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Article

A Study of the Phase $Mg_2Cu_6Ga_5$, Isotypic with Mg_2Zn_{11}. A Route to an Icosahedral Quasicrystal Approximant

Qisheng Lin and John D. Corbett*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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The new title compound was synthesized by high-temperature means and its X-ray structure refined in the cubic space group $Pm\bar{3}$, $Z = 3$, $a = 8.278(1)$ Å. The structure exhibits a 3-D framework made from a Ga_{14} and Mg network within which large and small cavities are occupied by centered $GaCu_{12}$ icosahedral and Cu_6 octahedral clusters, respectively. The clusters are well bonded within the network. Electronic structure calculations show that a pseudogap exists just above the Fermi energy, and nearly all pairwise covalent interactions remain bonding over a range of energy above that point. Analysis suggests that the compound is hypoelectronic with a four-electron deficiency per unit cell, and such a derivative with Sc substituting for Mg is an appropriate quasicrystal approximant ($Im\bar{3}$). Such characteristics seem to be key factors in the formation of icosahedral quasicrystals.

Introduction

Quasicrystal phases are a novel class of intermetallic compounds that exhibit rotational symmetries in their diffraction patterns that are incommensurate with translational periodicity.[1−3] Recently, intensive studies focusing on their discovery, structures, and properties have been carried out in a variety of binary, ternary, and quaternary systems.[4−9] However, to date there is still no general set of rules that can be used to predict which alloys and which compositions are susceptible to the formation of quasicrystalline phases. Examples that are extensively used to generalize experience in the search for new icosahedral quasicrystals encompass the known quasicrystals plus their presumed approximants. The latter are translationally normal crystalline compounds with large unit cells that contain condensed, high symmetry building blocks, such as icosahedra and dodecahedra, and that have compositions that lie close to those of quasicrystals. They commonly serve to model quasicrystal structures.[2,3] Quasicrystals are also generally recognized as electron phases, as described by Hume−Rothery stabilization rules,[10] and they thus exhibit restricted ranges of valence electron counts per atoms (*e/a*) and probable band gaps or pseudogaps at or near the Fermi energy.[11,12] Comparable sizes for component atoms also play an important role in forming tight 3-D networks that contain all atom types.[5,13]

Numerous studies of alkali-metal compounds of the triels Ga, In, and Tl have shown that these intermetallic compounds provide a rich collection of examples of isolated, centered, interbridged, and fused icosahedra.[14−17] These properly periodic compounds exhibit relatively flexible structures in order that the alkali-metal countercations can 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, Zn, Cd, etc., that also lie among the so-called “icosogen”[18] elements.

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* To whom correspondence should be addressed. E-mail: jcorbett@iastate.edu.

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One thing that aroused our interest in these systems was the evolution of structure and bonding from $Na_{15}K_6Tl_{18}M$ (M = Mg, Zn, Cd, Hg)[17] through $Na_2Au_6In_5$ [19] to $Mg_2Cu_6Al_5$ [20] and then to Mg_2Zn_{11}.[21] Nothing has been reported on the last two compounds since the original 1949 reports by Samson. All of these compounds have primitive cubic symmetry and are closely related to the Mg_2Zn_{11}-type structure, which consists of three different substructures: polyhedra of centered icosahedral Zn_{13} and octahedral Zn_6 plus a Zn_{14} network link with nominal Mg^{2+} cations. Naturally, the nature of the interactions among the linked networks of spacers and polyhedra in the above series undergoes dramatic evolution from $Na_{15}K_6Tl_{18}M$ to Mg_2Zn_{11} as the bonding character changes from predominantly ionic through heteronuclear covalent to mainly homonuclear covalent, a direction that also seems to be clearly associated with the formation of quasicrystalline phases. In this paper, we describe the structure and bonding of $Mg_2Cu_6Ga_5$, the first gallium compound in the Mg_2Zn_{11} family, and consider how to possibly tune the structure to that of a quasicrystalline phase. This pursuit is, in fact, encouraged by the discovery of the quasicrystalline Mg (Li)−Cu−Al[22] and $Mg_{32}(Cu,Zn,Al)_{49}$ [23] phases, which are described in terms of Bergman clusters[24] and more or less give connection to the Mg_2Zn_{11}-type structure.[25]

