

Sign of covalency in AlPdRe icosahedral quasicrystals obtained from atomic density and quasilattice constant

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Atomic density and quasilattice constant of AlPdRe icosahedral quasicrystals decreases and slightly increases, respectively, with increasing concentration of transition metals, which have smaller atomic radii. Average atomic packing could not be described simply by rigid sphere packing, that is, the covalent nature of icosahedral clusters may form in metallic bonds.

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Icosahedral AlPdRe quasicrystals possess the highest value of the electrical resistivity among all Al-based icosahedral quasicrystals, which reaches that of a heavily doped semiconductor.¹⁻³ The temperature coefficients of resistivity in this alloy system have the largest negative value. These nonmetallic characteristics, high resistivity and its negative temperature coefficient, have been explained by a combination of a Hume-Rothery pseudogap in the electron density of states at the Fermi level (E_F) and localization tendency of electrons near E_F .⁴ Nevertheless, the origin of pseudogap could be understood not only from the Hume-Rothery mechanism but also from the covalent nature of the icosahedral clusters. Atomic structures of the Al-based icosahedral phases have been described by quasiperiodic packing of the icosahedral multiple shell clusters such as Mackay icosahedron (MI) or Bergman cluster. Molecular orbital calculations have shown more covalent bonding nature for group III elements in a 12-atom icosahedral cluster without center atom, whereas a 13-atom one with center atom has more metallic one.⁵ Kirihara *et al.* reported a direct evidence of covalent bonds in the electron density distribution of nonmetallic α -AlMnSi icosahedral quasicrystalline 1/1 cubic approximant using MEM/Rietveld method.⁶ As shown in Fig. 1(a), the α -AlMnSi crystal has a bcc packing structure of the MI cluster, whose first shell is 12-atom icosahedron without a center atom.⁷ On the other hand, Al₁₂Re icosahedral quasicrystalline 1/0 cubic approximant has a bcc packing structure of 13-atom icosahedron, which is an Al₁₂ icosahedron with a central Re atom.⁸ It was found that in contrast with the covalent bonds in the 12-atom icosahedron in α -AlMnSi, no covalent bond exists for inter-Al atoms of the 13-atom icosahedron in Al₁₂Re. Variation in the bonding nature of the icosahedron in the approximant crystals could well depend on the center occupancy of the icosahedral cluster. Since MI cluster is also considered to be a basic space-filling unit of AlPdRe quasicrystal, the above bonding nature may be similar to the AlPdRe quasicrystal. Unfortunately, however, it is impossible to get electron density distribution for quasicrystal by the MEM/Rietveld method because of lack of periodicity in the atomic structure.

Kimura *et al.* suggested that metallic-covalent bonding conversion (MCBC) in icosahedral clusters of aluminum or boron is closely related to metal-nonmetal transition in both

Al-based icosahedral quasicrystals/approximants and B-based approximants.^{9,10} Three types of the atomic structure for the icosahedral approximants are shown in Fig. 1. The structural similarity up to the third shell between the Al-based approximants (a) α -AlMnSi, (b) α -AlLiCu,¹¹ and (c) β -rhombohedral boron (β -B) (Ref. 12) is clearly seen although the unit cell shapes of Al-based approximants and β -B are cubic and rhombohedral, respectively. The icosahedra in the first and the second shells are common in all three structures from (a)–(c). The soccer-ball-shaped cluster in the third shell is common in the structure of (b) and (c). As shown in Fig. 1, the atomic sites of the other clusters than icosahedron and soccerball in the second and third shells, which are occupied in case (a) and (b), are vacant in (c). β -B is a semiconductor whose electrical resistivity is 10^6 Ω cm at room temperature.¹³ As metallic atoms such as vanadium (V) are doped into the vacant site, which corresponds to exactly the dodecahedral site in the second shell of α -AlLiCu, the electrical resistivity and its temperature dependence approach to those of the Al-based icosahedral quasicrystals/approximants. The change in the electrical property was accompanied by hybridization of electronic states, i.e., metallic bond formation, between V and surrounding B atoms, which was suggested by ultra-violet photoemission spectroscopy and electron energy loss spectroscopy.¹⁴ We could expand the tendency of MCBC in the center of icosahedron into the vacant sites in the second and third shells. In α -AlMnSi, the vacant sites in β -B correspond to Al atom sites in the second and the third shell of the MI. Reduction of the occupancy of this Al atom sites may enhance the covalent bonding nature in the α -AlMnSi approximant and also in the AlPdRe quasicrystal.

