

Cubic approximants in the Al–Pd–Fe and Al–Pd–Ru systems

K. Sugiyama^{a,*}, K. Hiraga^a, K. Saito^b

^a Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan

^b Department of Materials Science and Engineering, Akita University, Akita 010-8502, Japan

Received 8 September 1999; accepted 25 February 2000

Abstract

The structures of cubic $\text{Al}_{66.8}\text{Pd}_{21.2}\text{Ru}_{12.0}$ ($Fm\bar{3}$; $a=15.6058(6)$ Å), $\text{Al}_{63.6}\text{Pd}_{30.2}\text{Fe}_{6.2}$ ($Fm\bar{3}$; $a=15.5187(9)$ Å) and $\text{Al}_{68.9}\text{Pd}_{17.1}\text{Fe}_{13.9}$ ($Im\bar{3}$; $a=15.3755(8)$ Å) phases, which are referred as the derivatives of 1/0-rational approximants for an icosahedral phase, were determined by means of the single crystal X-ray structural analysis. The edge-shared connection by (Pd,Ru)- and (Pd,Fe)-icosahedra is one of applicable descriptions for these 1/0 related structures and a variety of filling motifs inside the icosahedra produce the crystallographic difference for each structure. The structure of an 1/1-rational approximant of $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$ ($Pm\bar{3}$; $a=12.3773(8)$ Å) indicates a disordered atomic arrangement inside (Cu,Al)- and Ru-icosahedra. These features are similar to those found in disordered atomic arrangements inside the (Pd,Ru)- and (Pd,Fe)-icosahedra of the 1/0 related approximant structures. Such variation of Mackay atom clusters is suggested to play an important role against the stability region of the fundamental atom clusters with local icosahedral symmetry, together with the chemical and topological ordering found in the icosahedral phases. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Single-crystal X-ray diffraction; Structure; Al–Pd–Fe; Al–Pd–Ru; Crystalline approximant

1. Introduction

The crystalline structures displaying local icosahedral symmetry have directed much interest on complex crystalline phases. The Mackay icosahedra of α -Al–Mn–Si [1,2] and the triacontrahedron of $\text{Mg}_{32}(\text{Al,Zn})_{47}$ [3] were the classical examples, and atomic models of icosahedral phases were successfully deduced by using their structural features [4,5]. A series of structural analysis for γ -Al–Cu–Ru–Si [6], α -Al–Pd–Mn–Si [7] and β -Al–Pd–Mn–Si [8], which were referred as cubic 1/0-, 1/1- and 2/1-rational approximants for the F-type icosahedral phase, provide another fundamental image of a periodic packing of the dodecahedral atom clusters together with the τ -inflation rule in their sizes [9,10]. Through systematic studies on Al-based cubic phases nearby icosahedral phases, the structures of 1/0 related approximants $\text{Al}_{66.8}\text{Pd}_{21.2}\text{Ru}_{12.0}$ ($Fm\bar{3}$; $a=15.6058(8)$ Å), $\text{Al}_{63.6}\text{Pd}_{30.2}\text{Fe}_{6.2}$ ($Fm\bar{3}$; $a=15.5187(8)$ Å) and $\text{Al}_{68.9}\text{Pd}_{17.1}\text{Fe}_{13.9}$ ($Im\bar{3}$; $a=15.3755(8)$ Å) were determined by single crystal X-ray diffraction. Present paper reports the structural features of these 1/0-related approximants, together

with those of 1/1-rational approximant $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$ ($Pm\bar{3}$; $a=12.3773(8)$ Å) [11].

2. Experimental

The master alloy ingots of $\text{Al}_{68}\text{Pd}_{20}\text{Ru}_{12}$, $\text{Al}_{64}\text{Pd}_{31}\text{Fe}_5$ and $\text{Al}_{69}\text{Pd}_{17}\text{Fe}_{14}$ were prepared from pure metals of Al (99.999%), Pd (99.99%), Fe (99.9%) and Ru (99.9%) by using a conventional arc furnace in an Ar atmosphere. A solidified ingot was charged into an Al_2O_3 crucible sealed in an evacuated silica tube and annealed at selected temperatures followed by quenching in the ice water. Electron probe microanalysis (EPMA; JEOL JXA-8621MX) was used for the chemical analysis of crystalline phases and the results are summarized in Table 1, together with detailed annealing conditions. Single crystal samples were cut out from the annealed ingots and used for the following X-ray examination. Weissenberg photographs were taken by using the RAXIS-CS (Rigaku) system equipped with imaging plates and a rotating anode X-ray tube. Intensity patterns observed by monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) lead to a cubic cell with the space group of $Fm\bar{3}$ (No. 202) for $\text{Al}_{66.8}\text{Pd}_{21.2}\text{Ru}_{12.0}$ and $\text{Al}_{63.6}\text{Pd}_{30.2}\text{Fe}_{6.2}$. As for $\text{Al}_{68.9}\text{Pd}_{17.1}\text{Fe}_{13.9}$, the space group of $Im\bar{3}$ (No. 204) was selected. Intensity data sets for the following structural analysis were collected on a AFC7R (Rigaku) four-circle

