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## 論文内容要旨

After the discovery of an icosahedral quasicrystalline phase in a rapidly solidified  $Al_{86}Mn_{14}$  alloy by Shechtman *et al.* [1], a variety of structural studies have been done on quasicrystals and corresponding approximants phases in order to understand their unique structural features. A crystalline approximant has the local structure similar to that of the quasicrystalline phase. Therefore, structural analysis of approximants serves the important information on unique local atomic arrangements realized in the corresponding quasicrystals. The so-called Mackay type cluster (MC) which was found in  $\alpha$ -AlMnSi firstly is one of the classical atomic clusters for icosahedral quasicrystals by showing the first shell of Al icosahedron together with the second icosahedral shell of 12 Mn and the third icosidodecahedral shell of 30 Al [2-4]. However recent single crystal structural analysis of a variety of approximants provided several variations of MC [5,6,7]. These variants, called pseudo Mackay cluster (pMC), had topologically and chemically disordered first shells together with a center atom. This study pursues general understanding of the structure of Al based approximants demonstrating the detailed structural analyses of approximant crystals in Al-Pd-Co and Al-Pd-Re systems,  $R$ -AlPdCo [8],  $F$ -AlPdCoGe [9],  $\epsilon_6$ -AlPdCo,  $\epsilon_{16}$ -AlPdCo [10],  $W$ -AlPdCo [11] and  $\chi$ -AlPdRe [12], associated with pMCs and extending the discussion to other known Al based approximants.

In the second chapter, experiments that were used in this research are described. Sample alloys were prepared conventional arc melting. Pure metals of Al, Pd, Co, Ge and Re on water cooled Cu hearth were melted to the alloys in -55 mmHg Ar atmosphere by 10-300 A current using 20 V power-supply unit. The prepared ingots were crushed into carbon crucibles and some of them were sealed in evacuated  $SiO_2$  tube. Then they were annealed in Ar atmosphere to obtain single crystals. Single crystals were selected from the annealed alloys observed by optical microscope in  $\times 30 \sim 50$ . The single crystal X-ray diffraction data were collected by using  $Mo K\alpha$  ( $\lambda = 0.071073$  nm) radiation with Rigaku RAPID AUTO system equipped with an imaging plate mainly [13]. Initial structure model was introduced by Sir97, the direct method software [14]. Then the structural parameters were refined by SHELXL97, the least square process software [15]. Chemical compositional analyses were carried out by EPMA: electron probe micro-analyzer (JEOL JXA-8621MX).

A crystalline phase with the space group and lattice constants;  $R\bar{3}$  (No. 148),  $a = 2.91019(8)$  nm,  $c = 1.31854(4)$  nm was found in the sample alloys of  $\text{Al}_{72}\text{Pd}_{18}\text{Co}_{10}$ ,  $\text{Al}_{74}\text{Pd}_{14}\text{Co}_{12}$  and  $\text{Al}_{75}\text{Pd}_{16}\text{Co}_9$ . This was a new approximant phase for  $i$ -phase and was named  $R$ -phase. The structure of  $R$ -AlPdCo consists of four types of icosahedral cluster, Co(12)-pMC, Al(14)-pMC, Pd(1)-icosahedral unit and Pd(2)-icosahedral unit. The first shell of the Al(14)-pMC consists of an Al-octahedron and a Pd/Al-cube. The second shell is a distorted Al-icosidodecahedron and an icosahedron of Pd/Al and Co. Co(12)-pMC is composed of an irregular shaped Al-polyhedron together with the second shell of a Pd/Al-icosahedron and a heavily distorted Al-icosidodecahedron. All of atoms in the structure of  $R$ -AlPdCo are included in the four types of icosahedral cluster. This represents that the whole structure of  $R$ -AlPdCo can be shown by packing of the four types of icosahedral clusters (Fig. 1). The second shells of Co(12)-pMC and Al(14)-pMC are connected by their edges (Fig. 2). This can be described to connecting by sharing 2 fold axis. Looking at the third shell icosidodecahedrons of the pMCs, some Al is in the neighbor pMC. Geometrical feature of the third shell structures of the pMCs appear to reflect interaction between the third shell Al atoms of itself and the first shell atoms of the neighbors. The chemical ordering in the pMCs is suggested to be closely related to their polyhedral geometries. These two types of pMCs and the two Pd-icosahedral units are connected by sharing the faces in the third shell icosidodecahedrons. This can be described to connecting by sharing 3 fold axis. As described above, in section 3.2 we discovered a new approximant for  $i$ -phase,  $R$ -AlPdCo, and discussed the structure associating with connection of the four types of icosahedral clusters, Co(12)-pMC, Al(14)-pMC, Pd(1)-icosahedral unit and Pd(2)-icosahedral unit.