Experiment Section

Synthesis. Experience shows that gallium compounds generally cannot be obtained directly when a synthesis is carried out with the nominal composition sought; rather a shift of stoichiometries obtained in the process toward compounds poorer in gallium is generally observed.[15] This may have to do with gallium's particularly low melting point, and the physical segregation that results therefrom. Therefore, we have always used a self-flux method to grow crystals, and an internal sieve to separate crystals from the melts, as has been described elsewhere.[26]

Pure elements as Mg turnings (99.9%, Alfa), Cu powder (99.9%, Alfa), and Ga chunks (99.9%, Alfa) were used as received. An exploratory composition near 1:2:2 atom proportions was weighed in a glovebox under a nitrogen atmosphere and weld-sealed under an argon atmosphere into a tantalum container with a perforated disk sealed in the middle. This container was in turn held within an evacuated SiO_2 jacket to avoid air oxidation. The mixture was heated to 800 °C for 2 h to homogenize it, then cooled to 570 °C in 6 min, followed by slow cooling to 400 °C at a rate of 2 °C/h for crystal growth. The assembly was then inverted and rapidly centrifuged to filter the product from excess melt.

Table 1. Lattice Parameters of $Mg_2Cu_6Ga_5$

loaded composition			
at. %	($Mg_xCu_6Ga_y$)	a (Å)[a]	V (Å^3)
18/36/46	(3/6/7.7)	8.2751(4)	566.66(5)
10/40/50	(1.5/6/7.5)	8.2764(9)	566.9(1)
16.7/36.7/46.6	(2.7/6/7.6)	8.2761(6)	566.86(7)
15/40/45	(2.2/6/6.7)	8.2751(8)	566.66(9)
16/29/55	(3.2/6/11.3)	8.2754(5)	566.72(6)
12/32/55	(2.3/6/10.2)	8.2754(9)	567.7(1)

[a] From Guinier film data with Si as internal standard, $\lambda = 1.540598$ Å; 23 °C.

Table 2. Some Crystal Data and Structure Refinement for $Mg_2Cu_6Ga_5$

fw	778.46
cryst syst, space group, Z	cubic, $Pm\bar{3}$ (No. 200), 3
unit cell dimension, Å	8.278(1)
V, Å^3	567.3(1)
d (calcd), Mg/m^3	6.836
abs coeff (Mo Kα), cm^{-1}	340.6
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0477, wR2 = 0.1282
[all data]	R1 = 0.0480, wR2 = 0.1288

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

As-grown crystals were examined under a microscope inside a glovebox filled with purified nitrogen. They had a metallic luster and regular morphology and growth terraces, and the largest was about 0.3 × 0.3 × 0.3 cm^3. Crushed pieces were ground together with Si (NIST) as internal standard for Guinier powder diffraction examination. Products were found to contain two phases, ~70% $Mg_5Cu_6Ga_4$ [27] and ~30% of the title phase. Further experiments showed that higher yields of the title phase (~90−95%) were obtained using the same techniques if the atomic proportions of Mg/Cu/Ga were kept in the range ~(10−16)/(29−40)/(50−55). The highest yield came from the loaded composition $Mg_{3.3}Cu_6Ga_{11.3}$ (~$Mg_{16}Cu_{29}Ga_{55}$), at which point >95% was obtained. Table 1, which lists the cell parameters of $Mg_2Cu_6Ga_5$ crystals obtained from different reactions, shows how the cubic cell parameters of the filtered crystals remain substantially the same as the loaded compositions are changed (always with excess Ga). Even though the atomic radii of Cu and Ga are close (12 bonded radii: Cu, 1.276 Å; Ga, 1.404 Å[28]), this suggests that $Mg_2Cu_6Ga_5$ has a fixed composition with well differentiated lattice sites and no solid solutions. This is also supported by single crystal structure determinations.