* Corresponding author. Present address: Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo. Tel.: +81-3-5841-4544; fax: +81-3-3816-5714. E-mail address: kazumasa@eps.s.u-tokyo.ac.jp (K. Sugiyama).

Table 1
Experimental data of three derivatives for the 1/0-rational approximants

Chemical composition (EPMA)	Al _{66.8} Pd _{21.2} Ru _{12.0}	Al _{63.6} Pd _{30.2} Fe _{6.2}	Al _{68.9} Pd _{17.1} Fe _{13.9}
Chemical composition (X-ray)	Al _{65.1} (Pd,Ru) _{34.8}	Al _{61.9} Pd _{32.7} Fe _{5.3}	Al _{68.3} Pd _{19.2} Fe _{12.5}
Synthetic conditions	1273 K, 10 d	1323 K, 2 d	1323 K, 1.5 d
Crystalline size	0.08×0.09×0.09	0.07×0.07×0.08	0.08×0.09×0.15
Space group	<i>Fm</i> 3	<i>Fm</i> 3	<i>Fm</i> 3
<i>a</i> (Å)	15.6058(6)	15.5187(9)	15.3755(8)
<i>F</i> (000)	6131	5920	5163
<i>R</i> (<i>F</i> _{obs.} >4σ(<i>F</i> _{obs.}))	0.0313	0.0302	0.0392
<i>wR</i> 2 (all data)	0.0848	0.0797	0.1064
Data/parameters	766/36	758/36	1466/64

diffractometer by using monochromated Mo K α radiation in the ω -2 θ scan mode. After Lorentz and polarization corrections, an absorption correction was performed by means of an ordinary ψ -scan algorithm [12]. The program package SIR92 [13] based on direct methods was used in order to obtain an initial structural model and the model for each crystal was refined by the least-squares calculation of SHELXL-97 [14] coupled with the difference Fourier techniques. By introducing anisotropic temperature factors only for fully occupied positions and an extinction parameter of SHELXL-97, the refinement finally converged to $R(F)=0.03\sim 0.04$ for the reflections with $F_{\text{obs.}}>4\sigma(F_{\text{obs.}})$. The chemical compositions calculated from refined models correspond well with those determined by EPMA.

3. Results and discussion

The structure of Al_{66.8}Pd_{21.2}Ru_{12.0} is isostructural with that of γ -Al-Cu-Ru-Si [6]. As an example, atomic arrangements at the 4*a* and 4*b* sites and dodecahedral atom clusters at the 8*c* site of Al_{66.8}Pd_{21.2}Ru_{12.0} structure are shown in Fig. 1. The dodecahedral atom cluster, composed of an icosahedron and a dodecahedral shell, is connected to each other by sharing their edges along the $\langle 100 \rangle$ directions. Similar simple cubic arrangements of dodecahedral atom clusters are found in the structures of α -Al-Pd-Mn-Si and β -Al-Pd-Mn-Si, although their dodecahedral atom clusters are τ and τ^2 times, respectively, as large as that in the Al_{66.8}Pd_{21.2}Ru_{12.0} structure. The atomic arrangement of this structural type is also implied by the edge-sharing (Pd,Ru)-icosahedra around the 4*a* and 4*b* sites. Pointing out the heavily disordered arrangement at the first shell around the 4*b* site in particular, the structure may be constructed by the edge-shared (Pd,Ru)-icosahedra filled by the ordered rhombic dodecahedra (4*a*) and the disordered ones (4*b*). Let us recall the report on c-Al₆₈Pd₂₀Ru₁₂ (*P*23, $a=15.540(2)$ Å) [15]. Fundamental atomic arrangement of c-Al₆₈Pd₂₀Ru₁₂ is similar to that of the present Al_{66.8}Pd_{21.2}Ru_{12.0}, and the appreciable difference is the filling motif inside the (Pd,Ru)-icosahedra, only. These features readily allow us to predict that another structural type with different filling motifs existing among the Al-based

cubic 1/0 related approximant phases. The structure of Al_{63.6}Pd_{30.2}Fe_{6.2} is isostructural with γ -Al-Cu-Ru-Si and refined parameters for Al_{63.6}Pd_{30.2}Fe_{6.2} agree well with those reported in Ref. [16].