Sawada *et al.* reported that both the quasilattice constant (QLC) and the electrical resistivity increase with increasing the concentration of transition metal (TM: Pd or Re) in AlPdRe icosahedral alloys.¹⁵ QLC means the length of the edge of rhombohedra, which are the building blocks of the icosahedral quasilattice structure. If the metallic bonds are dominant in the bonding nature of icosahedral phase, the atomic packing can be described by rigid sphere packing. Since the atomic radius (Goldschmidt radius) of Pd and Re, is smaller than that of Al, QLC should decrease with increasing TM concentration in this case. The quasilattice expansion

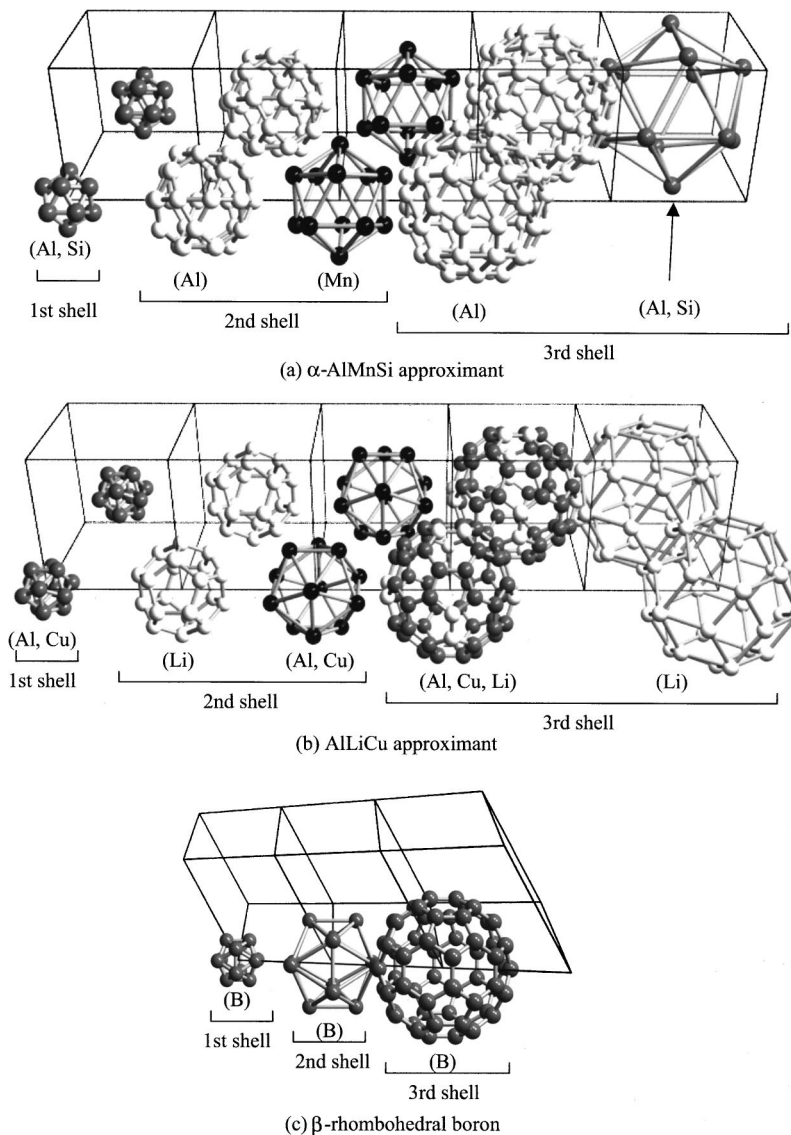


FIG. 1. Multiple shell structure of icosahedral quasicrystalline approximants. (a) α -AlMnSi 1/1 cubic approximant, (b) α -AlLiCu 1/1 cubic approximant, (c) β -rhombohedral boron (0/1-2/0 rhombohedral approximant).

reported by Sawada *et al.* means that the rigid sphere packing is not acceptable for the AlPdRe icosahedral alloys. Because of the lack of periodicity in quasicrystalline structure, it is not easy to determine specific atom sites where Al, Pd, and Re occupy and to get electron density distribution for the icosahedral quasicrystal. In order to discuss the bonding nature of AlPdRe quasicrystals, therefore, it is important to determine the atomic packing. The average atomic packing could be determined easily by atomic density, which is obtained from the absolute density measurement and the composition analysis of the phase.

In this paper, we report the atomic density together with the quasilattice constant. From these results, the characteristic of the average atomic packing and the bonding nature in AlPdRe icosahedral alloys are discussed.