Structure Determination. Single crystals from a reaction with a loaded composition of $Mg_{10}Cu_{40}Ga_{50}$ were selected and inserted in thin-walled glass capillaries for singularity checks with the aid of a Weissenberg camera. The best quality one, with dimensions of 0.20 × 0.18 × 0.20 mm^3, was selected for the structure determination. The crystallographic data were collected at 295 K with the aid of a Siemens APEX Platform CCD diffractometer and graphite-monochromatized Mo Kα radiation. The data were collected over a full sphere of reciprocal space to 56.36° in 2θ. The individual frames were measured with an ω rotation of 0.3° and an acquisition time of 10 s. The SMART software was used for the data acquisition and SAINT for the data extraction and reduction. The absorption correction was performed using SADABS. Some data collection and refinement parameters are given in Table 2. Another data set from a crystal from a 1:2:2 exploratory reaction was first collected with the aid of Rigaku AFC6R

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Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Mg_2Cu_6Ga_5$

atom	Wyckoff	symmetry	x	y	z	$U_{eq}{}^a$
Ga1	1*a*	*m*$\bar{3}$.	0	0	0	18(1)
Ga2	6*g*	*mm*2..	0.3364(2)	$^1/_2$	0	21(1)
Ga3	8*i*	.3.	0.2824(1)	x	x	22(1)
Cu1	6*h*	*mm*2..	0.2750(2)	$^1/_2$	$^1/_2$	20(1)
Cu2	12*j*	*m*..	0	0.1637(1)	0.2573(1)	19(1)
Mg	6*f*	*mm*2..	0.1812(6)	0	$^1/_2$	25(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

diffractometer, and the structure was also determined and refined. The resulting cell and atom parameters were within 3σ of those reported.

Structure solutions and refinements were performed with the SHELXTL package of crystallographic programs.[29] The lack of systematic absence conditions in the data set indicated a primitive lattice, and the indicated Laue group was *m*3, giving two possible space groups, *P*23 and *Pm*$\bar{3}$. However, the E-Stats model in the WinGX program[30] strongly indicated a centrosymmetric structure. Therefore, *Pm*$\bar{3}$ was chosen for the direct-methods structure determination. The first five heavy atom positions in the model were initially assigned to Ga atoms and a light one to Mg on the basis of both bond distances and peak heights. Refinements with isotropic thermal parameters proceeded smoothly except that the Ga atoms assigned to 6*h* and 12*j* sites exhibited ∼20% larger thermal parameters compared with those for the other three Ga atoms. This suggested that the former positions might be occupied by lighter Cu atoms, partially occupied by Ga atoms, or contain mixed Ga and Cu atoms. However, all attempts to establish that Ga and Cu atoms were mixing in the structure led to abnormal occupancies or thermal parameters. Thus, refinements with partial occupancies of supposed Ga atoms at 6*h* and 12*j* sites afforded values of 91(2)% and 92(1)%, respectively, and typical U_{eq} values, the former corresponding closely to the ratio of atomic numbers of Cu and Ga ($29/31 = 0.935$). Similarly, refinement of only Cu on the 1*a* position (the center of an icosahedron) gave an occupancy of 117%. Furthermore, semiquantitative EDX analyses yielded atomic proportions of Mg/Cu/Ga of about 2.0:5.9(1):4.8(8). Therefore, the possibilities for significantly mixed or partial occupancies of any positions were excluded in subsequent refinements. Only Cu was assigned to the 6*h* and 12*j* positions and Ga to 1*a*, which gives the empirical formula $Mg_2Cu_6Ga_5$ and a well segregated structure. The final converged refinement, with 24 variables and 280 independent reflections with $F_o{}^2 > 2\sigma(F_o{}^2)$, gave agreement factors of R1 = 0.048 and wR2 = 0.128. Residual electronic densities after convergence ranged between 1.48 e/$Å^3$ (0.95 Å from Ga1) and −2.23 e/$Å^3$ (0.05 Å from Cu1). Additional data are available in Tables 3 and 4.

