Composition-Dependent Electrical Resistivity in an Al-Re-Si 1/1-Cubic Approximant Phase: An Indication of Electron Confinement in Clusters

Ryuji Tamura, Takayuki Asao, and Shin Takeuchi

Department of Materials Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan

(Received 4 November 2000)

We report the synthesis of α-AlReSi and show that it is a 1/1-cubic approximant phase of the icosahedral quasicrystal with $a = 12.9$ Å. The trend of the resistivity of the new approximant phase shows a nonmetallic character, similar to those seen in the stable icosahedral phases. The resistivity depends sensitively on the Re concentration and the nonmetallic transport is observed only at the Re concentration close to 17.4 at. %, where the transition metal sites in the icosahedral cluster are exclusively occupied by Re atoms. In view of a recent *ab initio* calculation, the present result suggests strongly the formation of the virtual bound states, or confinement of electrons, in the icosahedral clusters of transition metal atoms.

DOI: 10.1103/PhysRevLett.86.3104 PACS numbers: 71.23.Ft, 72.15.–v

The insulatorlike behavior of the icosahedral phase (i-phase) such as seen in the i-AlPdRe [1–4] has been a challenging puzzle for modern physics. The experimental results suggest the proximity of the metal-insulator transition is due to the presence of localized states at the Fermi level (E_F). However, until now the question as to the origin of such localized states, whether it is due to the long-range quasiperiodicity or to the local structural environment or to some kind of structural disorder, has not been fully answered yet. On the other hand, the role of the d orbitals in the electronic transport is supposed to be of significance [5], since very high resistivity and its strong temperature variation have been observed only in i-phases containing transition metal (TM) atoms [6], such as i-AlCuTM (TM = Fe, Ru, Os) [7,8] and i-AlPdTM (TM = Mn, Re) [1–3,9]. In such quasicrystals the d band of the TM atoms lies close to E_F and, as a consequence, strong resonance between the d and sp orbitals near E_F is expected, which would give rise to resistivity to a substantial extent.

As for the origin of such enhanced resonance due to d orbitals, Trambly de Laissardiere *et al.* [10] discussed the formation of virtual bound states due to an icosahedral cluster of TM atoms and an icosahedral cluster of the TM clusters. They calculated the scattering property of these clusters embedded in a metallic medium by an *ab initio* method, using the same cluster radius as in the actual α-AlMnSi. According to their result, new fine resonance peaks with the width of a few tens of meV, which are not merely a superposition of the contributions from individual Mn atoms, appear in the cases of a Mn icosahedron and an icosahedron of 12 Mn icosahedra, indicating the formation of new virtual bound states due to clusters or confinement of electrons in clusters. The fine resonance peaks are associated with the fine peaks in the density of states observed in band structure calculations [11,12]. In addition, such fine resonance peaks are found to be very sensitive to the symmetry of the cluster; for instance, removing a TM atom from the icosahedron or any change in the symmetry of the TM cluster significantly reduces such resonance effect, implying that the resonance effect becomes strongest when the cluster has the icosahedral symmetry. In this view, the transport of the 1/1-cubic approximant is expected to be quite sensitive to the concentration of TM atoms and it is of great interest to investigate whether such cluster virtual bound states do exist in real 1/1-cubic approximant phase.

Formation of cubic $Al_{43}Re_{10}Si_4$, $a = 1.285$ nm, Pearson symbol $cI128$, has been reported in the literature [13]. From the view of the electronic transport, the phase is of particular interest since it contains the Re element, which is supposed to play a significant role in the insulating behavior of the i-AlPdRe. In the present paper, we first show that it is the $(1/1, 1/1, 1/1)$ rational approximant phase by studying its x-ray diffraction and electron diffraction patterns. Then the temperature dependence of its electrical resistivity is studied with varying the Re concentration. Finally, the role of the icosahedral cluster composed of Re atoms in the transport will be discussed in terms of the resonance effect due to the d orbital of the transition element.

Ingots of various compositions around $Al_{73}Re_{17}Si_{10}$ were prepared under an argon atmosphere with an arc-melting furnace. Thin ribbons were produced by melt spinning the alloys and then annealed at 1073 K for one hour in vacuum in a sealed quartz tube. The phases of the samples were studied by powder x-ray diffractometry with Cu $K\alpha$ radiation and transmission electron microscopy (TEM). It is noted that special care was taken for the characterization of samples since the electrical resistivity is very sensitive to the presence of any metallic phase such as fcc-Al. The resistivity was measured for samples of various Re concentrations by the four-probe method in the range between 12 and 300 K.

