Crystal structure of χ-AlNiRu containing pseudo-Mackay Clusters

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Abstract. χ-AlNiRu (H-AlNiRu), as determined by single crystal X-ray diffraction, crystallizes in the trigonal space group, $P31c$ (No.159), with unit cell parameters of a = 1.2095(1) nm, c = 2.6879(1) nm, and V = 3.4056(3) nm^3, and atoms/cell = 208.6. The refinement converged with $R(F)$ = 0.087 for 3915 observed reflections measured using Mo $K\alpha$ radiation (λ = 0.071073 nm). The structure of χ-AlNiRu is similar to that of χ-AlPdRe, wherein pseudo-Mackay type clusters are formed by the disordered distribution of Al in the heavy metal framework.

1. Introduction

Pseudo-Mackay clusters (pMC) are a common structural unit of quasicrystalline approximants, and a variety of linkages between pMCs have been described in previous reports [1–5]. For the ternary Al-Ni-Ru system, two types of decagonal phases (D-phases) have been reported, and high-resolution transmission electron microscopy and large-angle annular detector dark-field scanning transmission electron microscopy have been used for obtaining structural images of D-phases [6, 7]. Furthermore, an H-phase (hereafter, denoted χ-AlNiRu) with a chemical composition similar to that of the D-phase has been reported [8]. Herein, we report pMCs and their linkages within the structure of χ-AlNiRu. The Al-Ni-Ru system indicates the decagonal approximants of monoclinic and orthorhombic and cubic phases [9-11]. In comparison with the D-phases, an icosahedral AlNiRu phase has also been reported in the Ni-rich region [12].

2. Experimental

An alloy ingot with a composition of $Al_{77}Ni_{16}Ru_7$ was prepared by conventional arc melting in a purified Ar atmosphere. Fragments of the as-prepared ingot were charged into a carbon crucible, and the crucible was placed in an evacuated silica tube. The fragments were first heated to 1100 °C, subsequently cooled to 800 °C, and annealed at this temperature for 5 h. The annealed sample was mainly composed of χ-AlNiRu phase. Electron probe microanalysis (EPMA: JEOL JXA-8621MX) showed that the average chemical composition of χ-AlNiRu was $Al_{75.9}Ni_{16.2}Ru_{8.2}$. A small amount of a crystalline $Al_3Ni(Al_{74.1}Ni_{23.6}Ru_{2.1})$ phase was also found in the annealed sample. A single-crystal specimen of χ-AlNiRu was cut from the annealed sample and used for single-crystal X-ray diffraction analysis. Intensity data for 12997 reflections ($-8 \le h \le 15$, $-15 \le k \le 10$, $-34 \le l \le 34$) were collected using a Rigaku R-AXIS RAPID system equipped with an imaging plate. Data reduction, assuming trigonal $P31c$ symmetry yields 5187 reflections ($R_{int}(I)$ = 0.0394), among which 3915 reflections meet the condition of $F_o > 4.0\sigma(F_o)$. Lattice constants of a = 1.2095(1) nm and c = 2.6879(1) nm were

determined by least-squares method, as implemented in the RAPID-AUTO system. Absorption correction was carried out using an integration method, assuming an arbitrary shape for the specimen. An initial structural model for χ-AlNiRu was obtained by direct methods using SIR97 [13]. Subsequently, the structure refinement was carried out by least-squares method (SHELXL-97) [14].

Table 1. Fractional coordinates of trigonal χ-AlNiRu.