EHTB Calculations. Extended Hückel band calculations were carried out using the CAESAR program.[31] The following orbital energies and exponents were employed for all of the calculations (H_{ii} = orbital energy (eV), ζ = Slater exponent): Mg 3s, $H_{ii} = -9.00$, $\zeta = 1.1$; 3p, $H_{ii} = -4.50$, $\zeta = 1.1$; Cu 3d, $H_{ii} = -14.0$ eV, $\zeta_{11} = 5.95$, C1 = 0.5933, $\zeta_{22} = 2.30$, C2 = 0.5744; 4s, $H_{ii} = -11.40$, $\zeta = 2.2$; 4p, $H_{ii} = -6.06$, $\zeta = 2.2$; Ga 4s, $H_{ii} = -14.58$, $\zeta = 1.77$; 4p, $H_{ii} = -6.75$, $\zeta = 1.55$.[31]

Table 4. Bond Lengths (Å) in $Mg_2Cu_6Ga_5$

atoms	distances		atoms	distance (Å)	
Ga1−Cu2	2.525(1)	×12	Cu2−Ga1	2.525(1)	
Ga2−Cu2	2.466(1)	×2	Cu2−Ga2	2.466(1)	
Ga2−Cu1	2.649(2)	×2	Cu2−Ga3	2.545(1)	×2
Ga2−Ga2	2.709(3)		Cu2−Cu2	2.641(1)	×4
Ga2−Ga3	2.9848(4)	×4	Cu2−Cu2	2.710(2)	
Ga2−Mg	2.967(4)	×2	Cu2−Mg	2.850(3)	×2
Ga2−Mg	3.163(3)	×2	Cu2−Mg	2.854(2)	
Ga3−Cu2	2.545(1)	×3			
Ga3−Cu1	2.548(1)	×3	Mg−Ga2	2.967(4)	×2
Ga3−Ga2	2.9848(4)	×3	Mg−Ga2	3.163(3)	×2
Ga3−Mg	3.068(1)	×3	Mg−Ga3	3.068(1)	×4
Cu1−Ga2	2.649(2)	×2	Mg−Cu2	2.850(3)	×4
Cu1−Ga3	2.548(1)	×4	Mg−Cu2	2.854(2)	×2
Cu1−Cu1	2.634(2)	×4	Mg−Mg	3.000(1)	

Results and Discussions

Crystal Structure. The title compound can be usefully formulated as $Mg_6(Cu_6)(GaCu_{12})(Ga_{14})$ to make evident the three substructures beyond the six Mg atoms: a Ga_{14}-based network, one Cu_6 octahedron, and one Ga-centered Cu_{12} icosahedron. The symmetries of the three polyhedra are all *m*$\bar{3}$ in which the 3-fold axes lie on the cell diagonals (*Pm*$\bar{3}$). All nearest neighbor atoms in the environments around the Cu_6 octahedron and the $GaCu_{12}$ icosahedron are illustrated in Figure 1a,b, respectively. The Ga_{14} sheath about the octahedron, Figure 1a, consists of two distinct atoms distributed as $(Ga3)_8(Ga2)_{12/2}$ in a geometry that can be thought of as a distorted pentagonal dodecahedron. The eight Ga3 in a cube therein are somewhat collapsed onto the faces of the encapsulated Cu6 octahedron, thus defining a small hole with a diameter about 6.24 Å. Every Ga_{14} unit is connected to six others via shared Ga2−Ga2 extremities to generate a network, and this defines channels parallel to the three axial directions in which the clusters are bound, Figure 1c. Four similarly spaced atom pairs help define these channels, i.e, Ga2−Ga3 (2.9848(4) Å), Mg−Ga3 (3.068(1) Å), Mg−Ga2 (3.163(3) Å), and Mg−Mg (3.000(1) Å). These make the structure somewhat homogeneous and give some uniformity in bonding, evidently an important basis for tuning structures related to approximants and quasicrystals. A second cube of Ga3 atoms in the channels, Figure 1c, plus four Mg atom pairs define a larger hole in the lattice in which the $GaCu_{12}$ icosahedron is bound, Figure 1b. The Ga3 atoms thus cap faces on both Cu clusters whereas Ga2 atoms bond between these.

In terms of specific functions in and about the copper clusters, the surface Cu2−Cu2 separations on the icosahedron are 2.641(1) and 2.710(2) Å, whereas *d*(Cu1 − Cu1) in the octahedron is 2.634(2) Å. (These values are substantially the same as those inferred from the 1949 report on $Mg_2Cu_6Al_5$, 2.65 and 2.73 Å in the icosahedron and 2.64 Å in the octahedron.[20]) The Cu_{12} cluster is also centered by Ga1, *d*(Ga1 − Cu2) = 3.525(1) Å. All 20 triangular faces of the Cu_{12} icosahedron are capped by either Mg or Ga3 atoms at distances of 2.850(3) or 2.545(1) Å from Cu2, respectively. These atoms generate a larger Ga_8Mg_{12} pentagonal dodecahedron. In addition, each Cu2 vertex on the former polyhedra is exo-bonded to a Ga2 atom at 2.466(1) Å. (These Ga2 atoms thus also function as caps on the pentagonal faces of

