Crystal Structure of the C-AlRuNi Phase

Rayko Simura*, Kazumasa Sugiyama, Shota Suzuki and Toru Kawamata

Institute for Materials Research, Tohoku University, Sendai 980–8577, Japan

The structure of C-AlRuNi was determined by single-crystal X-ray diffraction (space group Pm\(\overline{3}\) (No. 200); \(a = 0.77088(4)\) nm; \(R = 0.0401\) for 268 independent reflections \(F_o > 2\sigma(F_o)\) measured by Mo \(K\alpha\) radiation). The fundamental structure of C-AlRuNi can be explained by the packing of two types of icosahedra. One is the regular icosahedron of transition metals (TMs; Ru and Ni) with a central TM atom at a 1\(\overline{1}\) site (H-ICO), and the other is the irregular icosahedron of TMs with a central TM atom at a 1\(b\) site (HM-ICO). An H-ICO is in contact with six H-ICOs and eight HM-ICOs in the directions of the twofold and threefold axes, respectively. The interstitial spaces among the TM distribution are filled by Al atoms. An HM-ICO contains an Al icosahedron (Al-ICO) inside the HM-ICO and a large Al-cube outside of it. An H-ICO has a small Al-cube inside the H-ICO and an Al distorted icosidodecahedron outside of it, indicating the atomic arrangement associated with a pseudo-Mackay cluster (pMC). The structure of C-AlRuNi can also be explained by the CsCl-like packing of pMCs and Al-ICO clusters. The pMC and Al-ICO are the key clusters for explaining the structures of the C1 and C2 phases in the Al–TM–TM ternary system.

Keywords: approximant, quasicrystal, Mackay cluster, cubic, aluminum ruthenium nickel, structural analysis, cluster distribution in the cell

1. Introduction

In the atomic arrangements of quasicrystalline approximants, a Mackay cluster (MC) and a pseudo-Mackay cluster (pMC) are among common building units. A variety of linkages of pMC units have been described well in the literature, and the distribution of MCs and pMCs provides an overview of the structural features of the approximants\(^1\)\(^2\). As an example, the recent structural analyses of R-AlPdCo\(^3\) and F-AlPdCoGe\(^4\) stressed the importance of the arrangement of pMCs, where pMCs are connected with each other by sharing the edges of two adjacent icosahedra composed of a transition metal (TM) element and the vertices of the outer Al icosidodecahedrons. Knowledge of the above approximant structures also allows us to suggest the importance of an Al icosahedron (Al-ICO) with a TM center as a glue cluster for the connection of pMCs. Such unique structures composed of the packing of pMCs and Al-ICOs are found in various approximants of Al–TM–TM ternary alloy systems\(^5\)\(^6\)\(^7\)\(^8\).

In the phase diagrams of Al–{(Cu, Ni, or Pd)–(Co, Ru, Rh, Fe, or Ir) systems\(^9\)}, so-called 1/0 approximants for the icosahedral phases were recognized in the compositional range of 60–80 mol% Al, and three cubic approximants of C (primitive lattice), C1 (body-centered lattice), and C2 (face-centered lattice) phases were reported. As shown in the phase diagram in Fig. 1, the C phase is located in the relatively Al-rich and TM-poor region compared to that for the C2 phase, and the C1 phase is realized in the middle region. This finding strongly suggests a significant relationship between the crystal structures and the chemical compositions for a series of 1/0 cubic approximants. The present paper reports the structural analysis of C-AlRuNi and discusses the structural features of three cubic phases.

2. Experimental Procedure

An alloy ingot with nominal composition of Al\(_{71.4}\)Ru\(_{16.5}\)Ni\(_{13.1}\) was prepared from Al (99.999%) droplets, Ru (99.9% up) powder, and Ni (99.9%) metal plates. Ru powder was pressed to form a tablet and was preliminarily melted using a conventional arc-melting furnace in a purified argon atmosphere. Then, a weighted mixture of these three metals was melted in the same arc-melting furnace. The as-prepared ingot was crushed into fragments, and some fragments were attached to an aluminum holder with carbon tape. The morphology of the obtained sample was observed by a Hitachi S-3400N scanning electron microscope (SEM). An aggregate of fine cubic crystals (hereafter referred as C-AlRuNi) with a size of 10–80 μm was clearly observed. A chemical analysis was carried out by using a JEOL JXA-8530F electron probe microanalyzer (EPMA) in the wavelength-dispersion mode with the following operating conditions: an accelerating voltage of 15 kV and a beam current of 1.2 nA. The chemical composition of C-AlRuNi was Al\(_{71.9}\)Ru\(_{17.9}\)Ni\(_{10.1}\). The Al\(_3\)Ni\(_2\) phase was found by the energy dispersive X-ray analysis with SEM (SEM-EDS).

