Ga_{52.66}$	
$(Cu,Ga)_{12}$ skeleton electrons $(fu)^{-1}$	$26 \times 4 =$	104	$26 \times 4 =$	104
$(Cu,Ga)_{12}$ exo bonding	$12 \times 4 =$	48	$12 \times 4 =$	48
$MgGa_{16}$ skeleton electrons	$36 \times 2 =$	72	$36 \times 2 =$	72
$MgGa_{16}$ exo bonding	$14.8 \times 2 =$	29.60	$14.3 \times 2 =$	28.7
bonding electrons required:	fu	253.6		252.7
	cell	1014.4		1010.6
electrons from composition:	fu	255.0		252.1
	cell	1019.9		1008.4
difference/cell		+5.5		−2.2

2 eV. A clear switch in the sign of the COOP data also occurs at this point. Likewise, the closo icosioctahedron is most stable with 36 skeletal electrons, which gives a gap of ~3.9 eV. This polyhedron is generally elongated, not spherical, and $2n + 4$ electrons are typically required.[19] This count remains unchanged whether the clusters are centered or not, as long as electrons on the centered atoms are counted in the former instance. Furthermore, a nido cluster with one vertex removed retains the same number of skeletal electrons, a condition that would seem to apply fairly well to the refined icosioctahedra in which an average of either 1.2 or 1.7 out of 8 Ga3 are missing. The only other effect of the missing Ga3 is to lessen the exo bonding of each to a like atom in an adjacent cluster, and so the only assumption made in tabulating the cluster requirements is that pairs of Ga3 vacancies be correlated between adjoining clusters.

As summarized in Table 5, the two refined crystals would require 253.6 and 252.7 electrons per formula unit or 1014.4 and 1010.6 electrons per cell ($Z = 4$), whereas the refined stoichiometries afford 1019.9 and 1008.4 electrons per cell, respectively. These comparisons correspond to small differences of ~5.5 and −2.2 electrons for the two structures, or +0.54% and −0.22% of the total electron counts. Of course, these phases may be metallic, in which case the closed shell concept is probably not meaningful.

According to Pauling's[21] metallic single bond radii of Cu and Ga (1.176 and 1.246 Å), single bond lengths for Cu–Ga should be around 2.418 Å, Ga–Ga ~ 2.490 Å, and Cu–Cu ~ 2.346 Å. The observed Ga2–Ga2 bonds between icosahedra are ~2.52 Å, the Cu–Ga1 bonds between icosahedra and icosioctahedra are ~2.45 Å, and the (fractional) Ga3–Ga3 bonds between icosioctahedra are 2.680 Å. Certainly, the first two comparisons are reasonable for 2c–2e bonds, whereas the third is long both here and relative to those in other Ga intermetallic phases. None of these distances change significantly between the two refined structures; $d(Ga3–Ga3)$ decreases the most, but by only 2.3σ as the Ga3 occupancy decreases 11(1)%. Disordered fractional occupancies of the Ga3 positions in this structure seem to be intrinsic.

The isotypic $Na_{35}Cd_{24}Ga_{56}$[18] is rather different in both atom distributions and electron count relative to the substantially ideal bonding in the present compound. The present Ga1 and Ga3 sites in the icosioctahedra become heavily admixed with Cd, 71 and 85%, respectively, for an assumed 100%
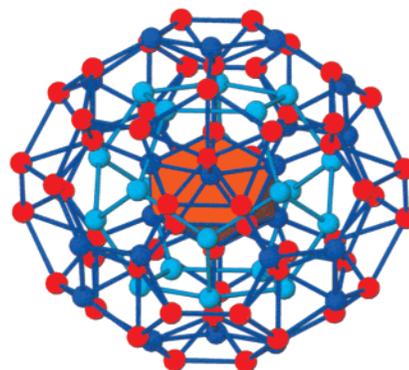
Figure 4. Samson polyhedron around the central Cu_6Ga_6 cluster with its Mg_{20} envelope, a large Ga_{12} polyhedron, and the $(Cu,Ga)_{60}$ fullerene. All bonds to Mg are omitted for clarity. The outward facing $(Cu,Ga)_6$ pentagonal pyramids at the surface are sections of other icosahedra. Cu, dark blue; Ga, red–orange; Mg, light blue.