In section 3.3 the structure of  $F$ -AlPdCoGe is discussed in detail. The lattice parameters and space group of  $F$ -AlPdCo was reported by Yurechko *et al.* [16]. This cubic phase was expected to be F-type approximant for  $i$ -phase because of the lattice parameters. The structure has three types of pMCs, Al(18)-pMC, Co(13)-pMC and Co(14)-pMC. The whole structure can be described by these pMCs and two Pd-icosahedral units as same as  $R$ -AlPdCo.

A variety of orthorhombic approximants associated with the Al-Pd decagonal quasicrystal had been found in Al-Pd-(Mn, Fe, Co, Rh) systems [16-19]. The lattice parameters of  $a = 2.35$  and  $b$  (pseudo-10 fold axis) = 1.68 nm are essentially similar to each other, nevertheless the corresponding  $c$  parameters are  $\sim 1.2, 3.2, 4.5$  and  $5.7$  nm for  $\varepsilon_6$  (Al<sub>3</sub>Pd phase [20-22]),  $\varepsilon_{16}$ ,  $\varepsilon_{22}$  and  $\varepsilon_{28}$ , respectively. The structural information of these  $\varepsilon$ -phases is expected to lead the structural models of atom columns realized in the decagonal phase with a period of 1.68 nm. So the  $\varepsilon$  series was expected to be good example for the purpose of this thesis. In section 3.4 structural analyses of  $\varepsilon_6$ -AlPdCo and  $\varepsilon_{16}$ -AlPdCo are described.  $\varepsilon_6$ -AlPdCo and  $\varepsilon_{16}$ -AlPdCo were found in the sample alloys of  $\text{Al}_{80}\text{Pd}_{11}\text{Co}_9$ ,  $\text{Al}_{73}\text{Pd}_{20}\text{Co}_7$  and  $\text{Al}_{72}\text{Pd}_{18}\text{Co}_{10}$ . HREM images and electron diffraction (ED) patterns were taken by a 200 kV electron microscope (TOPCON EM-002B) at a resolution of 0.14 nm. From the ED pattern we concluded that  $\varepsilon_6$ -phase,  $\varepsilon_{16}$ -phase and their intermediate phase occur in  $\text{Al}_{73}\text{Pd}_{20}\text{Co}_7$ ,  $\text{Al}_{80}\text{Pd}_{11}\text{Co}_9$  and  $\text{Al}_{72}\text{Pd}_{18}\text{Co}_{10}$ .

As a result of single crystal X-ray analysis  $R$  factor was  $R1 = 9.35$  %. This value indicates that we have something a little for refinement yet, but we think that this structural model is essentially correct on an empirical basis. Around of Co(12) pMC with the first shell of disordered shape was found. This pMC is connected to 1.68 nm direction with each other at a vertex. Looking at the second shell of icosahedron of heavy metals the 10 fold columnar structure which is characteristic structure of the D-phase approximants can be recognized in the structure of the pMCs' connection.

