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 $Fm\bar{3}$.

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$_{2.75}$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 quartz 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.

3. Results and discussions

3.1. XRD

Fig. 2 shows XRD patterns of (a) Al\(\frac{73}{27}\)Ir, (b) Al\(\frac{73.5}{26.5}\)Rh and (c) Al\(\frac{72.5}{27.5}\)Rh. 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\(\frac{73}{27}\)Ir, 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\(\frac{2.63}{2.63}\)Rh phase is observed in the composition range of Al70~74.5%. Indexed as a \(2a \times 2a \times 2a\) lattice, the indexes \((hFkFlF)\) satisfied the reflection condition \(hFkFlF; hF+kF, kF+lF, lF+hF = even\). It is possible that the superlattice structure possesses FCC lattice with a lattice constant \(a_F = 15.340\) Å. 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\(\frac{2.63}{2.63}\)Rh

Figure 3 shows selected area diffraction patterns of Al\(\frac{72.5}{27.5}\)Rh 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 \(2a \times 2a \times 2a\) F23 or \(Fm\bar{3}\). Therefore, the superlattice of Al\(\frac{2.63}{2.63}\)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 $2a \times 2a \times 2a$ lattice ($h, k, l \parallel c$). 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 ($h, k, l \parallel c$; $h + k + l = 2n$). Therefore, the superlattice structure of Al$_{2.75}$Ir is $2a \times 2a \times 2a$ $C2$ 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$_6$M $1/1$ 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.

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

Fig. 4.

![Bright field TEM image of Al_{2.75}Ir annealed at 723k for 3 days. (b) BF and (c) lattice images were taken along [100].](image)

Fig. 5 (a) Bright field TEM image of Al_{2.75}Ir 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 $Fm\overline{3}$. The composition dependence of superlattice reflections suggest that the superlattice structure is determined by the number of ordered Al atoms inside TM icosahedron.

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