A new superlattice structure in the $Al_{2.75}Ir$ and $Al_{2.63}Rh$ 1/0 approximants

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Abstract. We investigate the superstructure of binary $Al_{2.75}Ir$ and $Al_{2.63}Rh$ 1/0 approximants by X-ray diffraction method and transmission electron microscopy. $Al_{2.75}Ir$ possesses a $2a \times 2a \times 2a$ *C*-centred monoclinic lattice with space group *C2* or *Cm* or *C2/m*. $Al_{2.63}Rh$ possesses a $2a \times 2a \times 2a$ face centred lattice with space group *F23* or $Fm\bar{3}$.

1. Introduction

Binary $Al_{2.75}Ir$ and $Al_{2.63}Rh$ are 1/0 approximants of ternary Al-TM quasicrystals. The structure of $Al_{2.75}Ir$ and $Al_{2.63}Rh$ have been investigated by XRD, and $Al_{2.75}Ir$ and $Al_{2.63}Rh$ possess a primitive cubic lattice with space group *P23* (the lattice parameter $a = 7.674(1)$ Å and $a = 7.6692(1)$ Å, respectively) [1]. Fig.1 shows schematic crystal structure of (a) $Al_{2.75}Ir$ and (b) $Al_{63.3}Cu_{12.3}Ir_{24.4}$ phases. In the case of $Al_{2.75}Ir$, the primitive cubic lattice is composed by Ir_{12} (green circle) icosahedron containing central Ir atom and 9~10 Al atoms (small yellow circle). It should be noted that the Al sites inside the Ir icosahedron are partially occupied with a pentagon-dodecahedral like distribution and surround central Ir atom. In contrast, the structure of ternary Al-Cu-TM 1/0 approximants are different from the binary Al-TM 1/0 approximants. The ternary Al-Cu-TM 1/0 approximants possess the double $Fm\bar{3}$ lattice with the lattice constant =15.3844(2) Å $(2a \times 2a \times 2a)$ due to the ordered Cu site inside of the TM icosahedron [2, 3]. Therefore, the structure of Al-Cu-TM 1/0 approximant is a $2a \times 2a \times 2a$ FCC (space group $Fm\bar{3}$).

In the case of Al-Ir, the order-disorder phase transition of Al inside TM icosahedron is predicted by theoretical calculation using pair potentials fitted to an ab initio database [4]. Moreover, Mihalkovič reported that the ordered phase of $Al_{2.75}Ir$ is possibly insulate phase. Similarly, for $Al_{2.73}Ir$, very weak superlattice reflections were reported in the selected area electron diffraction patterns (SAED) [5]. Hence, it is necessary to investigate the superlattice structure of binary Al-TM(TM = Ir, Rh) 1/0 approximants.

In the present work, we have investigated the superstructure and the composition dependence of the $Al_{2.75}Ir$ and $Al_{2.63}Rh$ by the powder X-ray diffraction (XRD) method and transmission electron microscopy (TEM) study to understand the behaviour of atoms inside TM icosahedral clusters.

2. Experimental

Al-TM(TM=Ir, Rh) with composition ranging from 70 to 75 % Al were melted by arc method under an argon atmosphere (Al (99.99%), Rh (99.9%) and Ir (99.9%)). And the samples were annealed at 1373K for about 72 hours or 723K for 3 days in the quarts tube under the argon atmosphere, followed by water quenching. Powder X-ray diffraction experiments were carried out using Cu Kα to examine the phase constitution. Additionally, TEM study were performed by JEOL -TKP2 or TOPCON-002b operating at 200kV. The samples for TEM were crushed by agate mortar and dispersed on a copper micro-grid mesh.

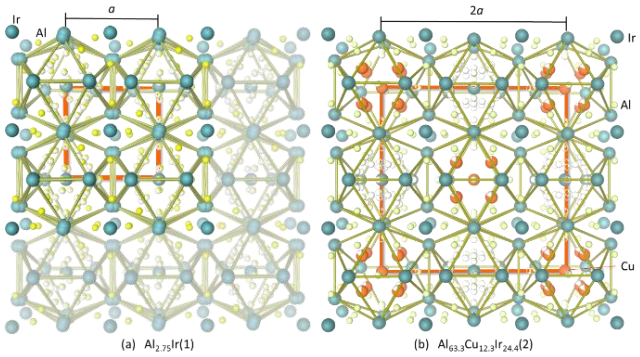

Fig. 1. Crystal structures of (a) $Al_{2.75}Ir$ with an $a \times a \times a$ lattice (space group *P23*) [1] and (b) $Al_{63.3}Cu_{12.3}Ir_{24.4}$ with an $2a \times 2a \times 2a$ lattice (space group $Fm\bar{3}$)[2]. The Al sites (small circle) inside the Ir icosahedron are partially occupied with a pentagon-dodecahedral-like distribution.