The cell parameters of  $\varepsilon_{16}$ -AlPdCo are  $a = 2.321(1)$ ,  $b = 1.6426(1)$  and  $c = 3.1941(8)$  nm and space group is  $B2mm$ . The structure is produced by stacking 8 layers perpendicular to the  $c$ -axis. Among them, 4 layers are independent and the others are generated by the mirror symmetry. The layers indicate the 5 fold tiling structure with pentagonal and ship-shaped tiles. Pentagonal and decagonal clusters are on the vertexes and some inner positions of the tiles. The structure of  $\varepsilon_{16}$ -AlPdCo can be explained by arrangement of 5 and 10 fold atom columns. pMC with the disordered first shell was found in  $\varepsilon_{16}$ -AlPdCo and it is connected at a vertex each other to  $b$  direct. From the discussion of the structures of  $\varepsilon_6$ -AlPdCo and  $\varepsilon_{16}$ -AlPdCo described in this section 3.4 it is disclosed that the columnar structure in D-phase approximants with 1.68 nm periodicity can be recognized in the structure of pMCs' connection to 1.68 nm periodic direction at a vertex.

W1-AlPdCo [23] and W2-AlPdCo discussed in the section 3.5 are approximant phases for D-phase with 0.8 nm periodicity. Space group and lattice parameters of W2-AlPdCo are  $Cm$  (No. 8),  $a = 3.9858(2)$ ,  $b = 0.8166(1)$ ,  $c = 2.3258(1)$  nm,  $\beta = 90.074(1)^\circ$ . The structure of W2-AlPdCo is described by two types of layer structure, flat layer A and puckered layer B. The structural model of W1-AlPdCo was discussed by using the model of W2-AlPdCo. The 0.8 nm periodic decagonal columnar structure was recognized in the structure of W2-AlPdCo but pMC was not found against the other approximants for D-phase and i-phase discussed in the above sections.

In the structure of  $\chi$ -AlPdRe ( $P31c$  (No. 159),  $a = 1.24$  nm,  $c = 2.74$  nm) pMC was found around Re(4). The first shell of the Re(4)-pMC is an disorder-shaped Al-polyhedron. The polyhedron consists of four Al sites and three Al split sites. Watching averaged shape, this pMC has a 3 fold axis. The second shell is composed of a Pd-icosahedron and an Al-icosidodecahedron similar to a typical MC. This pMC is connected with each other to  $c$  direction through the connection of two Al octahedrons sharing faces.

Structural features of approximants in Al-Pd-Co and Al-Pd-Re systems,  $R$ -AlPdCo,  $F$ -AlPdCoGe,  $\varepsilon_6$ -AlPdCo,  $\varepsilon_{16}$ -AlPdCo  $W$ -AlPdCo and  $\chi$ -AlPdRe have been discussed associating with pMCs and their connection in the above sections. This discussion was extended to other Al based approximants in the chapter 5. We have classified pMCs in the Al based approximants into the following five groups by the feature of the first shells; (1) averaged shape of the first shell is icosahedron, (2) averaged shape of the first shell is dodecahedron, (3) the first shell is composed of a cube and a octahedron, (4) the first shell has no apparent symmetry and (5) averaged shape of the first shell has a 3 fold axis. According to the above classification, pMC at (0,0,0) in  $\alpha$ -(Al,Si)CuFe and pMC at (0,0,0) in  $\alpha$ -AlCuRu belong to category (1). pMC at (1/2,1/2,1/2) in  $\alpha$ -AlCuRu and Co(14)-pMC in  $F$ -AlPdCoGe belong to the category (2). Al(14)-pMC in  $R$ -AlPdCo and Al(18)-pMC in  $F$ -AlPdCoGe belong to the category (3). Co(12)-pMC in  $R$ -AlPdCo and Co(13)-pMC in  $F$ -AlPdCoGe belong to the category (4). The structure of pMC in  $\chi$ -AlPdRe and  $Ir_9Al_{28}$  show that the first shells of them belong to the category (5). Category (2) pMC is surrounded by six pMCs of category (4) sharing edges of the second shell of icosahedron. Around the category (3) pMC octahedral coordination is performed by pMCs of the category (4). Category (4) pMC is coordinated by four pMCs of category (4), one pMC of category (2) and one pMC of category (3) sharing edges in the second shell of icosahedron. Category (5) pMC is connected with itself to one direction through two octahedrons of Al sharing faces.

