Atomic structure of the primitive cubic phase $P_{40}$ in the Al-Pd-Ru system

Y Hatakeyama$^1$, N Fujita$^{1,2}$ and A P Tsai$^{1,3}$

$^1$ Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
$^2$ JST, PRESTO, Kawaguchi, Saitama 332-0012, Japan
$^3$ National Institute for Materials Science, Tsukuba 305-0047, Japan

E-mail: nobuhisa@tagen.tohoku.ac.jp

Abstract. The atomic structure of the high-order cubic approximant $P_{40}$ in the Al-Pd-Ru system is determined by means of single-crystal X-ray diffraction.

1. Introduction

Icosahedral quasicrystals (iQC’s) in Al-Pd-TM systems, where TM stands for transition metal elements (e.g., Mn, Re, Ru, Os), are among the oldest families of thermodynamically stable F-type iQC’s [1, 2]. These quasicrystals continue to offer attractive challenges to unravel their atomic structures because of a number of uncertainties in their fine structural details. Albeit the study of approximant phases generally provides information that can help us understand local atomic arrangements in the iQC’s, suitable approximants have seldom been reported in a compositional proximity to the iQC’s. In the relevant ternary phase diagrams, there often exist one or a few cubic phases (C, C$_1$ and/or C$_2$ phase) known as the 1/0 cubic approximants lying next to the iQC’s. Still, the stability ranges of the C-phases are somewhat detached from those of the iQC’s, and besides their unit cells may be too small to abstract many of the complex features of the iQC’s.

Perhaps, more insights could be given by higher order approximants, which for instance have been reported in ternary Al-Pd-Co [3] and Al-Pd-Re [4] systems and also in quaternary Al-Pd-Mn-Si [5, 6], Al-Pd-Cr-Fe [7] and Al-Pd-Ge-Co [8] systems. These authors have derived a few kinds of atomic cluster which may potentially constitute the stable iQC’s in Al-Pd-TM systems. However, the things may not work out as we expect because views on the constituent clusters are not necessarily consistent among these papers. Another concern is that any of these approximants does not accompany a stable iQC in its immediate proximity of composition. For elucidating the structural relationship between the iQC’s and approximants, a sensible approach would be to focus on an alloy system in which both an iQC and a high-order approximant lie in close proximity to each other in the phase diagram.

In the Al-Pd-Ru alloy system, the stability range of the iQC roughly extends between the compositions Al$_{73}$Pd$_{11.5}$Ru$_{15.5}$ and Al$_{70}$Pd$_{22}$Ru$_8$ at a temperature between 790°C and 900°C [9]. At the high-Ru end of this range lies a narrow region of a large cubic approximant, $P_{40}$, with $Pn\bar{3}$ space group and a lattice constant of about 40Å[9]. At the low-Ru end on the other hand lies a narrow region of another approximant, $P_{20}$, which is often called the 2/1 cubic approximant,
Figure 1. (a) Powder diffraction patterns with synchrotron X-ray (wave length=0.652802 Å) taken from the single-crystal part (upper panel) and polycrystalline part (lower panel). The inset is a photo image of the sample, in which the single-crystal part is indicated with a dotted circle. (b) A selected area electron diffraction pattern taken from the single-crystal part with the ⟨100⟩ incidence, indicating the formation of the P40 phase.

with a lattice constant of about 20Å[10, 11]. Because of the compositional proximity between the iQC and the two approximants, the present system offers a rare opportunity to investigate the structural relationship between them. So far, however, the structural details of both the P40 and P20 phases have yet to be clarified.

In this study, the crystal structure of P40 is elucidated for the first time using single-crystal X-ray diffraction. The aim of this paper is to provide a short account of the structure analysis, while more details will be presented in a separate paper. In fact, remarkable similarities can be recognized between published electron diffraction patterns for P40 [9] and ones for the Al-Pd-Cr-Fe approximant [7]. Our present results ensure that the crystal structures of the two approximants are identical.