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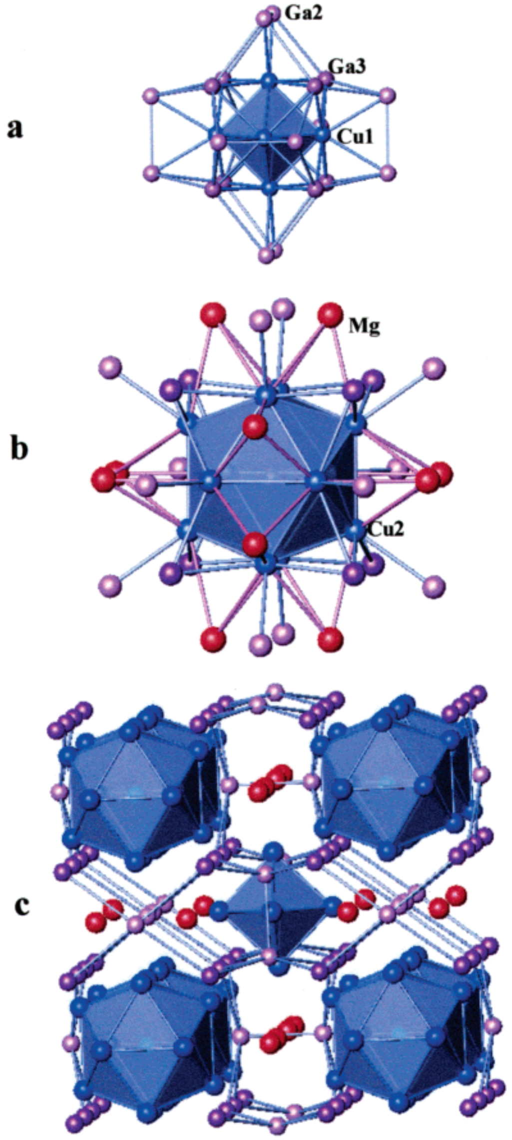

Figure 1. (a) The Cu1 octahedron encapsulated by a Ga_{14} linking unit, (b) the Ga1-centered Cu2 icosahedron and bonded neighbors, and (c) the unit cell with separate Ga_{14} and Mg network and the copper clusters, without any interbonding. The larger nonbonded polyhedron defined by capping atoms in a and b and the Mg−Ga interconnections in b and c have been omitted for clarity, see text. The Cu, Ga3, Ga2, and Mg atoms are denoted by blue, purple, lavender, and red circles, respectively.

the above Ga_8Mg_{12} dodecahedron.) According to the angle Ga1−Cu2−Ga2, 177.04(6)°, the Ga2 atoms lie nearly on the radial lines (pseudo-5-fold axes) from the centering Ga1 atom through the 12 Cu2 atoms of the central icosahedron to the exo Ga2, thus geometrically defining an even larger $(Ga2)_{12}$ icosahedron on which the Ga vertices are naturally not directly bonded. The total constitutes a 45-atom three-shell cluster.

Regarding the $(Cu1)_6$ octahedron, every face is capped by a Ga3 atom at a Cu−Ga distance of 2.548(1) Å, and each vertex is also exo-bonded to two Ga2 atoms at 2.649(2) Å. These face-capping and exo-bonded atoms together generate the distorted pentagonal dodecahedron of the gallium network, every face of which is also approximately capped by a Mg atom. Interconnection of these well separated Mg atoms similarly defines an ideal icosahedron that is comparable to the large Ga_{12} icosahedron mentioned above. This group as a whole can similarly be identified as a 40-atom cluster. The Mg atoms in this structure are not members of a bonded polyhedron; rather, their clear functionality is to cap faces on two adjacent $(Cu2)_{12}$ clusters (Figure 2) as well as to bond to 4 Ga2 and 4 Ga3 atoms in the linked network, thus providing some more polar "glue" that holds the structure together. The last connections are not drawn in Figure 2 in order to give improved clarity, but the Mg environment is illustrated in the Supporting Information. We have recently noted a similar role of Sc in bonding together multiple endohedral cluster shells in $ScZn_6$ and related approximants.[32]

