Electron Tuning of Mg2Cu6Ga5. A Route to Crystalline Approximant and Quasicrystalline Phases

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Quasicrystals (QCs) exhibit high long-range order but lack translational periodicity, not even the underlying lattice of an incommensurate structure. After their debut in 1984, QCs aroused extensive interest among scientists from divergent fields. Prospective applications of these novelties as hydrogen storage, catalytic, thermoelectric, and biomaterials, and as surface coatings have been widely studied over the past two decades. However, there are still no definite guidelines for the discovery of new QC systems. Fortunately, most QCs have normal crystalline mates—approximants (ACs)—with structures and compositions that are presumed to be close to those of corresponding QCs. Three types have been classified in terms of the cluster-based building blocks in the assumed ACs, the Mackay- and the Bergman-types plus the newer symmetry-breaking (Tsai) type. They are generally recognized as electron phases that may be described by Hume-Rothery rules with sharply restricted ranges of valence electron concentrations (VEC) per atom (e/a), approximately 1.75 for the Mackay-type, about 2.1–2.2 for the Bergman-type, and close to 2.0 for the Tsai-type. Likewise, they appear to have pseudogaps in the densities-of-states (DOS) near the Fermi energy ($E_F$), consistent with their generally poor electronic conductivities. With these aspects in mind, we have discovered both QC and AC phases in the Sc$_3$Cu$_{48}$Ga$_{34}$ system. The discovery has been enabled by the nominal cubic parent structure, Sc$_3$Zn$_6$, which has a similar composition to the binary ScZn$_6$. Meanwhile, related QCs of Sc$_{15}$M$_{10}$Zn$_{75}$ (M = Ag, Au, Pd, Pt)$_4$ and Sc$_{12}$Mg$_{32}$-Cu$_6$Ga$_{43}$ have also been found in the same system. This naturally raises questions as to how to judge whether a new or known structure is a good candidate for QC tuning or not. To this purpose, we have been investigating new systems starting from somewhat more distant structures, utilizing the concept that pseudogaps in the DOS are general features of QC and, evidently, ACs as well, and this paper describes a major advance in this effort.

We noted that the $e/a$ values that favor icosahedral QCs partially overlap those for intermetallics containing a main group metal, a late transition metal, and a heavy triel element (Ga, In, Tl). Our interest was particularly aroused by the structure and bonding evolution of Mg$_2$Zn$_{11}$-type compounds from K$_2$Na$_{13}$Ti$_3$M (M = Mg, Zn, Cd, Hg) through Na$_2$Au$_3$In$_5$ and Mg$_2$Cu$_6$Al$_5$ to Mg$_2$Zn$_{11}$. The bonding character within these undergoes a dramatic evolution from predominantly ionic in K$_2$Na$_{13}$Ti$_3$M through heteronuclear covalent to mainly homonuclear covalent in Mg$_2$Zn$_{11}$, a direction that seems to be clearly necessary and consistent with the formation of quasicrystalline phases. Alternatively, these structures may be described as a primitive cubic packing of endohedral clusters, for example, as Al@Cu$_{13}$@Al$_4$M$_{12}$@Al$_{12}$ in Mg$_2$Cu$_6$Al$_5$, which geometrically also resembles an incomplete Bergman-type cluster. We have recently synthesized and structurally established Mg$_2$Cu$_6$Ga$_5$ as a new member of the Mg$_2$Zn$_{11}$ family.

Moreover, EHTB calculations on it show both a pseudogap in the densities-of-states (DOS) and empty bonding states according to the crystal-orbital-overlap-population (COOP) data just above $E_F$ ($e/a = 1.92$). Four more electrons per cell would accordingly fill all bonding states and shift the $E_F$ to the pseudogap ($e/a = 2.03$). The phase was therefore considered as a candidate for electronic tuning to a QC phase, assuming that a rigid band may still apply with a structure change.

Our first tuning that modified the Cu/Ga ratio as Mg$_2$Cu$_{6-x}$Ga$_{5+x}$, to add 4 e/cecell resulted in the synthesis of Mg$_2$Cu$_{5.5}$Ga$_{5.5}$. A new Laves-like phase that contains interpenetrating Bergman clusters. However, its fcc symmetry did not seem to afford a likely route to an icosahedral symmetry according to the group—subgroup theorem. In this paper, we report success of the alternative means: replacement of Mg in Mg$_2$Cu$_6$Ga$_5$ by Sc, which yields both the desired bcc AC and QC phases.

Exploratory reactions of Sc$_{29}$Mg$_{57-x}$Cu$_{6-x}$Ga$_{39}$ ($x = 3, 4, 5$) aimed at optimizing the bonding as above were reacted as before. Sc was selected because it has one more valence electron than and a similar metallic radius to Mg. The XRD pattern (Supporting Information) for the $x = 5$ sample showed 85–90% of a phase very similar to the bcc Sc(CuZn)$_6$. Quench treatments did not decrease the crystalline quality. Structure determination showed this phase is isostructural with Sc$_2$Zn$_6$. The refined composition Sc$_{15}$M$_{10}$Cu$_{48}$Ga$_{34}$ ($e/a = 1.99$), is close to the value (2.03) predicted from Mg$_2$Cu$_6$Ga$_5$. Meanwhile, a quenched sample of Sc$_{13}$Mg$_{57}$Cu$_{49}$Ga$_{33}$ ($e/a = 2.01$), in which the (Cu + Ga) proportion had been decreased ~5% contained a major amount of a QC phase, suggesting this was the right direction for fine-tuning. Accordingly, the compositions, now expressed in atomic percentages, were tuned with small increments in Cu:Ga as Sc$_{12}$Mg$_{57}$Cu$_{49}$Ga$_{33}$ ($e/a = 2.01$), then Mg$_2$Cu$_6$Ga$_5$. All samples were quenched after homogenization at 800 °C for 3 days.

