Cluster covering structure in a 3/2-2/1-2/1 rational approximant to Bergman type icosahedral quasicrystals

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Icosahedral quasicrystals (iQCs) with Bergman type clusters have attracted much attention in recent years due to superconductivity has been discovered for Al-Zn-Mg iQC [1]. Their atomic structure is however still far from complete understanding. To elucidate atomic structure of iQCs, it is useful to investigate rational approximant crystals (RACs) whose local structure is similar to that of the corresponding QC. For this purpose, it is desirable to study higher-order RACs, but their existence is scarce compared to lower-order 1/1 and 2/1 cubic RACs. Here each fraction consists of adjacent Fibonacci numbers and approximates the golden ratio $\tau = (1+\sqrt{5})/2 = 1.618\cdots$.

It is known that a 3/2-2/1-2/1 orthorhombic RAC forms in Mg-Ga-Al-Zn system by a powder X-ray diffraction study [2]. We have synthesized a high-quality 3/2-2/1-2/1 RAC and determined its atomic structure (Fig.1) by means of single crystal X-ray diffraction. The structure was successfully refined to $Mg_{35.1}Ga_{17.5}Al_{3.7}Zn_{40.0}$, $Cmc2_1$, a = 36.9590(1) Å, b = 22.8517(1) Å, c = 22.9821(1) Å, N_{ind} = 27692 (26234 $F_o>4\sigma(F_o)$); N_{var}= 1301, R_1/wR_2 = 0.024/0.059). The structure has less positional disorder than the 3/2-2/1-2/1 RAC in Mg-Ga-Zn system [3] and is characterized by three types of rhombic triacontahedron (RTH) clusters. The network of the clusters consists of not only usual b- and c-linkages [4], but also b'-linkage ($b' = b/\tau$), where b- (b'-) linkage runs along a two-fold axis and c-linkage a three-fold axis, respectively. It is shown that the 3/2-2/1-2/1 RAC structure can be regarded as a covering structure of RTH clusters. The present result is consistent with a resent observation in Zn-Mg-Tm iQC [5] and suggests a possible covering model for Bergman-type iQCs.

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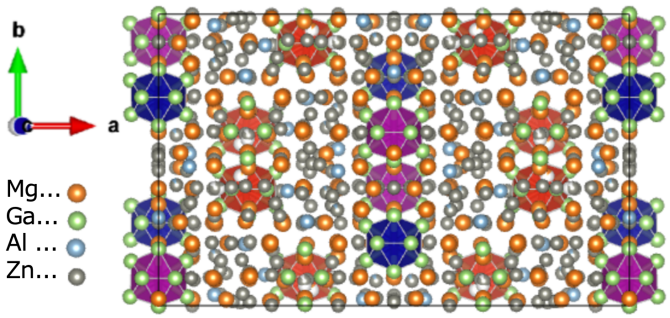

Fig.1: Atomic structure model of the 3/2-2/1-2/1 RAC. Only Ga icosahedra are shown.

A tale of two similar 1/1 Tsai-type quasicrystal approximants in RE-Au-Ge systems

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This study aims to explore the new quasicrystals and approximants in RE-Au-Ge systems (RE = Y, Ce, Gd, and Yb). Our systematic investigation reveals the atomic structures, formation conditions, compositions, and temperatures for Tsai-type phases in the RE-Au-Ge systems. The atomic structures of the phases have been determined from single-crystal X-ray diffraction data and described using concentric atomic clusters with icosahedral symmetry. We hypothesize the presence of pseudo-Tsai phases is a more common phenomenon that occurs in more approximants. The pseudo-Tsai phases are structurally similar yet physically different from the Tsai phases.