A 20 × 20 × 20 mm\(^3\) single crystal was cut from a prepared alloy ingot and used for single-crystal X-ray diffraction (XRD) by using Mo \(K\alpha\) radiation and Rigaku VariMax with Confocal Max-Flux® (CMF) optics. The intensity data of 3041 reflections were collected, and absorption correction (ABSCOR)\(^10\) was performed by considering the shape of the single-crystal specimen after Lorentz and polarization corrections. The refined cell constants and diffraction patterns allowed us to select a cubic cell of \(a = 0.77088(4)\) nm with the space-group symmetry of P\(_m\)\(_3\) or P\(_23\). Since a structural analysis of P\(_23\) did not improve the structural model, we selected P\(_m\)\(_3\) for the present analysis. The diffraction patterns recorded on an imaging plate featured no supercell reflections indicating C1 or C2 phases. Data reduction according to the space group P\(_m\)\(_3\) yields 285 independent reflections, among which 268 reflections meet the condition \(F_o > 2.0\sigma(F_o)\). The experimental details are summarized in Table 1. The figures for the description of the crystal structure were illustrated by the CrystalMaker software\(^11\).

*Corresponding author, E-mail: ray@imr.tohoku.ac.jp

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3. Structural Analysis

The initial structural model for the C-AlRuNi phase was obtained by using the direct method (SIR9712). A least-squares refinement was performed using SHELXL-9713 on the WinGX platform14. The TM sites M(1), M(2), and M(3) were considered as the mix sites with Ru and Ni, and the remaining three sites were considered as partially occupied Al sites, Al(4), Al(5), and Al(6). The refinement with the anisotropic displacement parameters finally converged at $R_{\text{final}} = 0.0401$ for the 268 observed reflections. The maximum and minimum residual electron densities were 1.9 and $-2.3 \times 10^{-3}$ e/nm$^3$, respectively. In particular, the Al(6) site on the mirror plane shows a very large anisotropic displacement parameter normal to the mirror plane ($U_{11} = 0.30 \times 10^{-2}$ nm$^2$), which corresponds to an ellipsoid with a dimension of 0.054 nm in the [100] direction. The present structural model indicates a short distance between Al(6) and M(3) equal to 0.215 nm (symmetry code ii: y, z, x), and this value is unusually shorter than the common Al–Ru/Ni bond distances (0.241–0.257 nm15). This inconvenience also supports the structural disorder associated with the Al(6) site. These features indicate the feasible introduction of the split-site model for the Al(6) site; nevertheless, such structural modeling did not remove such inconvenience. Thus, the extraordinary anisotropic Al(6) site was employed in the model. It should be also noted that the present structural refinement utilized a chemical constraint to maintain the compositional ratio of Ru/Ni at 5.1/2.9. This procedure allows us to obtain the chemical composition of the structural model Al$_{20.5}$Ru$_{5.1}$Ni$_{2.9}$, which is compatible with Al$_{20.5}$Ru$_{5.1}$Ni$_{2.9}$ obtained by EPMA. The final atomic coordinates and anisotropic displacement parameters are listed in Table 2 and Table 3.

