A structural reinvestigation of α-AlCuRu as merohedric twins

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α-AlCuRu [1] is often referred to as the 1/1 cubic approximant to the F-type icosahedral phase, *i*-AlCuRu [2]; see also [3]. It is a rare instance of an approximant in Al-Cu-M (M: transition metal) icosahedral alloys if the lowest order 1/0 approximants are disregarded, so that it could give us invaluable insights into the atomic structure of related icosahedral phases. The first model structure of α-AlCuRu obtained using single-crystal X-ray analysis was depicted using two Mackay-cluster-like motifs in the CsCl-type arrangement [4]. A similar structure was also reported for α-AlMnSi [5] or the 1/1 cubic approximant to the P-type icosahedral phase, *i*-AlMnSi [6]. The space group $Pm\bar{3}$ was assumed for both the α-phases [4,5] which were deemed isostructural.

In this report, the atomic structure of α-AlCuRu is reinvestigated in light of our updated knowledge on related approximants in Al-transition metal alloys. Recent publications on the structure analysis of novel high-order approximants in Al-Pd-M icosahedral alloys [7–10] have revealed a certain construction principle for related structures. More specifically, the description of these approximants is commonly based on two cluster motifs, sometimes called pseudo-Mackay and mini-Bergman clusters (Fig.1), which are centered at the vertices of a tiling composed of four polyhedral proto-tiles called the canonical cells (Fig.2) [11]. This construction principle when combined with the catalogue of canonical-cell tilings will immediately give us a number of hypothetical polymorphs of approximants. Then, there arises a natural conjecture: *The same principle applies to ALL icosahedral approximants in Al-transition metal alloys.* In fact, however, it is rather easy to find counter examples in the literature; some of the reported approximants that include α-AlCuRu [4] clearly disprove it. If one would stick to this fancy conjecture, she or he would go ahead and ask *if anything was wrong with the previous refinements of these counter examples*.

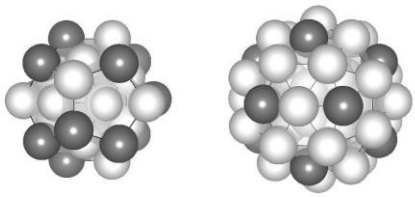

Figure 1. Two kinds of cluster: mini-Bergman (left) and pseudo-Mackay (right).

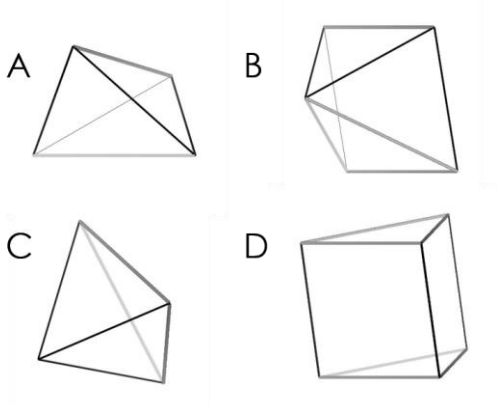

Figure 2. The canonical cells: A, B, C, and D cells.

Indeed, this is what we intend to do in this study of α-AlCuRu. We start by synthesizing a good-quality specimen by annealing an arc-melted ingot with a nominal composition of $Al_{57.3}Cu_{31.4}Ru_{11.3}$ under Ar atmosphere at 750°C for 360~720h. We then obtain mm-sized single grains of α-AlCuRu, dark-field electron microscopy images of which however indicate microscopic texture patterns comprising many single crystal domains of over 100nm in diameter (Fig.3). Here, in fact, the diffraction peaks from neighbouring domains

fully overlap. Interestingly, many of the twin boundaries are parallel to two crystallographic planes: {100} and {110}. We also collect single-crystal X-ray diffraction data from the present sample of α-AlCuRu. Due to the merohedric twinning, however, it seems unlikely that direct methods can give us a proper starting model for a structure refinement. Hence, an initial structure model is prepared instead by replicating cluster motifs (Fig.1) at the vertices of the relevant canonical-cell tiling (known as the 2/1 cubic packing [11]). For the refinement, we assume that the sample texture comprises twin domains taking four independent orientations and that the space group of each individual domain is $R3$.

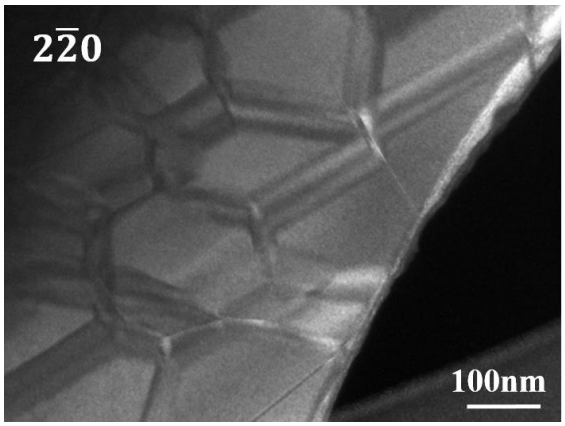

Figure 3. A TEM dark field image showing 100 nm-size twin domains in α-AlCuRu annealed at 750 °C for 360 hours.

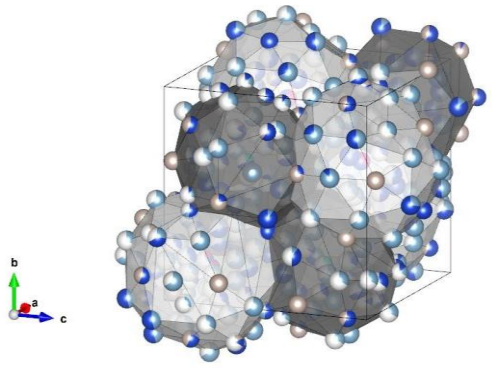

Figure 4. The refined structure of α-AlCuRu, where twinning was taken care of. The two kinds of cluster are distinguished by color.

The refinement finally converges when a reasonable value of the reliability factor, $R_F \approx 10.4\%$, is attained, where the packing of the two cluster motifs looks inert despite emergent splitting sites within individual clusters demand further physical interpretations. We argue that a twin boundary either parallel to {100} or {110} can arise without much cost of energy if an extra layer of canonical cells is inserted into the tiling. Finally, it is confirmed that if we chose $Pm\bar{3}$ as the space group and did not care about the merohedric twinning, we would end up with the crystal structure that was reported previously [4].

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