In Fig. 1, we present an example of x-ray diffraction spectra of $Al_{72.5}Re_{17.4}Si_{10.1}$, together with a pattern of the 1/1-cubic approximant phase calculated by the projection method with the lattice parameter of 12.9 Å and

 0031-9007/01/86(14)/3104(4)$15.00

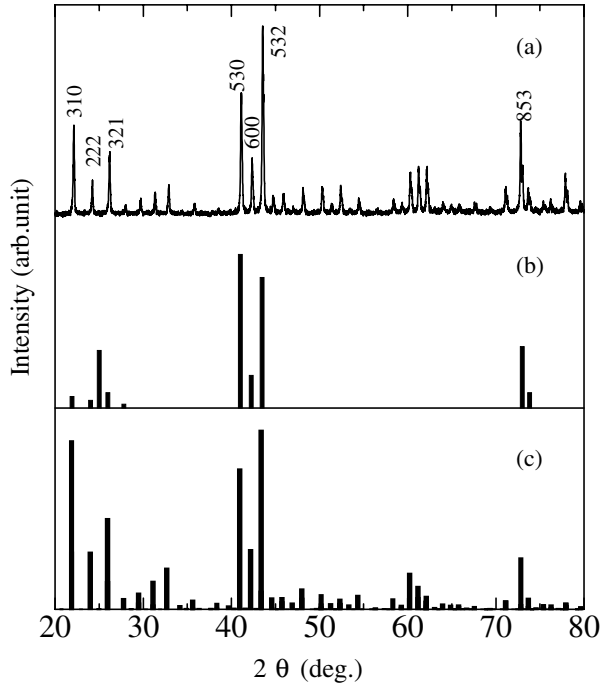

FIG. 1. Powder x-ray diffraction spectrum of $Al_{72.5}Re_{17.4}Si_{10.1}$ (a) and calculated patterns of the $(1/1, 1/1, 1/1)$ rational approximant by the projection method (b) and using the structural model of α-AlMnSi (c).

with that calculated using the structural model for the $Al_{72.5}Mn_{17.4}Si_{10.1}$ by placing Re atoms at the Mn sites of the model [14]. As is shown in the figure, the observed spectrum can be described as the $1/1$-cubic approximant phase and its structure is closely related to that of α-AlMnSi. Here all the peaks can be indexed as a primitive cubic lattice with $a = 12.9$ Å, showing that a single phase with no metallic impurity phases has been successfully obtained. As also shown in the figure, all the prominent reflections satisfy $h + k + l = 2n$; therefore, the phase is almost body centered and nearly the same structural entities are located at the origin and the body center of the unit cell. The result of the electron diffraction measurement (not shown) also confirms that it has a primitive cubic lattice, which is in agreement with the case of α-AlMnSi. By an analogy with $Al_{72.5}Mn_{17.4}Si_{10.1}$, it is considered that an icosahedron of 12 Re atoms is located at the origin and at the body center of the unit cell also in $Al_{72.5}Re_{17.4}Si_{10.1}$.

Figure 2 presents the nominal compositions of the samples studied in the resistivity measurement. A single phase with no trace of second phases such as fcc-Al has been obtained at these compositions. It is noted that not all the studied compositions are presented here but only the compositions at which a single phase is obtained are shown in the figure. In fact, we have prepared and studied samples in a wide composition region, from 7 to 19 at. % for the Re concentration, which entirely covers the region shown in the figure. X-ray studies on the samples have shown that in a Re-poor region, precipitation of aluminum

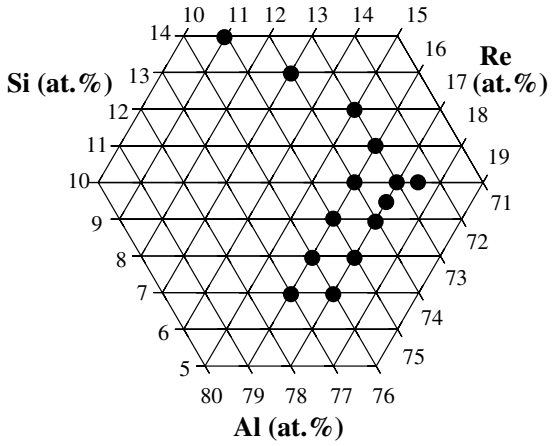

FIG. 2. Nominal compositions of the samples studied in the resistivity measurement.