4. Results and Discussion

The structure of the C phase is mainly composed of a three dimensional (3-D) framework consisting of two types of icosahedra composed of TM atoms, and the interspaces of the framework are filled by Al atoms (Fig. 2). One type of icosahedron is a regular icosahedron (H-ICO; Fig. 3, (a-ii)) composed of twelve M(3) sites with a center M(1) site, and the other type is a distorted icosahedron (D-ICO; Fig. 3, (a-i)). The present structural model indicates a short distance between Al(6) and M(3) equal to 0.215 nm (symmetry code ii: y, z, x), and this value is unusually shorter than the common Al–Ru/Ni bond distances (0.241–0.257 nm15). This inconvenience also supports the structural disorder associated with the Al(6) site. These features indicate the feasible introduction of the split-site model for the Al(6) site; nevertheless, such structural modeling did not remove such inconvenience. Thus, the extraordinary anisotropic Al(6) site was employed in the model. It should be also noted that the present structural refinement utilized a chemical constraint to maintain the compositional ratio of Ru/Ni at 5.1/2.9. This procedure allows us to obtain the chemical composition of the structural model Al$_{20.5}$Ru$_{5.1}$Ni$_{2.9}$, which is compatible with Al$_{20.5}$Ru$_{5.1}$Ni$_{2.9}$ obtained by EPMA. The final atomic coordinates and anisotropic displacement parameters are listed in Table 2 and Table 3.
the other is the irregularly shaped icosahedron (HM-iICO; Fig. 3, (b-ii)) composed of M(3) sites with a center M(2) site. Since the center sites M(1) and M(2) are located at 1a and 1b (corresponding to m3 in site symmetry; Fig. 2), respectively, an H-ICO is connected to six neighboring H-ICOs in the direction of the twofold axis, sharing an edge, and to eight HM-iICOs in the direction of the threefold axis, sharing a triangular face. An HM-iICO is also connected to six HM-iICOs, sharing an edge in the direction of the twofold axis, and to eight H-ICOs, sharing a triangular face in the direction of the threefold axis.

The H-ICO has the inner shell of an Al-cube (Fig. 3, (a-i)) composed of eight Al(5) sites, and the outer shell of the Al distorted icosidodecahedron (Al-ICSID: Fig. 3, (a-iii)) is composed of thirty-two Al(4) and eight Al(6) sites, indicating the atomic arrangement of a pseudo-Mackay cluster (pMC). An Al-ICSID of a pMC is connected to a neighboring Al-ICSID, sharing five Al vertexes including four Al(4) sites and one partially occupied Al(6) site (Fig. 4, (a-iii)-(a-iii)). The structure determined for C-AlRuNi is very similar to the structures of IrAl2.75 and RhAl2.638), which also have a systematic distribution of pMCs, and one pMC is connected to a neighboring pMC along [100]. Two Al-ICSIDs of a pMC in IrAl2.75 and RhAl2.63 interpenetrate each other, sharing four Al sites corresponding to Al(4) of C-AlRuNi, and the Al position at the midpoint of the connection between pMCs corresponding to Al(6) of C-AlRuNi is not present in IrAl2.75 and RhAl2.63. The pMCs of IrAl2.75 and RhAl2.63 have dodecahedral first shells having 9.88 and 9.04 Al atoms considering occupation, respectively, and the space inside the TM icosahedron is tight. However, C-AlRuNi has a very compact cubic first shell (Al-cube) having 5.9 Al atoms considering occupation, and the space inside the H-ICO seems loose. Considering the structural disorder of Al(6) along the twofold axis suggested by the very large component of the anisotropic parameter, the first shell of C-AlRuNi then has 8.23 atoms (i.e., 0.74 (atoms/site for Al(5)) × 8 (sites) + 0.77 (atoms/site for Al(6)) × 2 (one Al(6) site is shared by two pMCs) × 6 (sites) = 8.23 atoms). This value is comparable to the values for IrAl2.75 and RhAl2.63. Thus, some positional variation is suggested for the Al(6) atom.

On the other hand, an HM-iICO has an inner shell of an Al-ICO (Fig. 3, (b-ii)) composed of twelve Al atoms of Al(4) sites and an outer shell of a large Al-cube (Al-cube; Fig. 3, (b-iii)) composed of eight Al(5) sites. From the viewpoint of the Al distribution, the Al-ICO and Al-ICSID are also located at m3, and one Al-ICO is connected to six neighboring Al-ICOs in the direction of the twofold axis (Fig. 3, (a-iii)=(a-iii)) and eight Al-ICSIDs in the direction of the three-fold axis (Fig. 3, (a-iii)=(b-ii)).