The XRD patterns (Figure 1a) show high yields (>95%) of AC phase at about $z = 46.0$ and 48.5, whereas the intermediate $z = 48.0$ yields the QC as a line compound. All 30 peaks in this pattern can be indexed with six integers according to Elser’s method, indicating a substantially pure phase. The experimental quasilattice constant, $a_0 = 4.9073(6)$ Å, is in excellent agreement with the value $a_0 = 4.9052(3)$ Å predicted from the AC. The inset in Figure 1 shows the electron diffraction pattern of QC along the 5-fold axis. The QC composition by EDX is Sc$_{15}$Mg$_{57}$Cu$_{49}$Ga$_{33}$ ($e/a = 2.00$), a little Mg-poorer than that reported by Kaneko et al. Note that Mg is essential for QC formation, as only the AC phase forms in its absence (Supporting Information).

The structure of the AC, as before, exhibits the bcc packing of multiply endohedral clusters, a disordered tetrahedron, a pentagonal dodecahedron, an icosahedron, an icosidodecahedron, and a Pauling triacontahedron from the center out (Figure 1b). The main structural difference between the AC structures of the $x = 5$ and $y = 46.0$.
In summary, replacement of Mg in Mg$_2$Cu$_6$Ga$_5$ with the electron-richer Sc gives strong p–d orbital mixing that enhances the depth of the pseudogap and results in the formation of the icosahedral QC. The achievements of electronic tuning to afford both AC and QC phases via pseudogap and empty bonding state predictions represent a promising route to new QCs, especially when ACs are not already known. The surprising fact that the method works across phase changes may result because of the similarities of the clusters and the structures. This route closely correlates the pseudogap and bonding with the Hume–Rothery concepts. Before these developments, the search for QC systems has relied more on Hume–Rothery ideas, experience, and luck. Parallel tuning starting with Na$_2$Au$_6$In$_5$ and the parent Mg$_2$Zn$_{11}$ phases works well too.\(^{21}\)

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Supporting Information Available: Details of synthesis, phase identification and EDX analysis results, the observed Fourier map for ACs in the Ca$_2$Mg$_6$Cu$_6$Ga$_5$ system.\(^{20}\) From the COHP curves (Supporting Information), Ga bonding states are optimized at $E_F$, consistent with the predictions based on Mg$_2$Cu$_6$Ga$_5$. Besides providing valence electrons, an important feature of Sc is, as expected, its low-lying d orbitals around $E_F$. Fatband analyses (Supporting Information) clearly show that the formation of the pseudogap arises from orbital mixing of Cu and Ga p with Sc d plus some small contributions from Cu d orbitals. The p–d orbital mixing at $E_F$ may also increase the magnitude of the pseudogap compared with that for Mg$_2$Cu$_6$Ga$_5$. The same mechanism is believed to account for the formation of other Sc–M–Zn i-QCs mentioned above.\(^{7,9}\)

References


(8) This corrects the erroneous Sc$_2$Zn$_{17}$ see ref 7a.


(17) Single-crystal data were collected on a Bruker APEX Platform SMART CCD diffractometer, from which the space group is $I_{4}2d$ and the high dimensional indices, respectively. (b) Multiply endohedral clusters for the AC.

Figure 1. (a) XRD for Sc$_{2}$Mg$_{6}$Cu$_{6}$Ga$_{5}$, quenched samples; $y = 46.0$ and 48.5 samples are identified as AC, $y = 48.0$ as the QC, and $y = 47.0$ as a mixture of QC and Sc$_{2}$Cu$_{5}$Ga$_{2}$. The inset and the six integers show the ED pattern of QC along 5-fold axis and the high dimensional indices, respectively. (b) Multiply endohedral clusters for the AC.

Figure 2. The densities-of-states (DOS) of the approximant.

In summary, replacement of Mg in Mg$_2$Cu$_6$Ga$_5$ with the electron-richer Sc gives strong p–d orbital mixing that enhances the depth of the pseudogap and results in the formation of the icosahedral QC. The achievements of electronic tuning to afford both AC and QC phases via pseudogap and empty bonding state predictions represent a promising route to new QCs, especially when ACs are not already known. The surprising fact that the method works across phase changes may result because of the similarities of the clusters and the structures. This route closely correlates the pseudogap and bonding with the Hume–Rothery concepts. Before these developments, the search for QC systems has relied more on Hume–Rothery ideas, experience, and luck. Parallel tuning starting with Na$_2$Au$_6$In$_5$ and the parent Mg$_2$Zn$_{11}$ phases works well too.\(^{21}\)