Atom	Site	Occupation	*x*	*y*	*z*	$U_{eq.}$ ($U_{iso.}$)
Ru1	6*c*	1	0.5383(2)	0.4614(2)	0.1615(2)	0.0123(5)
Ni/Ru2	6*c*	0.86/0.14(3)	0.1196(3)	0.2397(3)	0.3768(2)	0.0118(11)
Ni/Ru3	6*c*	0.88/0.12(3)	0.4088(3)	0.2045(3)	0.0283(2)	0.0073(11)
Ni/Ru4	2*a*	0.94/0.06(4)	0	0	0	0.0057(12)
Ni5	6*c*	0.51(5)*	0.2373(9)	0.103(2)	0.2496(3)	0.0093(6)*
Ni5′	6*c*	0.49(5)*	0.2366(10)	0.134(2)	0.2495(3)	0.0093(6)*
Ru/Ni6	2*b*	0.86/0.14(5)	1/3	2/3	0.1033(3)	0.0165(13)
Ru/Ni7	6*c*	0.58/0.42(4)	0.4097(3)	0.2051(3)	0.4683(2)	0.0214(11)
Ni8	6*c*	1	0.2272(4)	0.4544(1)	0.2481(3)	0.0088(4)
Ni/Ru9	2*b*	0.51/0.49(5)	1/3	2/3	0.3937(3)	0.0102(15)
Ru/Ni10	6*c*	0.74/0.26(4)	0.5389(2)	0.4607(2)	0.3355(2)	0.0084(8)
Ni11	6*c*	1	0.1201(3)	0.2405(3)	0.1207(2)	0.0131(7)
Al1	2*a*	1	0	0	0.2496(6)	0.0168(17)
Al2	6*c*	1	0.1622(7)	0.0810(7)	0.1638(3)	0.0095(13)
Al3	6*c*	1	0.4274(8)	0.2127(7)	0.3048(4)	0.0138(17)
Al4	6*c*	1	0.0027(8)	0.3892(7)	-0.0005(3)	0.0172(14)
Al5	6*c*	1	0.3864(7)	0.3890(7)	-0.0005(3)	0.0166(14)
Al6	6*c*	1	0.2156(7)	0.4311(7)	0.0616(4)	0.0135(13)
Al7	6*c*	1	0.3465(8)	0.2891(8)	0.1035(3)	0.0163(16)
Al8	6*c*	1	0.0891(7)	0.5442(7)	0.0879(4)	0.0234(15)
Al9	6*c*	1	0.3465(7)	0.0583(8)	0.1034(3)	0.0166(17)
Al10	6*c*	1	0.3466(7)	0.2936(7)	0.3949(3)	0.0108(14)
Al11	6*c*	1	0.3462(7)	0.0539(7)	0.3950(3)	0.0120(15)
Al12	6*c*	1	0.115(1)	0.234(2)	0.2211(6)	0.075(4)
Al13	6*c*	1	0.1636(8)	0.0818(9)	0.3366(4)	0.0204(17)
Al14	2*b*	1	1/3	2/3	0.0140(12)	0.092(9)
Al15	6*c*	0.50(1)*	0.1588(14)	0.4543(14)	0.1591(6)	0.026(2)*
Al15′	6*c*	0.50(1)*	0.2946(14)	0.4529(14)	0.1593(6)	0.026(2)*
Al16	6*c*	1	0.5894(7)	0.4120(7)	0.0689(3)	0.0083(13)
Al17	2*b*	1	2/3	1/3	0.1523(5)	0.009(2)
Al18	2*b*	1	2/3	1/3	0.3435(5)	0.016(3)
Al19	6*c*	1	0.5900(8)	0.4114(8)	0.4265(3)	0.0171(16)
Al20	6*c*	1	0.5866(9)	0.4129(9)	0.2482(4)	0.0105(8)
Al21	6*c*	1	0.4468(8)	-0.1063(8)	0.3865(4)	0.0421(19)
Al22	6*c*	1	0.4228(10)	0.2106(9)	0.1892(4)	0.027(2)
Al23	2*a*	0.77(2)*	0	0	0.0879(5)	0.010(2)*
Al23′	6*c*	0.23(3)*	0.156(3)	0.063(3)	0.0660(10)	0.010(2)*
Al24	6*c*	1	0.0403(9)	0.3375(9)	0.3020(4)	0.0385(19)
Al25	6*c*	1	0.2960(9)	0.3370(9)	0.3020(4)	0.0383(19)
Al26	6*c*	1	0.4590(9)	0.5406(9)	0.2560(4)	0.0365(19)
Al27	6*c*	0.60(1)*	0.1587(13)	0.0731(13)	0.4337(5)	0.0222(19)*
Al28	6*c*	0.60(1)*	0.2078(14)	0.4143(13)	0.4354(6)	0.0222(19)*
Al29	2*b*	1	1/3	2/3	0.2993(14)	0.111(12)
Al30	2*b*	0.47(2)*	1/3	2/3	0.4877(9)	0.015(2)*
Al30′	6*c*	0.53(2)*	0.5859(11)	0.4135(11)	-0.0247(5)	0.015(2)*
Al31	2*b*	1	1/3	2/3	0.2012(7)	0.044(4)
Al32	6*c*	0.40(1)*	0.1113(16)	0.2230(17)	0.4708(7)	0.0222(9)