The single crystal structure analyses on a variety of approximants for i-phase and D-phase in Al-Pd-Co and Al-Pd-Re systems are performed in detail. Pseudo Mackay clusters (pMC), a variations of Mackay cluster (MC) which is the classical icosahedral structure, were classified

into five categories by the features of their first shells. It was disclosed that the structural features of the Al based approximants for i-phase and D-phase with 1.68 nm periodicity can be described by the structure of pMCs' connection. This thesis leads the study on general understanding of quasicrystals including i-phase and D-phase.

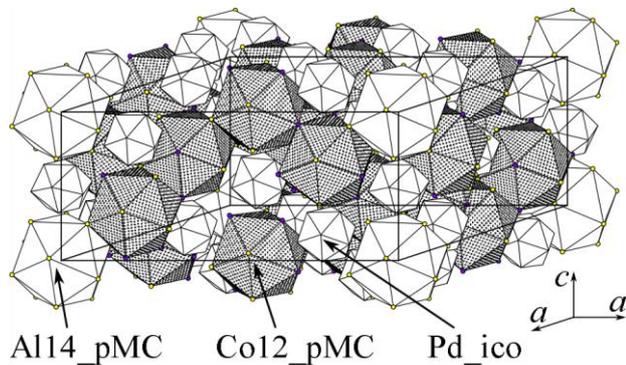


Fig. 1 Whole structure of R-AlPdCo can be shown by Al(14)-pMC, Co(12)-pMC and Pd-icosahedral unit.

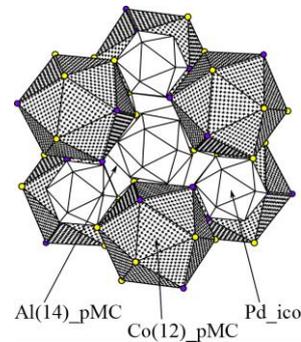


Fig. 2 Al(14)\_pMC is surrounded by Co(12)\_pMCs octahedral coordination and cubic coordination of Pd\_icosahedral units.

#### References

- [1] Shechtman, D., *et al.*, *Phys. Rev. Lett.* **53** (1984) 1951-1953.  
 [2] Mackay, A. L., *Acta Cryst.* **15** (1962) 916-918.  
 [3] Cooper, M. and Robinson, K., *Acta Crystallogr.* **20** (1966) 614-617.  
 [4] Sugiyama, K., *et al.*, *Acta Crystallogr.* **C54**(5) (1998(a)) 445-447.  
 [5] Puyraimond, F., *et al.*, *Acta Crystallogr. A* **58** (2002) 391-403.  
 [6] Sugiyama, K., *et al.*, *J. Alloy. Compd.* **229** (2000) 169-174.  
 [7] Katrych, S., *et al.*, *J. Alloy. Compd.* **407** (2006) 132-140.  
 [8] Simura, R., *et al.*, *Mat. Trans.* **54** (2008) 1385-1391.  
 [9] Sugiyama, K., *et al.*, *Acta Physica. Polonica* **A126** (2014) 588-593.  
 [10] Yubuta, K., *et al.*, *Aperiodic Crystals* (2013) 231-236.  
 [11] in press.  
 [12] Suzuki, S., *et al.*, *Phil. Mag.* **91** (2011) 2610-2616.  
 [13] *RAPID-AUTO*, Rigaku Corporation, Tokyo, 2001.  
 [14] Altomare, A., *et al.*, *J. Appl. Crystallogr.* **32** (1999) 115-119.  
 [15] Sheldrick, G. M., SHELXL-97, University of Göttingen, Germany (1997).  
 [16] Yurechko, M., *et al.*, *J. Alloys Compd.* **337** (2002) 172-181.  
 [17] Boudard, M., *et al.*, *Phil. Mag.* **A 74** (1996) 939-956.  
 [18] Balanetskyy, S., *et al.*, *J. Alloy. Compd.* **376** (2004(c)) 158-164.  
 [19] Przepiorzynski, B., *et al.*, *Intermetallics* **14** (2006) 498-504.  
 [20] Matsuo, Y. and Hiraga, K., *Philos. Mag. Lett.* **70** (1994) 155-161.  
 [21] Hiraga, K., *et al.*, *J. Electron. Microsc.* **49** (2000) 729-733.  
 [22] Saito, K., *et al.*, *J. Alloy. Compd.* **342** (2002) 126-129.  
 [23] Yubuta, K., *et al.*, *Phil. Mag.* **75** (1997) 273-284.

