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Electronic Tuning of $Mg_2Cu_6Ga_5$. 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.[1] After their debut in 1984,[2] 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.[3] 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[1] plus the newer symmetry-breaking (Tsai) type.[4] 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*),[5] approximately 1.75 for the Mackay-type, about 2.1−2.2 for the Bergman-type,[5] and close to 2.0 for the Tsai-type.[4] Likewise, they appear to have pseudogaps in the densities-of-states (DOS) near the Fermi energy (E_F),[6] consistent with their generally poor electronic conductivities. With these aspects in mind, we have discovered both QC and AC phases in the $Sc_3Cu_xZn_{18-x}$ system.[7] The discovery has been enabled by the nominal cubic parent structure, $ScZn_6$,[8] which has a similar composition to the binary $Ca_{15}Cd_{85}$ QC and is isostructural with its AC $CaCd_6$.[4] Meanwhile, related QCs of $Sc_{15}M_{10}Zn_{75}$ (M = Ag, Au, Pd, Pt)[9] and $Sc_{15}Mg_3Cu_{48}Ga_{34}$[10] 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).[11] Our interest was particularly aroused by the structure and bonding evolution of Mg_2Zn_{11}-type compounds from $K_6Na_{15}Tl_{18}M$ (M = Mg, Zn, Cd, Hg) through $Na_2Au_6In_5$ and $Mg_2Cu_6Al_5$ to Mg_2Zn_{11}.[12] The bonding character within these undergoes a dramatic evolution from predominantly ionic in $K_6Na_{15}Tl_{18}M$ through heteronuclear covalent to mainly homonuclear covalent in Mg_2Zn_{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 $Al@Cu_{12}@Al_8Mg_{12}@Al_{12}$ in $Mg_2Cu_6Al_5$, which geometrically also resembles an incomplete Bergman-type cluster. We have recently synthesized and structurally established $Mg_2Cu_6Ga_5$ as a new member of the Mg_2Zn_{11} family.[13] 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 $Mg_2Cu_{6-x}Ga_{5+x}$ to add 4 e^-/cell resulted in the synthesis of $Mg_{35}Cu_{24}Ga_{53}$,[14] a novel Laves-like phase that contains interpenetrating Bergman clusters. However, its fcc symmetry did not seem to afford a likely route to icosahedral symmetry according to the group−subgroup theorem.[15] In this paper, we report success of the alternative means: replacement some of Mg in $Mg_2Cu_6Ga_5$ by Sc, which yields both the desired bcc AC and QC phases.

Exploratory reactions of $Sc_{x/3}Mg_{2-x/3}Cu_6Ga_5$ (x = 3, 4, 5) aimed at optimizing the bonding as above were reacted as before.[14] Sc was selected because it has one more valence electron than and a similar metallic radius[16] to Mg. The XRD pattern (Supporting Information) for the x = 5 sample showed 85−90% of a phase very similar to the bcc $Sc(CuZn)_6$.[7] Quench treatments did not decrease the crystalline quality. Structure determination[17] showed that this phase is isostructural with $ScZn_6$,[7] $Im\bar{3}$, a = 13.5005(4) Å. The refined composition $Sc_3Mg_{0.17(4)}Cu_{10.5}Ga_{7.25(4)}$, corresponding to a *e*/*a* = 1.99, is close to the value (2.03) predicted from $Mg_2Cu_6Ga_5$. Meanwhile, a quenched sample of $Sc_{15}Mg_5Cu_{47}Ga_{33}$ (*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 $Sc_{15}Mg_3Cu_yGa_{82-y}$ (y = 46.0, 47.0, 48.0, 48.5, with *e*/*a* = 2.05, 2.03, 2.01, and 2.00, respectively). 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,[18] indicating a substantially pure phase. The experimental quasilattice constant, a_6 = 4.9073(6) Å, is in excellent agreement with the value 4.9052(3) Å predicted from the AC.[19] The inset in Figure 1 shows the electron diffraction pattern of QC along the 5-fold axis. The QC composition by EDX is $Sc_{15.9(2)}Mg_{1.3(2)}Cu_{49.4(4)}Ga_{33.4(3)}$ (*e*/*a* = 2.00), a little Mg-poorer than that reported by Kaneko et al.[10] 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,[7] 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