*See text

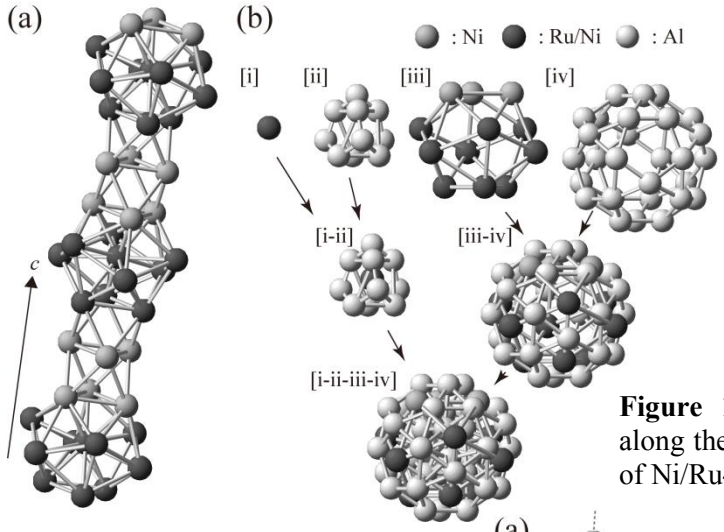

Figure 1. (a) The linkage of Ni/Ru4-pMC along the *c*-axis and (b) detailed shell structure of Ni/Ru4-pMC.

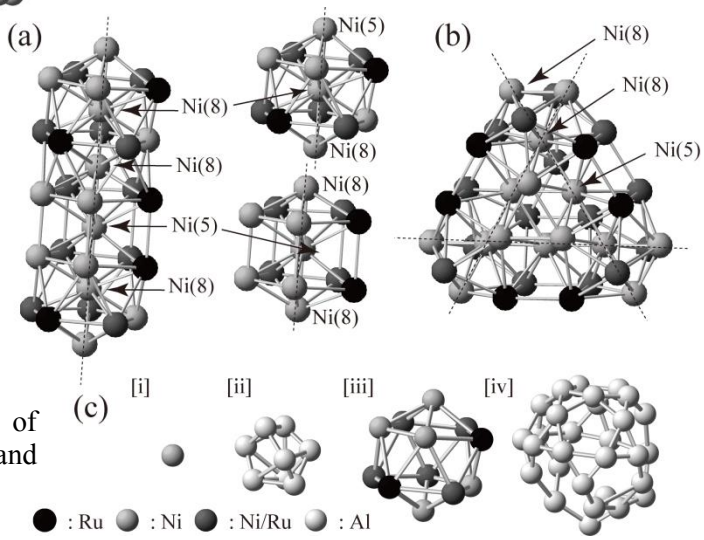

Figure 2 (a) The columnar structure of heavy metal polygons, (b) i3 cluster, and (c) imperfect Ni8-pMC.