Fig. 2 shows an atomic arrangement at the 2*a* and 6*b* sites and dodecahedral atom clusters at the 8*c* site in the body-centered structure of Al_{68.9}Pd_{17.1}Fe_{13.9}. The fundamental features of the edge-shared arrangement of dodecahedral atom clusters along the $\langle 100 \rangle$ direction are realized again like those in face-centered phase. Most interesting point of this Al_{68.9}Pd_{17.1}Fe_{13.9} structure is another type of filling motif inside the (Pd,Fe)-icosahedra. The six (Pd,Fe)-icosahedra indicate a heavily disordered atomic arrangement and remaining two possess the ordered rhombic dodecahedral one in the body-centered structure of Al_{68.9}Pd_{17.1}Fe_{13.9}. This is the third example of the derivatives for the cubic 1/0-rational approximant phases with a cell parameter of about 15.5 Å. It should be added that the structures of Ir₂Al₅ (*P*23, $a=7.7$ Å) and Rh₂Al₅ (*P*23, $a=7.7$ Å) [17] are classified as the simplest 1/0 approx-

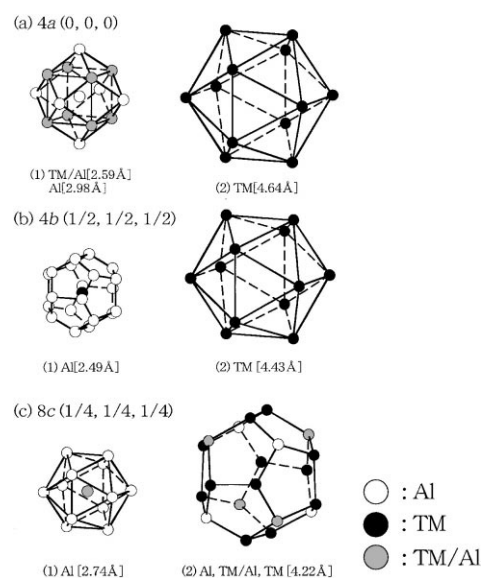


Fig. 1. Atom clusters at the 4*a* site (a) and the 4*b* site (b) together with the 8*c* site (c), of Al_{66.8}Pd_{21.2}Ru_{12.0} structure. The values indicate averaged distances of constituents from the center of the cluster.

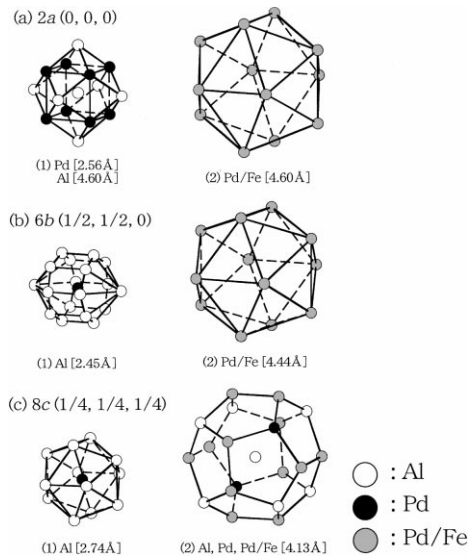


Fig. 2. Atom clusters at the $2a$ site (a) and the $6b$ site (b) together with the $8c$ site (c), of $\text{Al}_{68.9}\text{Pd}_{17.1}\text{Fe}_{13.9}$ structure. The values indicate averaged distances of constituents from the center of the cluster.

imant structure and referred as an averaged structure of $\text{Al}_{66.8}\text{Pd}_{21.2}\text{Ru}_{12.0}$, $\text{Al}_{63.6}\text{Pd}_{30.2}\text{Fe}_{6.2}$, $\text{Al}_{68.9}\text{Pd}_{17.1}\text{Fe}_{13.9}$, $c\text{-Al}_{68}\text{Pd}_{20}\text{Ru}_{12}$ and Al-Cu-Rh [18].