2. Synthesis
An ingot with the composition Al72.6Pd13Ru14.4, which has been reported to be the one for P40[9], was prepared by ordinary arc-melting under an argon atmosphere. Three parts of the ingot were annealed at 900 °C, 1000 °C and 1100 °C for a few days. All the samples were found to contain multiple phases including the P40 and C2 phases, while powder X-ray diffraction indicated that the sample annealed at 1000 °C had the largest amount of P40. Hence, another ingot was prepared with the same composition and annealed at 1000 °C for 20 days. As shown in the inset of Fig. 1(a), a part of the sample revealed a single-crystal grain 3 mm in diameter wrapped in a polycrystalline matrix. Using powder X-ray diffraction Fig. 1(a) and selected area electron diffraction Fig. 1(b), the single crystal was confirmed to be that of P40[9], while several kinds of crystallites are in the polycrystalline part. It seems that the single crystal has grown in a melt of residual components, which have turned into fine crystallites upon cooling. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to analyze the composition of the single-crystal part, indicating the composition to be Al72Pd16.4Ru11.6. The deviation from the nominal composition may be too large to be explained on a mere assumption that the initial ingot was somewhat inhomogeneous. Considering that no previous report (cf. [9]) used a single crystal to analyze the composition, our result should indicate the right composition of P40.
3. Measurement and analysis

The single-crystal X-ray diffraction experiments were carried out at room temperature on a fragment (roughly in the shape of a cube with edge length being slightly less than 0.1 mm) of the single-crystal, using a SMART APEX diffractometer (Bruker) mounting CCD area detector with Mo Kα radiation and graphite monochromator (wavelength 0.71073Å). Indexing and empirical absorption correction were performed using the Bruker software package (SMART, SAINT and SADABS)[12]. The Bravais lattice was identified to be primitive cubic while the lattice constant was estimated to be 40.67Å.

The indexed diffraction intensities were analyzed using the software package JANA2006 [13]. The space-group was unambiguously determined to be Pn3 (No. 205) with Rint (obs/all) being 8.26/21.14. There were 59904 independent reflections within a 2θ range of 1.12 ~ 40.64 °, wherein 12604 were classified as observed (i.e., I > 3σ(I)). The initial model for the structure refinement was obtained using the SUPERFLIP program [14] called from the JANA2006 platform. The refinement converged reasonably well with R(F) = 9.65 %, Rw(F) = 10.00 % (σ weight) and (∆ρmax, ∆ρmin) = (7.46, −4.99) e/A³. In the final model, each unit cell contains 4824 atomic sites among which 208 are symmetrically unique, whereas the number of refined parameters is 1073. The composition calculated from the refined model is Al71.40 Pd16.68 Ru11.92, which agrees well with the result of ICP-AES. Since each unit cell corresponds to 4320 atoms, the density is calculated to be 5.23 g/cm³.

4. Crystal structure

The refined structure exhibits a dense packing of atomic clusters, which are called pseudo-Mackay clusters (pMC’s) and mini-Bergman clusters (mBC’s). Whereas these clusters are joined together by sharing atoms, three kinds of linkage between clusters are observed. The first two kinds are parallel to 2-fold symmetry axis with the cluster centers separated by about 7.8Å. The other kind of linkage is parallel to 3-fold axis and the separation is about 6.7Å. The former two linkages connect the same kind of cluster (pMC-pMC and mBC-mBC), whereas the third linkage connects distinct cluster types (pMC-mBC). The cluster network thus determined can be represented as a tiling composed of four kinds of polyhedra called the canonical cells [15], where the edges of the cells correspond to the inter-cluster linkages. The kind of cluster at each node is determined unambiguously by the parity of the node. The present tiling can be understood as a 2 × 2 × 2 superstructure of the standard 3/2-cubic packing [15].

We find that the centers of the clusters are mostly occupied by Pd or Ru while the inner shells mostly by Al. It is important to note that each pMC-pMC linkage involves a weak inter-penetration of the two pMC’s, such that an outer-shell atom of either pMC is enforced to be dimpled in to lie on the outer shell of the other pMC. The inner shell of each pMC is not fully occupied but is occupied by 6 to 8 atoms (mostly Al), which also belong to the outer shells of adjacent mBC’s connected through pMC-mBC linkages. It turns out that the present crystal structure is identical to that of the Al-Pd-Cr-Fe approximant [7].