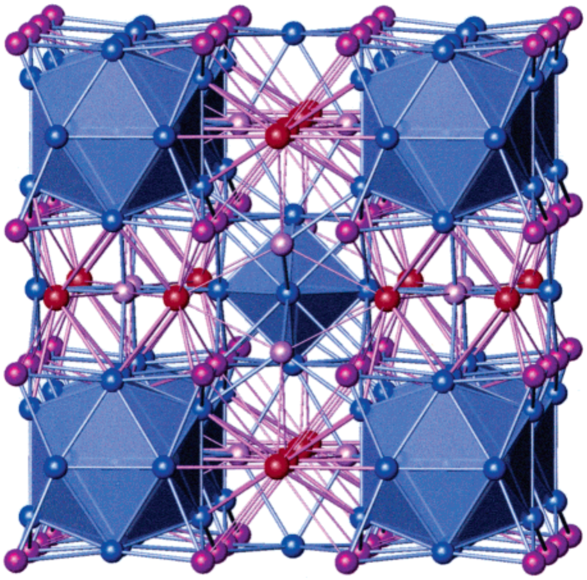

Figure 2. ~[010] view of the unit cell of $Mg_2Cu_6Ga_5$ showing the network formed through interconnections of Ga_{14} spacers, Mg, and the icosahedral and octahedral copper clusters. All pairwise neighboring interactions are marked. The atom coloring scheme is the same as in Figure 1.

Alternatively, the structure can be viewed as a simple cubic packing of the three-shell 45-atom clusters noted above together with the Cu_6 octahedra at the center. The outer shell of the 45-atom cluster, a geometric unit rather than a formal building block, is also a rhombic triacontahedron of 30 rhombi or a capped pentahedron dodecahedron of 60 triangles. This unit is also found in metallic compounds such as the Frank−Kasper phases[33] and, naturally, in the cubic Mg_2Zn_{11} phase of Samson.[21] The structure may, therefore, serve as a precursor or a useful guide to a quasicrystal phase. For example, if the vertices of the outer nonbonded Ga_{12} icosahedron in the 45-atom cluster are truncated, a shell of 60-atom "soccer ball" results. This 105-atom hierarchical shell (or 104 atoms when the center is empty) is frequently seen in crystalline approximants (of Bergman type quasicrystals) with space group $Im\bar{3}$, as in (Al, Zn)$_{49}$Mg$_{32}$,[34] R-Li_3CuAl_5,[35] and $Li_3Cu_6Ga_{21}$.[36]

Of particular interest, therefore, is the attainment of structures derived from or showing the higher symmetry of the $Im\bar{3}$ space group. To get such a bcc structure from the

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present primitive example, the most substantial change needed would be the replacement of the octahedron in the present structure by an icosahedron related by *I*-centering. Consider the clusters in Figure 1, in which the differences are mainly size and geometry; the central Cu_6 octahedron is too small with respect to the 20-atom pentagonal dodecahedron. In other words, the cavities formed by the Ga_{14} links plus the Mg cations that define the size and distribution of structural units are too unequal. What is needed is an icosahedron at the site of octahedron that might be expected to increase the symmetry to bcc $Im\bar{3}$.