3. Results and discussions

3.1. XRD

Fig. 2 shows XRD patterns of (a) $Al_{73}Ir_{27}$, (b) $Al_{73.5}Rh_{26.5}$ and (c) $Al_{72.5}Rh_{27.5}$. The most peaks are indexed by an $a \times a \times a$ lattice with reported space group *P23*, but weak superlattice peaks appeared. In Fig. 2, superlattice peaks are indicated by black circles and open circles. For $Al_{73}Ir_{27}$, the superlattice peaks can be indexed as $2a \times 2a \times 2a$ lattice. In addition, the peaks parallel to the (100) seem to be split into two peaks, when the $K\alpha_2$ removed. Then, it is possible that the superlattice structure is monoclinic.

On the other hand, for Al-Rh, $Al_{2.63}Rh$ phase is observed in the composition range of Al70~74.5%. Indexed as a $2a \times 2a \times 2a$ lattice, the indexes ($h_Fk_Fl_F$) satisfied the reflection condition ($h_Fk_Fl_F$; h_F+k_F, k_F+l_F, l_F+h_F = even. It is possible that the superlattice structure possesses FCC lattice with a lattice constant a_F (= $2a$) = 15.340Å. Additionally, superlattice peaks disappeared in the poorer Al compositions below Al72.5%. The composition dependence on the superstructure suggests that the number of Al inside the TM icosahedron contribute to the superstructure.

3.2. TEM

3.2.1 $Al_{2.63}Rh$

Figure 3 shows selected area diffraction patterns of $Al_{72.5}Rh_{27.5}$ taken along [100], [110] and [111]. We observed the superlattice reflections at h/2 k/2 l/2 positions indicated by open triangle in the [110] SAED pattern. In the [111], there are no superlattice reflections, suggesting that the superlattice structure is cubic lattice. All the superlattice reflections can be indexed by considering a $2a \times 2a \times 2a$ lattice ($h_Fk_Fl_F$), and satisfy the FCC reflection condition ($h_Fk_Fl_F$; h_F+k_F, k_F+l_F, l_F+h_F = 2n). Therefore, the superlattice of $Al_{2.63}Rh$ can be explained as $2a \times 2a \times 2a$ *F23* or $Fm\bar{3}$.

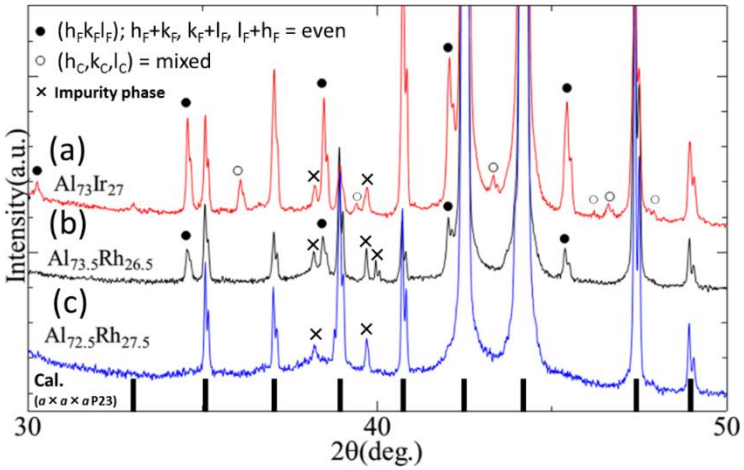

Fig. 2. XRD patterns of (a) $Al_{73}Ir_{27}$, (b) $Al_{73.5}Rh_{26.5}$ and (c) $Al_{72.5}Rh_{27.5}$.

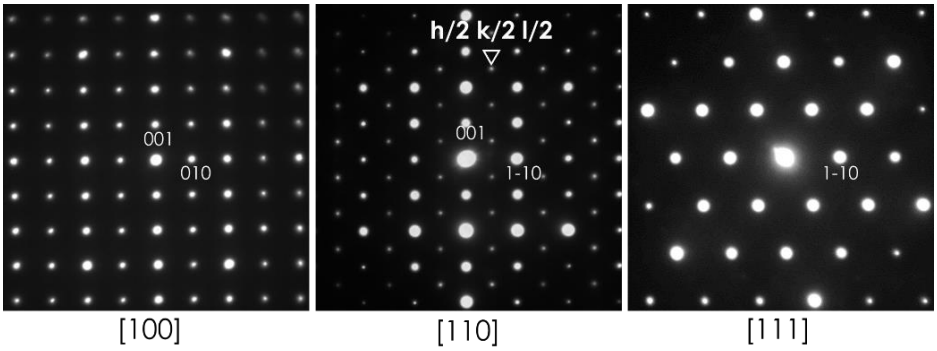

Fig 3. Selected area electron diffraction patterns of Al-Rh taken along [100], [110], [111] and (b) a bright field TEM image.