Tsai-type phases are distinguished by a cluster unit made up of four concentric polyhedral shells (Fig.1) [1]. The first shell is a dodecahedron composed of Au and Ge atoms, which is followed by an icosahedron that exclusively constitutes RE atoms. The third and fourth shells are an icosidodecahedron and a rhombic triacontahedron, respectively, again composed of Au and Ge atoms. The cluster is typically centered by an orientationally disordered $(Au, Ge)_4$ tetrahedral unit. However, there exists a variant in (Ca, Yb)–Au–Ge [2], RE-Au-Si [3] systems. Where the central tetrahedron of the Tsai clusters is replaced by a single RE atom. This 1/1 Tsai-type approximant variant has been termed pseudo-Tsai phases. Tsai and pseudo-Tsai cluster types can be found coexisting in the approximants. The structural differentiations between Tsai and pseudo-Tsai phases exhibit strong correlations between lattice parameters, cluster sizes, particular site occupancies, and valence electron counts.

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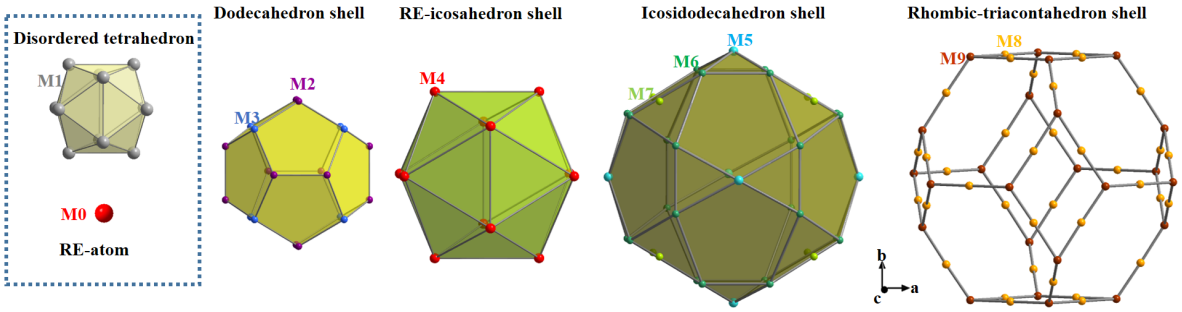

Fig.1: Concentric polyhedral shells of the Tsai-type cluster unit: From left to right, a disordered tetrahedron or (RE-atom), dodecahedron, RE-icosahedron, icosidodecahedron, and rhombictriacontahedron, respectively.

Investigation of chemical order in $Gd_{14}Au_xAl_{86-x}$ quasicrystal 1/1 approximant and its correlation to magnetic properties

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The effect of chemical composition on the magnetic behavior of $Gd_{14}Au_xAl_{86-x}$ ACs has been recently reported[1]. In particular, it was found that with increasing Au concentration, the magnetic transition changes from Spin Glass (SG) behavior to FM, then AFM (see Fig. 1a). The lattice parameter *a* across the total Au concentration shows an overall Vegard-like behavior. However, we notice that there are several line segments with different slopes separated by inflection points in both the trends of the lattice parameter and the paramagnetic Curie-Wiess temperatures (see Fig.1a). These inflection points reflect structural changes that take place as the amount of Au increases. In order to better understand the underlying reasons for the observed magnetic properties, it was deemed necessary to determine in detail the crystal structures of $Gd_{14}Au_xAl_{86-x}$ 1/1 AC samples for a broader range of x. In this work, we select several compositions from the different segments and synthesized the corresponding phase pure single crystals. By comparing them, we observe that some atomic sites show strong chemical preferences while others are resilient (Fig. 1b). The specifics of the chemical ordering phenomena and the effects of the structural changes on the magnetic ordering in $Gd_{14}Au_xAl_{86-x}$ 1/1 ACs will be discussed.