Samples were prepared from elemental constituents by arc melting in an Ar atmosphere. The alloy ingots were turned over and remelted several times for homogenization. Bulk samples cut from the ingots were wrapped by Ta films, which act as oxygen getters, and sealed in quartz tube in Ar with low pressure (<100 Pa). Annealing condition was

950°C for 12 h. Annealed samples were quenched in water. The phase of samples was identified by x-ray diffraction. Microstructure investigations were performed using field emission type scanning electron microscope. The local composition was probed by energy dispersive x-ray spectroscopy. We have measured the variation of QLC and atomic density with increasing the concentration of transition metals. The atomic density can be estimated by the ratio of the absolute density to the average atomic weight. The absolute density was measured by the pycnometer (Shimatzu AccuPic 1330), using a helium displacement technique. The helium gas is filled up to a vessel, which the sample was inserted, and then expanded into an adjoining vessel. Since the volumes of these vessels are already known, the sample volume is estimated by change in the pressure with the expansion of the gas. This technique could avoid some experimental errors, which come from the viscosity or wettability between the liquid and the sample, occasionally facing in Archimedes method. Using this technique, reliable data can be provided even for the powder samples. In order to eliminate the closed pores in the sample, the bulk samples were ground into pow-

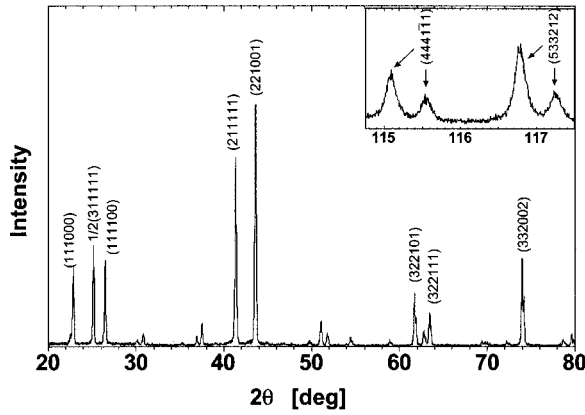


FIG. 2. X-ray powder diffraction pattern of AlPdRe icosahedral phases using Cu $K\alpha$ radiation. Inset shows the diffraction pattern in the high angle range for the analysis of quasilattice constant. Diffraction peaks from $K\alpha_2$ radiation are not subtracted.

der before the density measurements. The sample composition was analyzed by the inductive-coupled plasma emission spectrometry (ICP) and used for the calculation of the average atomic weight. The analyzed concentration of Al, Pd and Re are 67.6–74.8, 17.7–23.0, and 7.3–10.4 at.%, respectively. The powder x-ray diffraction patterns were measured using Cu $K\alpha$ radiation. The samples were mixed with Si powder (5N) as internal standard. The QLC was estimated using 2θ values of (444111) peak and (533212) peak in the 2θ range of 114° to 118° . These 2θ values of the samples were corrected by Si (531) peak position involved in the same range.

Figure 2 shows the powder x-ray diffraction pattern of AlPdRe icosahedral phase. The pattern in the 2θ range from 114.7° to 117.5° reveals that Cu $K\alpha_1$ profile can be easily distinguished from the Cu $K\alpha_2$ to determine the peak positions and QLC. Full width at half maximum was $0.09(1) \text{ nm}^{-1}$ for (533212) diffraction peak. Figure 3 shows TM concentration dependence of QLC and average atomic radius. Since Pd and Re have smaller atomic radius, 0.137 nm, than that of Al, 0.143 nm,¹⁶ the average atomic radius decreases with increasing the concentration of Pd and Re. Despite that, the QLC slightly increases with increasing the TM

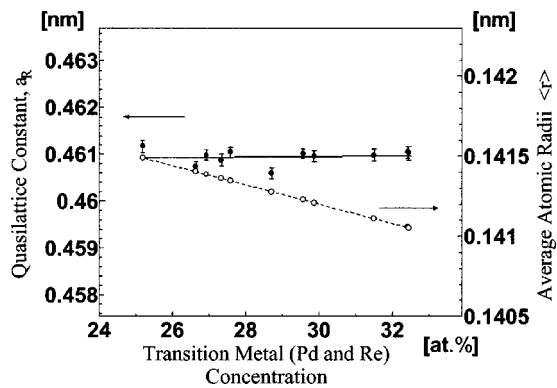


FIG. 3. Transition metal concentration dependence of quasilattice constant of icosahedral phases (closed circles). Open circles show the average atomic radii estimated by the sample composition.