# 論文審査結果の要旨

物質中の原子配列を特定する手段がなかった時代から、物質の規則的な形はごく微小な粒子の規則的な配列が反映されたものであると予想されてきた。規則性とは原子の並進規則つまり周期的配列であると理解が進み、その学理は結晶学として体系化されてきた。そして結晶学は、X線回折法など回折法を用いた原子配列を決定する技術の進展とともに発展し、現在では我々の文明を支える材料科学の基礎学問として機能している。Shechtman *et. al.*, (1984)によって、結晶の並進対称性と共存できない5回回転対称性を有する正二十面体相(icosahedral phase; I相)が発見されてより、結晶とは異なる準周期規則性を持つ準結晶が物質科学の新しい研究分野として注目を集めている。準結晶の原子配列の理解には、準周期配列を近似できる近似結晶相の構造解析が極めて有効であり、近似結晶に見いだされる正二十面体クラスターが準周期配列したものが準結晶であると考えられている。本研究は、Al-Pd-Co および Al-Pd-Re 系三元合金に着目し、準結晶の構造ユニットとして注目されている擬マッカイクラスターとその連結様式という観点から近似結晶群の原子配列の特徴を総括した論文である。

本研究では、合金調整・熱処理・EPMA 化学分析による近似結晶試料の作製、単結晶構造解析法を駆使した近似結晶相の構造決定そして構造解析結果の総括を行なっている。第一章では、準結晶発見の歴史とその原子配列決定に関する様々な研究アプローチを解説している。第二章では、試料調整、化学分析さらに通常の単結晶試料と異なる複雑な原子配列を示しその構造決定が困難である近似結晶相の研究に際して、結晶育成条件の最適化および迅速な散乱強度測定ができるイメージングプレートを搭載したX線回折装置を駆使することによって問題解決を図る実験方法の詳細をまとめている。論文第三章では、Al-Pd-Co 三元系合金近似結晶相の構造解析を進め、2種類の擬マッカイクラスターから構成されるR相および3種類の擬マッカイクラスターから構成されるF相の構造解析を完了している。さらに、 $\epsilon$ 系近似結晶層の解析に挑戦し、これらの近似結晶相の構造も擬マッカイクラスターの連結によって説明可能であることを記述している。第四章では、Al-Pd-Re 三元系合金近似結晶相の構造解析を進め、本近似結晶の構造は擬マッカイクラスターと類似の重原子配列を示すI3クラスターを特徴とすることを説明している。第五章では、これらの一連の構造解析結果をまとめて、これまで準結晶近似結晶相に記載された擬マッカイクラスターを明晰に分類しその構造の特徴と化学組成の特徴に関して整理をしている。さらに擬マッカイクラスターの原子配列とその連結様式を例示し、擬マッカイクラスターの連結による中距離領域構造の形成メカニズムを的確に整理記述している。そして第六章では、本研究で得られた結果を総括すると同時に、準結晶の化学組成とクラスタータイプに関する整理をしている。

論文提出者が着目する擬マッカイクラスターの構造特性とその連結様式に関する構造科学的研究成果は、準結晶の構造や物理化学的特性を議論するために不可欠な情報である。そして、これまで整理されていなかった擬マッカイクラスターの原子配列の詳細とその連結様式を明晰な視点で整理し議論した本研究は、知能デバイス材料学の発展に寄与するところがすくなくない。

よって、本論文は博士(工学)の学位論文として合格と認める。