The obtained structural model indicates a similar atomic arrangement to that of χ-AlPdRe [15], yielding 47 independent atomic sites per unit cell. Ten heavy metal sites and thirty-one Al are fully occupied by the respective elements, whereas the other sites are either partially occupied or disordered. After several least-squares iterations, the Fourier maps indicated the location of the possible paired sites at Ni5/Ni5′, Al15/Al15′, Al23/Al23′, Al27/Al32, Al28/A32, and Al30/Al30′. Because the short calculated distances exclude simultaneous occupation of these paired sites, we introduced a restriction that the sum of the occupancies for each pair is 1.0. During the structural refinement, the isotropic temperature factors for the paired Al sites were constrained to be equal. After modeling the disorder and refining the fully occupied heavy metal sites anisotropically, the refinement finally converged to an $R(F)$ of 0.086 for all observed reflections. The maximum and minimum residual electron densities are 4.66 and -2.24 eÅ^{-3}, respectively. The obtained chemical composition $Al_{74.1}Ni_{17.1}Ru_{8.8}$ is consistent with $Al_{75.9}Ni_{16.2}Ru_{8.2}$, as determined by EPMA. The final atomic coordinates and isotropic or equivalent temperature factors are listed in Table 1. The calculated atomic distances are reasonable except for the previously mentioned paired sites.

3. Results

The distribution of heavy metal sites of χ-AlNiRu can make a unique substructure with space group symmetry $P6_3/mmc$. Nevertheless, the remaining Al sites reside in the interstitial space of the substructure, resulting in the symmetry reduction toward subgroup symmetry $P31c$. This feature in the mode of elemental distribution leads to a local structure without direct bonding between heavy metals

in the first nearest neighbor region. Notably, the substructure composed of heavy metal sites is isotypic with the structures of χ-AlPdRe and Ir_9Al_{28} [16] and significant structural differences are only present in the distribution of Al sites. Figure 1(a) shows the connected heavy metal icosahedra around Ni/Ru4 along the *c*-axis via the Ni5 or Ni5′ triangles, and a pMC with a heavy metal center is realized around Ni/Ru4. As shown in Fig. 1(b), the first irregular coordination shell is composed of disordered Al sites Al23, Al23′, Al27, and Al32. The second shell (Fig. 1(b-iii-iv))) may be grouped into two sub-shells. An icosahedron is produced by Ni/Ru2, Ni/Ru3, Ru/Ni7, and Ni11 and each vertex of the icosahedron is coordinated by five outer Al atoms, forming Al-icosidodecahedrons. It may be added that similar pMC with a disordered inner shell are also found in the approximants of *R*-AlPdCo [1] and χ-AlPdRe. Figure 2(a) shows the substructure units of Ni8-centered icosahedrons and Ni5(Ni5′)-centered bi-capped pentagonal prisms composed of heavy metals. The Ni8-centered icosahedra interpenetrate, producing an I-type connection (Fig. 2(b)) [17]. Such I-type connections are further connected via a common vertex at Ni5 (Ni5′) forming a pentagonal columnar structure along the *a*-axis. Figure 2(c) shows the Al distribution of the inner and outer area of the Ni(8)-centered icosahedrons. The first irregular coordination shell is composed of Al12, Al15′, Al15′, Al24, Al25, Al26, Al29, and Al31, similar to the case of the pMC around Ni/Ru4. The second shell is ranked into sub-shells of a heavy metal icosahedron and an imperfect Al-icosidodecahedron. The heavy metal icosahedron is composed of Ru1, Ni/Ru2, Ni5 (Ni5′), Ru/Ni6, Ni8, Ni/Ru9, Ru/Ni10, and Ni11 (Fig. 2(c-iii)). Interestingly, the pseudo five-fold axes along the neighboring Ni8 is broken in the outer Al-icosidodecahedron. Nevertheless, the distribution of Al in other directions indicates some similarities with Mackay cluster geometry.

4. Conclusion

The crystal structure of χ- AlNiRu was determined using single-crystal X-ray diffraction. The Heavy metal distribution corresponds to that in χ-AlPdRe and Ir_9Al_{28}, wherein the Al sites at the interstitial spaces of heavy metals are disordered. The atomic arrangement of the heavy metals is well featured by the unit structure composed of Ni/Ru4 and Ni8-centered pMCs. In particular, the Ni8-pMC shows the linkage of pMCs toward the five-hold direction running parallel to the *a*-axis and an aggregation of three pMCs in the I3 cluster. The knowledge of these structural units and their linkage would provide an image leading the structure of D- and I-phases of the AlNiRu system.

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