3.2.2 $Al_{2.75}Ir$

Figure 4 presents SAED patterns of $Al_{73}Ir_{27}$ taken along [100], [001]. [110]. [011] and [111]. We observed the superlattice reflections at h/2 k/2 l/2, h/2 k/2 0 and 0 0 l/2 positions indicated by open and filled triangles. Thus, all the superlattice reflections can be indexed by considering a $2a\times2a\times2a$ lattice ($h_Ck_Cl_C$). In the case of [111], the superlattice reflections appeared at the point to break the cubic 3-fold symmetry. It indicates that the superlattice structure are not cubic lattice. Considering the XRD result, it is possible that the $Al_{2.75}Ir$ possesses a monoclinic lattice. Moreover, all reflections satisfy the *C*-centred lattice reflection condition ($h_Ck_Cl_C$; $h_C+k_C=2n$). Therefore, the superlattice structure of $Al_{2.75}Ir$ is $2a\times2a\times2a$ *C2* or *Cm* or *C2/m*.

Fig 5 shows TEM images of $Al_{7.25}Ir$ annealed at 723K for 3 days ((a, b) and (c) a HRTEM image. (b) and (c) were taken along [100]). In Fig. 5(a), dark contrast line indicates domain boundary of ordered phase due to the structural phase transition. The structural phase transition might be same mechanism of order-disorder phase transition of Cd_6M 1/1 approximants at about 100 K [6]. The domain structure is the rectangular shape of about a few 100 nm. Also, in the SAED taken from domains (Fig.5b), there are diffuse streaks along [001]. Additionally, many dark parallel lines generated by stacking faults can be recognized thickly at intervals of a few dozen nm parallel to (001) in the domains (Fig. 5b). It implies that the stacking of ordered clusters tend to easily disarranged to [001]. To obtain the insulate

phase for Al-Ir phase, it is interesting to investigate the electronic state of superlattice structures and lattice defects.

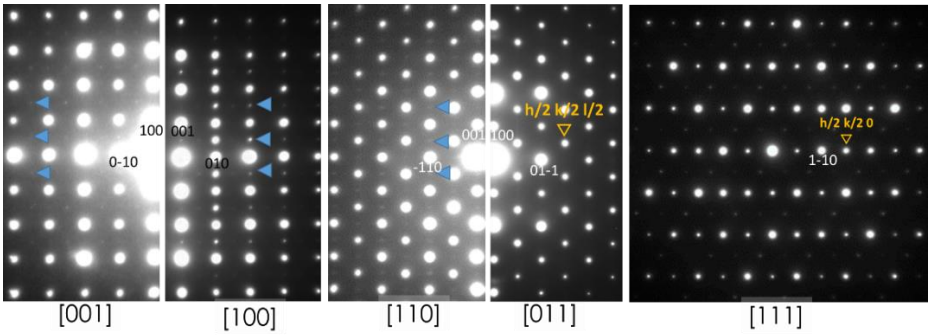

Fig 4. Selected area electron diffraction patterns of $Al_{7.25}Ir$ taken along [100], [110], [011] and [111] annealed at 1373K for 72h.

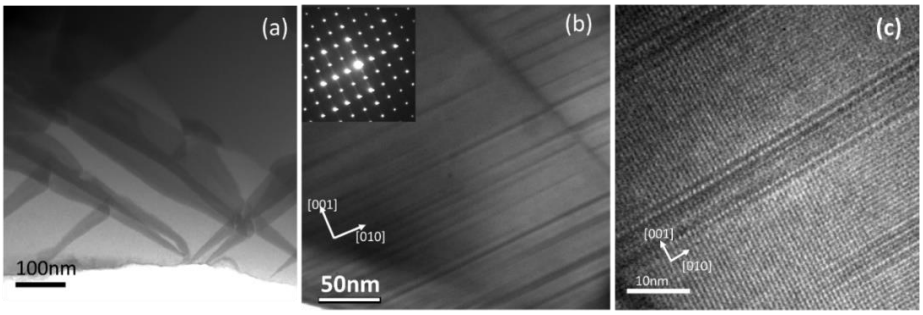

Fig. 5 (a) Bright field TEM image of Al2.75Ir annealed at 723k for 3 days. (b) BF and (c) lattice images were taken along [100].

In this work, we reported the new superlattice structure of binary $Al_{2.75}Ir$ and $Al_{2.63}Rh$ phases, which was effected by number of Al atoms in side TM(TM = Ir, Rh) icosahedron cluster. $Al_{2.75}Ir$ possesses a $2a \times 2a \times 2a$ monoclinic lattice with space group *C2* or *Cm* or *C2/m*. $Al_{2.63}Rh$ possesses a $2a \times 2a \times 2a$ face centred lattice with space group *F23* or $Fm\bar{3}$. The composition dependence of superlattice reflections suggest that the superlattice strucuture is determined by the number of ordered Al atoms inside TM icosahedron.

Acknowledgements

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