Fig. 3(a) shows an atom cluster at the origin ($1a$ site) of the cubic $1/1$ -rational approximant of $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$

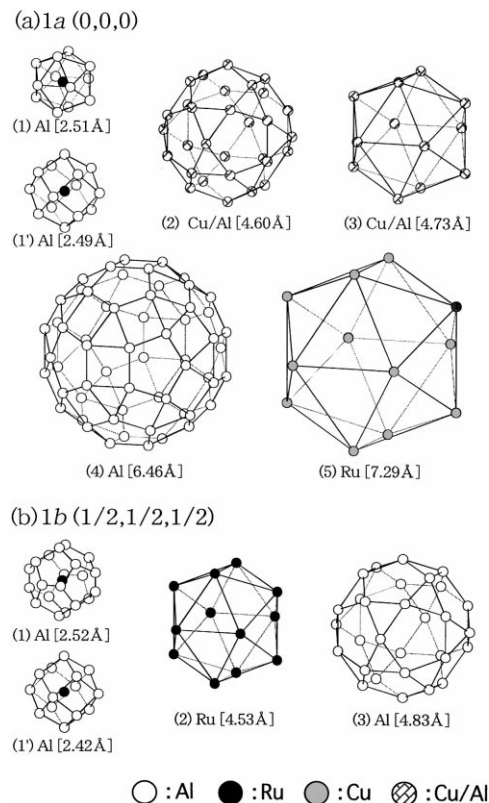


Fig. 3. Atom clusters at the origin (a) and the center (b) of the $1/1$ rational approximant of $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$. The values indicate averaged distances of constituents from the center of the cluster.

[11]. The atomic arrangements of Fig. 3 (a2)–(a5) are similar to those of $\alpha\text{-Al-Mn-Si}$. Most striking difference of the $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$ structure from the classical $\alpha\text{-Al-Mn-Si}$ one is the location of Ru at the origin and heavily disordered nature at the first shell of Fig. 3 (a1) and (a1'). Fig. 3(b) indicates an atom cluster at the center ($1b$ site) of the $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$ structure. The location of Ru at the center and the heavily distorted first shell are realized again, although the atomic arrangements at the second and third shells indicate the close similarity with those of $\alpha\text{-Al-Mn-Si}$. In these contexts, the Mackay atom clusters of $\text{Al}_{57.3}\text{Cu}_{31.5}\text{Ru}_{11.3}$ are suggested to be strongly disordered by the Cu/Al- and Ru-icosahedra and their Ru centers. These disordered motifs indicate close similarity to those of derivatives for the $1/0$ -rational approximants and indicate a harmony of the local icosahedral symmetry and the rhombic dodecahedral symmetry. Such variation of the Mackay atom clusters is suggested to play an important role against the stability region of the fundamental atom clusters with local icosahedral symmetry, together with the chemical and topological ordering found in the icosahedral phases.

Acknowledgements

This work has been financially supported by a Grant-in-Aid for Scientific Research (B) (No. 11440101) from the Ministry of Education, Science and Culture of Japan and also by JSPS's fund.

References

- [1] M. Cooper, K. Robinson, *Acta Cryst.* 20 (1966) 614.
- [2] K. Sugiyama, N. Kaji, K. Hiraga, *Acta Cryst.* C53 (1998) 445.
- [3] G. Bergman, J.L.T. Waugh, L. Pauling, *Acta Cryst.* 10 (1957) 254.
- [4] V. Elser, C.L. Henley, *Phys. Rev. Lett.* 55 (1985) 2883.
- [5] M. Audier, P. Guyot, *Phil. Mag.* B53 (1986) L43.
- [6] K. Sugiyama, T. Kato, K. Saito, K. Hiraga, *Philos. Mag. Lett.* 77 (1998) 165.
- [7] K. Sugiyama, N. Kaji, K. Hiraga, T. Ishimasa, *Z. Kristallogr.* 213 (1998) 90.
- [8] K. Sugiyama, N. Kaji, K. Hiraga, T. Ishimasa, *Z. Kristallogr.* 213 (1998) 168.
- [9] K. Hiraga, K. Sugiyama, T. Ohsuna, *Phil. Mag.* 78 (1998) 1051.
- [10] K. Hiraga, T. Ohsuna, K. Sugiyama, *J. Phys. Soc. Jpn.* 66 (1997) 3700.
- [11] K. Sugiyama, K. Kato, T. Ogawa, K. Hiraga, *J. Alloy. Comp.* 299 (2000) 169–174.
- [12] A.T.C. North, D.C. Phillips, F.S. Mathews, *Acta Cryst.* A24 (1968) 351.
- [13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* 27 (1994) 435.
- [14] G.M. Sheldrick, SHELXL97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [15] F.J. Edler, V. Gramlich, W. Steurer, *J. Alloy. Comp.* 269 (1998) 7.
- [16] S. Mahne, W. Steurer, *Z. Kristallogr.* 211 (1996) 17.
- [17] Y. Grin, K. Peters, U. Burkhardt, K. Goltzman, M. Ellner, *Z. Kristallogr.* 212 (1997) 439.
- [18] X.-Z. Li, K.T. Park, K. Sugiyama, K. Hiraga, *Metallur. Mater. Trans. A.* 29A (1998) 1559.