This is not just whimsical. The space group changes with composition in the Al−(Mn,Fe)−Si system well exemplify the case. This system contains an icosahedral quasicrystalline phase with composition $Al_{74}Mn_{17.6}Fe_{2.4}Si_6$ [37] and an approximant phase $(Al,Si)_{82}Mn_xFe_{18-x}$.[38] The space group of the latter is a function of x; for $x \leq 0.29$, the alloys crystallize in the simple cubic lattice of $Pm\bar{3}$, whereas for $0.32 \leq x \leq 0.69$, the structure becomes $Im\bar{3}$. Obviously, this transformation from a primitive to a body-centered cubic system with composition well illustrates a structure tuning driven by electron count and composition. In another example, the reverse process, a body-centered to primitive cell transformation is achieved by introduction of elements with different valences. The phase $Na_4A_6Tl_{13}$ (A = K, Rb, Cs), the $Im\bar{3}$ analogue, is constructed of Tl-centered icosahedra, Tl_{13}.[39] For $Na_{14}K_6Tl_{18}M$ (M = Mg, Zn, Cd, Hg), this transforms into the $Pm\bar{3}$ relative containing the same units, centered Tl_{12} icosahedra plus Na-centered Tl_6 octahedra, on change of the Na/K proportions and the introduction of a divalent centering cation M.[17] The latter compound was noted at that time to be completely analogous to Mg_2Zn_{11} when the latter is enumerated as $Zn_{14}Mg_6(Zn_{13}Zn_6)$, but this contains clearly more suitable elements for bonding in a more covalent lattice. The alkali-metal cations play the same structurally critical bridging roles, but they bring about a greater charge separation, producing a less covalent extended lattice than is evidently necessary for quasicrystal or approximant phases. We suspected that the primitive $Mg_2Cu_6Ga_5$ lattice might also be tuned to a bcc lattice and eventually perhaps to a quasicrystal phase. To understand the electronic requirements for this tuning, we turned to the following band structure analysis.

Band Structures. The densities-of-states (DOS) and crystal orbital overlap population (COOP) data for the title compound according to the extended Hückel approach are shown in Figure 3. A total of 75 valence electrons per cell ($Z = 3$) fill the states to a Fermi energy of −7.82 eV. (Cu 3d is not included in this total as these states fall below −14 eV.) Not surprisingly, a metallic behavior for the compound is indicated. The s orbital contributions to DOS are very small for all atoms, indicating that s−p mixing is not large. Judging from the COOP curves, the DOS bands right below E_F contain some strong bonding, but more importantly, the unfilled energy region just above, between −8 and −6 eV, also contains a relatively large number of bonding states that fall in a sharply declining DOS, indicating that the present compound is located near a pseudogap. Further, the approximate bonding characters, which order Cu−Ga > Cu−Cu > Ga−Ga in this region (ignoring overlap differences), gradually change from bonding to antibonding with increasing energy, whereas the Mg−Cu > Mg−Ga interactions remain bonding over the whole energy region. In this sense, the compound appears to be electron deficient. Calculations on approximant crystals such as Al−Mg−Zn, Cu_5Zn_8, and Al−Cu−TM (TM = transition metal) have shown that a pseudogap appears to be one key factor in the formation of icosahedral quasicrystals.[12] Therefore, the present structure affords some interesting clues about the design of the corresponding crystalline approximants and even icosahedral quasicrystals.

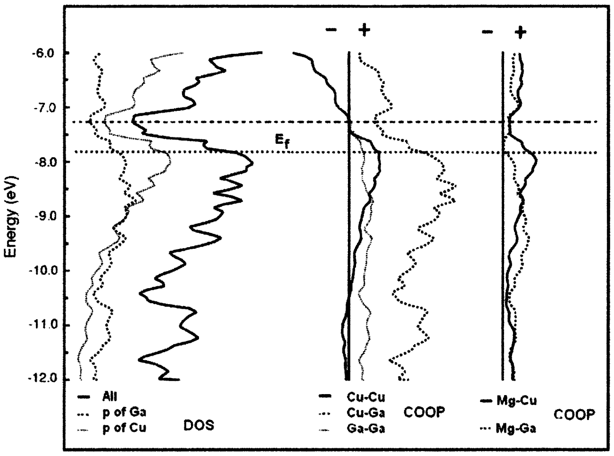

Figure 3. DOS and COOP data for $Mg_2Cu_6Ga_5$. Note the pseudogap $4e^-$/cell above E_F.