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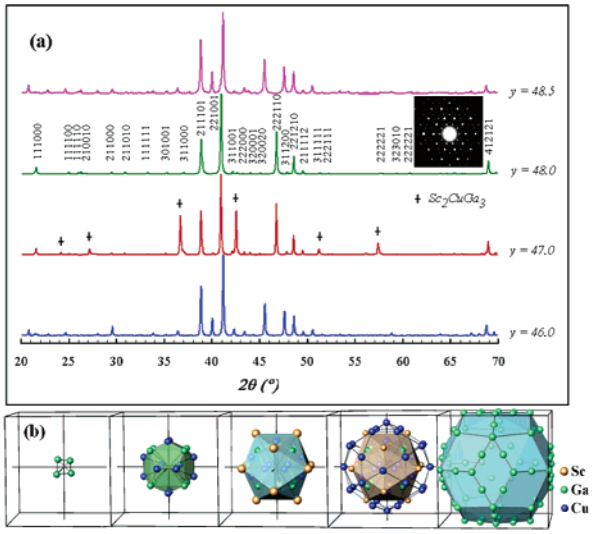

Figure 1. (a) XRD for $Sc_{15}Mg_3Cu_yGa_{82-y}$ quenched samples; $y = 46.0$ and 48.5 samples are identified as AC, $y = 48.0$ as the QC, and $y = 47.0$ as a mixture of QC and Sc_2CuGa_3. The inset and the six integers show the ED pattern of QC along 5-fold axis and the high dimensional indices, respectively. (b) Multiply endohedral clusters for the AC.

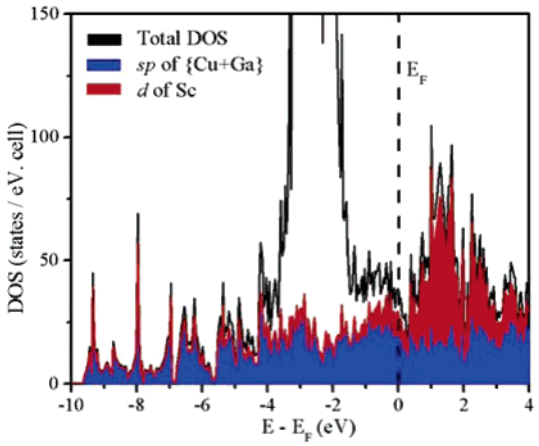

Figure 2. The densities-of-states (DOS) of the approximant.

samples is that the occupancy of an extra 8c position in the latter is about 16(2)% (Supporting Information). This is not changed even by annealing for 20 days at 400 °C.

LMTO-ASA calculations for the AC show widely spread s−p orbitals of Cu and Ga and d orbitals of Sc over the valence/conduction bands (Figure 2). A prominent feature of the DOS curves is that E_F ($e/a = 2.00$) lies on the shoulder of the pseudogap but not the minimum ($e/a \sim 2.08$). A similar feature has been found experimentally by photoemission spectroscopy on the isostructural ACs in the Ca−Cd system.[20] From the COHP curves (Supporting Information), Ga−Ga bonding states are optimized at E_F, consistent with the predictions based on $Mg_2Cu_6Ga_5$. 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 $Mg_2Cu_6Ga_5$. The same mechanism is believed to account for the formation of other Sc−M−Zn *i*-QCs mentioned above.[7,9]

In summary, replacement of Mg in $Mg_2Cu_6Ga_5$ 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 $Na_2Au_6In_5$ and the parent Mg_2Zn_{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 the disordered $(Ga4)_4$, and the CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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