In fact, pMC and mBC may serve as the fundamental building units of the iQC as well as the P20 phase, in which the arrangement of clusters may be represented as another canonical-cell tiling. Moreover, number of hypothetical crystal structures are derived from the same principle, which may thus act as a universal framework for describing the cluster-packing geometry in Al-Pd-TM alloys. Indeed, it can be shown that the Al-Pd-Co [3] and Al-Pd-Ge-Co approximants [8] exhibit the same kind of cluster-packing geometry. Still, one may be puzzled to find that the two Al-Pd-Mn-Si approximants, usually referred to as 1/1 and 2/1 cubic approximants, have so far been described in incompatible manners [5, 6]. Here, apart from that the reported clusters are neither pMC nor mBC, the relationship between the two approximants is left unclear. In addressing this issue, a detailed structure analysis of P20, which exhibits the same crystal symmetry as the 2/1 approximant in Al-Pd-Mn-Si, could give us valuable hints.
Figure 2. (a) The crystal structure of P$_{40}$ represented as a packing of clusters. pMC’s and mBC’s are shown in light and dark gray, respectively. White spheres represent Al, while gray spheres Pd or Ru. (b) The cluster network extracted from panel-(a). Each sphere represents a cluster, where the two kinds of cluster are distinguished by color. Edges of the unit cell are represented as dashed lines, while cluster linkages as cylindrical bars. (c) The shell structures for pMC and mBC. Panel-(a) and panel-(b) corresponds to Figs. 7 and 9 in Ref.[7].

Acknowledgments
The authors thank Akira Sato for technical assistance in the single-crystal X-ray diffraction measurements. The synchrotron powder X-ray diffraction experiments were performed at the BL15XU beamline of SPring-8 with the approval of National Institute for Materials Science (NIMS) (Proposal No. 2015A4901). N F thanks Marek Mihalkovic for helpful discussions and comments on related subjects. Financial support from JSPS (Grant-in-Aid for Scientific Research(C) no. 25400354) and JST (PRESTO) is gratefully acknowledged (N F).

References
[1] Tsai A P, Yokoyama Y, Inoue A and Masumoto T 1990 Jpn. J. Appl. Phys. 29 L1161
[2] Asao T, Tamura R and Takeuchi S 2002 Philosophical Magazine Letters 82 217
[3] Simura R, Suzuki S, Yubuta K and Sugiyama K 2013 Mater. Trans. 54 1385
[4] Suzuki S, Simura R and Suzuki K 2011 Philosophical Magazine 91 2610
[5] Sugiyama K, Kaji N and Hiraga K 1998 Zeitschrift für Kristallographie 213 168
[6] Sugiyama K, Kaji N and Hiraga K 1998 Zeitschrift für Kristallographie 213 90
[7] Fujita N, Takano H, Yamamoto A and Tsai A P 2013 Acta Cryst. A 69 322
[8] Sugiyama K, Yubuta Y, Yokoyama Y, Suzuki S and Simura R 2014 Acta Phys. Pol. A 126 588
[9] Pavlyuchkov D, Grushko B and Velikanova T Y 2009 Journal of Alloys and Compounds 469 146
[10] Tamura R, Asao T, Tamura M and Takeuchi S 1999 J. Phys.: Condens. Matter 11 10343
[11] Shibuya T, Asao T, Tamura M, Tamura R and Takeuchi S 2000 Mater. Sci. Eng. A 294-296 61
[12] Bruker 2001 SMART (v. 5.625), SAINT (v. 6.45) and SADABS Bruker AXS Inc., Madison, Wisconsin, USA
[13] Patricek V, Dusek M and Palatinus L 2006 JANA2006: The Crystallographic Computing System http://jana.fzu.cz/ (Institute of Physics, Prague, Czech Republic)
[14] Palatinus L and Chapuis G 2007 J. Appl. Cryst. 40 786
[15] Henley C L 1991 Phys. Rev. B 43 993