Focusing on the pMCs and Al-ICO clusters, both are also located at m3 in C-AlRuNi; therefore, the pMCs and Al-ICO clusters are distributed similarly to the CsCl structure, as shown in Fig. 4(a). In other words, the pMC is distributed at the lattice point of the simple cubic lattice with the glue cluster Al-ICO for the C phase. The manner of pMC packing with the glue cluster Al-ICO is also found in C1-AlPdFe4), as shown in Fig. 4(b), (c), (d), and (e), respectively.

It is interesting to discuss the chemical compositions for the 1/0 approximants by using the structural variation in the pMCs. There are two types of pMCs having different first shells. The first shell of one pMC (pMC-A, hereafter) is composed of a body-centered cubic (b.c.c.) arrangement with TM and Al atoms, and the other pMC (pMC-B, hereafter) is composed of Al polyhedron around a central atom3,4,6). The pMC in the C phase is categorized as pMC-B. The structural features in the first shells of the pMCs indicate that pMC-A has more TM atoms than pMC-B. The pMC-As of the C1 and C2 phases are distributed at the lattice points of a b.c.c. lattice (Fig. 4(b)) and face-centered cu-

### Table 2

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<th>Atom</th>
<th>Site</th>
<th>Occupation</th>
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<td>M(2)</td>
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<td>1/2</td>
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* The M(1), M(2), and M(3) sites are mixed sites, and their occupations (M = Ru/Ni) were refined by the mixed-site model.

### Table 3

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<th>Atom</th>
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<th>$U_{33}$</th>
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<td>M(3)</td>
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<tr>
<td>Al(4)</td>
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<td>0.0095(8)</td>
<td>0.0112(8)</td>
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<td>Al(5)</td>
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<td>$-0.0091(8)$</td>
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<td>0.012(4)</td>
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bic lattice (Fig. 4(c)), respectively. Thus, the ratio \( pMC-A / pMC-B \) in the C2 phase is greater than that in C1 phase. It is consistent that the C2 phase is located in the more TM-rich region of the phase diagram than the C1 or C phases (Fig. 1).

5. **Summary and Concluding Remarks**

The structure of C-AlRuNi \((Al_{20.2}Ru_{5.1}Ni_{2.9})\) was determined by single-crystal X-ray diffraction. The structure can be explained by a framework composed of TM icosahedral clusters around M(1) and M(2), and the interspaces in the TM framework are filled by Al atoms. The icosahedral cluster around M(1) is a regularly shaped icosahedron of a TM (H-ICO). An H-ICO includes an inner Al cube (Al-cube) and is covered by the large outer Al cube (Al-Lcube). The (a-iii)-(a-iii) and (a-iii)-(b-i) connections are also shown.

Fig. 3 Regular icosahedron around M(1) (=Ru/Ni) sites (H-ICO; (a-ii)). An H-ICO has an inner Al cube (Al-cube; (a-i)) and an outer Al distorted icosidodecahedron (Al-ICSID; (a-iii)). They form a pseudo-Mackay cluster. The irregularly shaped icosahedron around the M(2) sites (HM-iICO; (b-i)) is also drawn. An HM-iICO has an inner Al icosahedron (Al-ICO; (b-ii)) and is covered by the large outer Al cube (Al-Lcube; (b-iii)). The (a-iii)-(a-iii) and (a-iii)-(b-i) connections are also shown.

Fig. 4 Distribution of pMCs (spheres) with glue cluster Al-ICOs (icosahedra) for (a) C-AlRuNi, the (b) C1 and (c) C2 phases of AlPdFe\(^{3}\), (d) R-AlPdCo\(^{3}\), and (e) F-AlPdCoGe\(^{3}\).
cludes a small Al-ICO and is covered by an Al-Lcube. M(1) and M(2) are located at \(m\bar{3}\), and the clusters around M(1) and M(2) are distributed similar to the CsCl structure. Focusing on the pMCs and Al-ICO clusters, the structure of C-AlRuNi can be explained by the packing of pMCs with the glue cluster Al-ICO. The packing of pMCs with the glue cluster Al-ICO is also realized in the C1 and C2 phases, and the manner of packing must be a common one for the cluster distribution in the approximant of Al–TM ternary system, irrespective of the crystal system.

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REFERENCES