About four more electrons would appear to be necessary to fill all of the bonding levels in Figure 3; that is, the optimum number of valence electrons would be about 79 rather than 75 per cell, as marked. To optimize the bonding, one might adjust the ratios of Mg, Cu, and Ga, such as to $Mg_2Cu_{4.33}Ga_{6.67}$. However, this has led instead to a new cubic $Fd\bar{3}m$ phase $Mg_{35.2}Cu_{24}Ga_{52.6}$ containing icosahedra and icosioctahedra, evidently not the typical $Im\bar{3}$ approximant needed.[40] On the other hand, one might replace part of the Mg cations with other elements that are similar chemically and in size but with more valence electrons. For example, if two-thirds of the six Mg atoms per cell were to be replaced by Sc, the four additional electrons would push the Fermi energy to a level at which orbital interactions are changing from bonding to antibonding in character (neglecting the effects of different sizes and types of atoms). As a matter of fact, we have recently so obtained such a quaternary phase $Sc_{2.6}Mg_{0.4}Cu_{11}Ga_7$ ($\sim Sc_{1.4}Mg_{0.2}Cu_6Ga_{3.8}$ or $Sc_{12.4}Mg_{1.9}Cu_{52.4}Ga_{33.3}$), and its single crystal structure determination reveals

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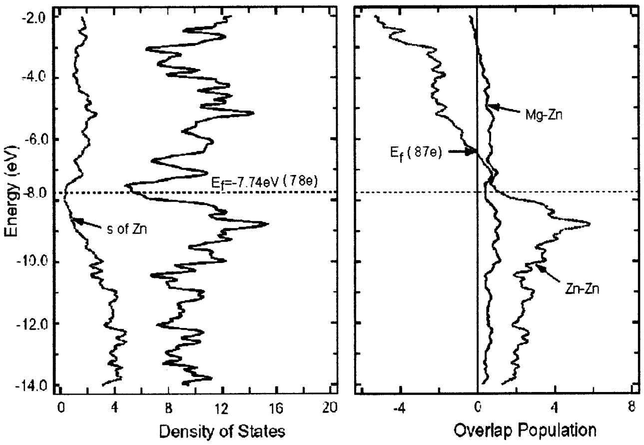

Figure 4. DOS and COOP results for Mg_2Zn_{11}.

that it indeed has the desired larger bcc lattice constructed of icosahedra in space group $Im\bar{3}$ (a = 14.94 Å). It appears that this would qualify as the 1/1 crystalline approximant of the recently discovered, nominal $Sc_{15}Mg_3Cu_{48}Ga_{34}$ icosahedral quasicrystal[8] in terms of the composition, structure, and the numeric relationship between the above cell parameter and the 6D quasilattice constant.[40] These results enable us to conclude that because of a pseudogap just above E_F and unfilled bonding levels, the primitive $Mg_2Cu_6Ga_5$ structure or, in a broader sense, the Mg_2Zn_{11} parent structure type may be tuned to bcc lattices and perhaps even serve as precursors to new icosahedral quasicrystals.

This conclusion is further supported by another recent discovery of the nominal $Sc_{15}Mg_5Zn_{80}$ icosahedral quasicrystal.[7] Our band structure calculations on Mg_2Zn_{11}, Figure 4, show DOS and COOP curves similar to those for the present $Mg_2Cu_6Ga_5$, Figure 3, but with relatively higher densities-of-states and strong bonding characters just below E_F (−7.74 eV). Although the pseudogap is already achieved, the bonding character for Zn−Zn thereabove again gradually changes from bonding to null bonding between −7.7 and −3.0 eV, whereas Mg−Zn bonding remains unchanged over a larger range. To optimize the former bonds in the structure, three more electrons would be required per Zn_{11} unit or nine per cell (for a rigid band). The generation of such a suitable approximant has not been tried experimentally, but the change is in the right direction toward the new icosahedral quasicrystalline $Sc_{15}Mg_5Zn_{80}$.[7]

Conclusions. The newly discovered metallic compound $Mg_2Cu_6Ga_5$ ($\sim Mg_{23.1}Cu_{46.2}Ga_{38.5}$) is an ordered ternary derivative of the Mg_2Zn_{11}-type structure with a primitive cubic packing of copper icosahedra and octahedra in a Zn−Mg network. Extended Hückel electronic band structure calculations reveal that the bonding is not optimized and a pseudogap falls just above the Fermi energy. This type of structure provides important atomic and electronic structure information for tuning to higher symmetry bcc lattices and perhaps to icosahedral quasicrystals. Recent experimental results show that substitution of Sc for Mg in the system justifies what is expected from the band structure analysis.[40]

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Supporting Information Available: Tables of crystallographic details, anisotropic displacement ellipsoids, and a figure of the Mg environment. This material is available free of charge via the Internet at http://pubs.acs.org.

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