total occupancy. The Cu site changes to all Ga, whereas the Mg4 site becomes 50% occupied by Na. Differences in the Mulliken electronegativities for the Cu–Ga and Cd–Ga pairs are nearly the same (for the neutral atoms),[30] but Cd is appreciably larger than Cu, 1.38 versus 1.18 Å in metallic radii. This may be responsible for the rather different distributions of the minor components Cu and Cd, although a complete calculation would be necessary to check the site populations. Electron counting for the Cd phase indicates that it is a good deal less ideal. For the more precisely refined composition $Na_{35}Cd_{23.8}Ga_{56.8}$, there are now 20 fewer electrons per cell relative to the ideal Cd–Ga polyhedral network. Clearly, changes in the electron counts associated with the switch from Cu to Cd are insufficient to compensate for the larger change associated with the switch from Mg to Na as the more cationic component. Na is certainly more electropositive and is generally believed to be less effective than Mg in its participation in complete network bonding,[4] as also appears to be the case in the electron-deficient Bergman ($Im\bar{3}$) phase $Na_{13}(Cd_{0.70}Tl_{0.30})_{27}$.[31]

How Far to a Quasicrystalline Phase? As alluded to before, three facts make the present structure interesting in this respect. First, the compound contains condensed icosahedra and icosioctahedra without any isolated or weakly bonded spacers; second, bonding in the structure tends to be fairly homogeneous; and third, the electron concentration can be varied (at least slightly) by changing the composition. All of these seem to be characteristics of quasicrystals, or at least of their better quantified approximants.[5] However, whether the title compound is really close to the quasicrystal phase or not is unknown because no quasicrystal phase has been discovered in the Mg–Cu–Ga ternary phase to date. (One is not certain that the system has even been searched.)

The present structure can also be described as a condensed packing of the so-called Samson polyhedra,[32] which are sometimes used as guides to this chemistry. Figure 4 represents the hierarchy of such a giant cluster, namely,

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successive concentric polyhedra from a $(Cu,Ga)_{12}$ icosahedron, the Mg_{20} pentagonal dodecahedron framework, a larger Ga_{12} icosahedron, and the $(Cu,Ga)_{60}$ Buckminster fullerene. However, in this case, the polyhedra cut through recognizable clusters, for example, the icosahedra around the outer shell that appear here as pentagonal pyramids. Hence, this representation does not really fit in with the customary cluster-based descriptions.

The electron content per atom (e/a) might be a useful indicator. The e/a value of the title compounds is ~2.26, which is within the generally considered favorable range of 2.0−2.3 for icosahedral quasicrystals.[4,5,9,33] (The e/a value of the unique Ga quasicrystal $Mg_{32}Zn_{52}Ga_{16}$ is 2.16.[34]) Attainment of an ideal e/a value for the title phase might be achieved by changing the proportion of Mg and Ga. In this case, the correct direction toward icosahedral quasicrystals should probably be via a structural evolution from the icosioctahedra. The limited composition variations studied (Table 1), largely with limited Cu, suggest that Ga variation may be the more likely method, but one should presumably look for a change in the structure type as well. As a matter of fact, fcc lattices have not proven to be favorable for crystalline icosahedral approximants; rather, symmetry-breaking bcc ($Im\bar{3}$) lattices[4,9,33,35] should be more interesting, or even lattices with as low as $R\bar{3}$ symmetry, which have a common subgroup relationship to both cubic space groups, may prove more favorable. The cubic $Li_{13}Cu_6Ga_{21}$ ($Im\bar{3}$)

phase that was synthesized 10 years ago[36] has a similar structural motif and elemental composition and has an electron concentration (2.05) close to that of the R−Li_3CuAl_5 (2.11)[37] crystalline approximant and the i−Li_3CuAl_6 (2.20) icosahedral quasicrystal,[38] but no corresponding quasicrystal phase with Ga has been reported. Once again, it may be that "first comes the synthesis", as undirected as that may be.

Conclusions. In this paper, we present the synthesis and structure of the title compounds. Single-crystal structure determinations reveal that the compounds crystallize in the cubic space group $Fd\bar{3}m$, with $Z = 4$. They contain two kinds of building blocks, empty $(Cu,Ga)_{12}$ icosahedra and centered $MgGa_{16}$ icosioctahedra. These are bonded in different sized cavities within a 3-D Mg framework to the clathrate-II host structure. Some of these features appear to be related to structure tuning to quasicrystal phases.

Supporting Information Available: Structural data as cif files. Tables of crystallographic details, anisotropic displacement ellipsoid parameters, drawings of the Ga3−Ga3 and Mg environments, a [111] view of the Mg network, and MO calculational results for the isolated clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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