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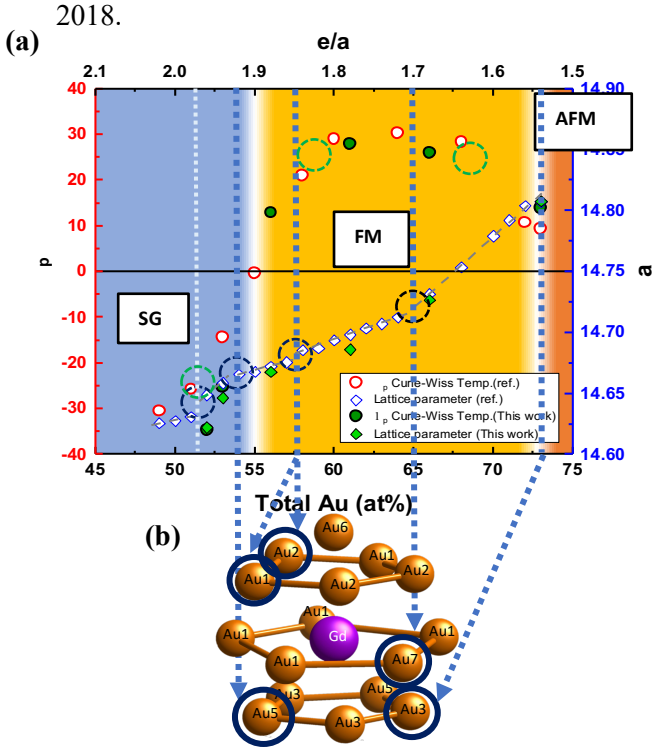

Fig.1: **(a)** Paramagnetic Curie-Weiss temperatures (circle icon) and lattice parameters (diamond icon) across as a function of Au concentration. The background colouring highlights the different magnetic regimes, from Spin Glass (SG) to Ferromagnetic (FM) and Antiferromagnetic (AFM), which was adopted from [2]. The green icons are the data from this work, while the white icons are the reference data from [1]. The blue dotted circles show the inflection points in the trend of the lattice parameter, and the green dot circles are the inflection points in the trend of Curie-Weiss temperature. Each inflection point is linked to occupancy saturation event in the different atomic positions. **(b)** An illustration of the Au and Al atoms surrounding a Gd atom.

The decagonal AlCuRh quasicrystal modelled with five atomic surfaces – high-temperature XRD data analysis

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Since the beginning of research on the structure of quasicrystals, the challenging question about the stability of these phases has not been answered with a clear answer [1]. The use of two competing mechanisms of structure stabilization (through entropy or energy minimization) in quasicrystals finds only partial theoretical and experimental verifications. In our presentation, we will present the results of the refinement of the Al-Cu-Rh decagonal structure model based on high-temperature data [2] using a new phason approach [3,4] and a generalized Penrose tiling (GPT) as a quasilattice [5]. Diffraction data were collected at temperatures 293 K and 1013-1223 K. A correlation was observed between lattice parameters and the maximum residual electron density was observed, indicating a phase transformation at around 1083-1153 K. At the same temperatures, the minima of values of moments, which model the phasonic flips, are observed, leading to the conclusion that the transition to a more stable phase is related to phason disorder.

The occurrence of the additional 5th atomic surface in GPT can be obtained by phasonic fluctuation in the ideal structure. In the consecutive refinement we observed that the atomic distribution of an 5th atomic surface correlates with the stability of a structure at the temperature of approximately 1153 K, which could indicate the influence of the phason disorder on the stabilization of the structure [6] (see Fig. 1).

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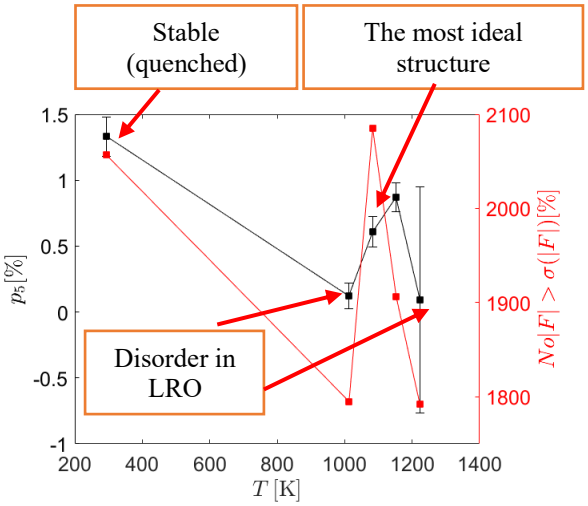

Fig.1: Occupation of the 5th atomic surface correlates with the highest stability of the system and anomalous thermal lattice expansion.