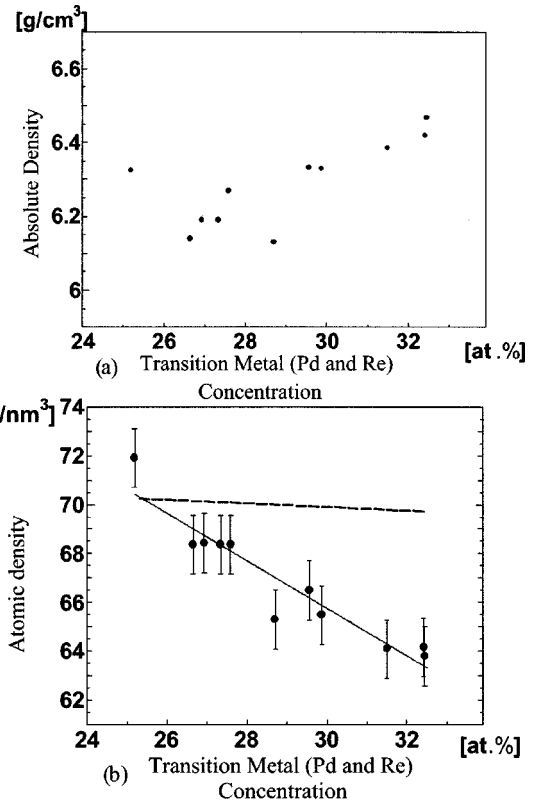


FIG. 4. Transition metal concentration dependence of (a) absolute density and (b) atomic density of icosahedral phases.

concentration. This tendency is similar to the results of the previous work.¹⁵ Figure 4 shows TM concentration dependence of (a) the absolute density and (b) the atomic density. The atomic density was determined from the absolute density divided by the average atomic weight and is represented by number of atoms per cube with 1 nm side length. When QLC increases without any change of atomic structure, number of atoms in the quasiunit cell is constant and atomic density decreases proportionally to QLC^{-3} . A dotted line in Fig. 4(b) shows the decrease of the atomic density caused by the expansion of quasilattice shown in Fig. 3. The atomic density determined from the absolute density decreases more rapidly than that estimated from the quasi-lattice expansion accompanied with the increase of the concentration of transition metals.

The above fact means a decrease in the occupancy of the specific atom site in the icosahedral quasicrystal. In spite of the occupancy reduction, i.e., the introduction of vacancy, the quasilattice constant slightly increases as shown in Fig. 3. Since atomic packing fraction is smaller for covalent bonding system than for metallic one, this is considered to be an increase of the covalent bonding nature in AlPdRe icosahedral quasicrystal. A net decrease in the atomic density was obtained where the TM concentration increases from 25.2 to 32.4 at.%. The decrease in the atomic density by the quasi-lattice expansion was subtracted. Because of the difficulty of structural analysis, as discussed above, we assumed that the local atomic structure model in AlPdRe icosahedral phase is MI cluster. Under this assumption, we estimated the decrease

in the number of atom per unit cell of 1/1 cubic approximant, in which the MI clusters have bcc packing. The unit cell size of the 1/1 cubic approximant was calculated using quasilattice constant of the AlPdRe samples. The decrease in the number of atoms, where the TM concentration increases from 25.2 to 32.4 at. %, is about 14.8 in 1/1 cubic unit cell. We could propose some candidates for the specific atomic sites with reduced occupancy, from the atomic structure shown in Fig. 1(a). The center of the icosahedral cluster should be a candidate for the specific atomic sites but number of this site is only two in 1/1 cubic unit cell. For α -AlMnSi structure, reduction of the occupancy of Al atom sites in second or third shell that corresponds to the vacant site in β -B may also enhance the covalent bonding nature as mentioned in the section of Introduction. We suppose that occupancy change, i.e., structural vacancy in these candidate atom sites could induce MCBC phenomena in the AlPdRe icosahedral quasicrystal. On the other hand, because the con-

centration of TM site in 1/1 α -AlMnSi cubic approximant structure is 17.4 at. %, TM should be substituted in Al (Si) sites for AlPdRe quasicrystal. When the TM concentration increases from 25.2 to 32.4 at. %, occupancies of TM in Al (Si) sites are considered to increase.

Tamura *et al.* recently reported the Re concentration dependence of lattice constant, electrical resistivity and its temperature coefficient of the α -AlReSi which is isostructural to α -AlMnSi.¹⁷ They showed that if the Re concentration increases from 11 to 17 at. %, the lattice constant enlarges 0.1% and the resistivity and its temperature coefficient rapidly increase. Lattice expansion of α -AlReSi with increasing the Re concentration is very similar behavior to our results in AlPdRe quasicrystal. We reported covalent bonds between Mn and Al (Si) in α -AlMnSi.⁶ When occupancy of Re in Mn site of Mackay icosahedron increases, covalent bonding nature should increase.

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