has been observed for less than 11 at. % Re and that of an $Al_{2.4}Re_{17.5}Si_{9.5}$ ternary compound for more than 17.4 at. % Re. For samples of 11 and 17.4 at. % Re which were subjected to the resistivity measurement as presented in the following figures, they were investigated thoroughly by TEM. No second phase nor glassy state has been recognized at all, and the regions we examined all show well defined spots from the cubic approximant phase. Next, we investigated the effect of Re substitution on the structure by studying the lattice constant for compositions $(Al, Si)_{100-x}Re_x$ $(x = 11-17)$. It is clearly seen from Fig. 3 that the lattice constant systematically varies in accordance to the Re concentration, confirming that Re sites are partially occupied by Al and Si atoms, and its dependence is such that it increases almost linearly with increasing Re content. Since the concentration of Re is varied while keeping changes in the concentration of Al and Si the same, the observed behavior may be due to the difference between the atomic radius of a Re atom (1.38 Å) and that averaged for Al(1.43 Å) and Si(1.32 Å) atoms.

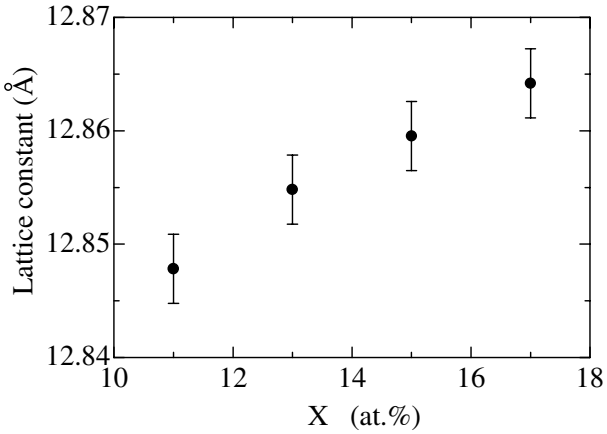

FIG. 3. The lattice constant as a function of the Re concentration X in $(Al, Si)_{100-X}Re_X$.

First of all, an overall feature of the resistivity with widely varying the Re concentration from 11 to 17.4 at. % has been investigated and the result is shown in Fig. 4. In the figure and what follows, the resistivity is normalized to its 300 K value, which is considered to be a good quantity to characterize a sample without an experimental error. As is clearly seen, the trend of the resistivity becomes nonmetallic when the Re concentration is increased. In Fig. 5, we plot the resistance ratio and the $\rho_{300\ \mathrm{K}}$ value as a function of the occupancy of the TM sites in the icosahedral clusters; by an analogy with the case of $Al_{72.5}Mn_{17.4}Si_{10.1}$ [14], the TM sites are fully occupied by Re atoms with the concentration of 17.4 at. %. The value of the $\rho_{300\ \mathrm{K}}$ is 50 $\mu\Omega$ cm for 11 at. % Re, and it rapidly increases with increasing Re concentration and reaches 4960 $\mu\Omega$ cm for 17.4 at. % Re. Such a large resistivity and a large resistance ratio of $\rho_{12\ \mathrm{K}}/\rho_{300\ \mathrm{K}} = 2.1$ are quite anomalous for the low order approximant phase, and they are well comparable with those of the stable *i*-phases. The observed nonmetallic behavior of the α-AlReSi confirms the result of the α-AlMnSi [15], where the similar anomalous resistance ratio of $\rho_{0.5\ \mathrm{K}}/\rho_{300\ \mathrm{K}} \sim 2$ has been observed at $Al_{72.5}Mn_{17.4}Si_{10.1}$. Since there is no long-range quasiperiodicity in the 1/1-cubic approximant phase, the observed nonmetallic behavior of $Al_{72.5}Re_{17.4}Si_{10.1}$ is mainly attributed to the local atomic environment of the length scale of about 13 Å. Considering that at lower Re concentrations the Re icosahedron at the origin and the body center of the unit cell are partially occupied by Al or Si atoms, decreasing the Re content results in breaking the icosahedral symmetry of the potential in the TM cluster. According to the *ab initio* calculation [10], any symmetry breaking of the icosahedral clusters significantly reduces the resonance effect due to the TM clusters. Therefore the observed trend of the resistivity of α-AlReSi agrees with what is expected from the calculation.

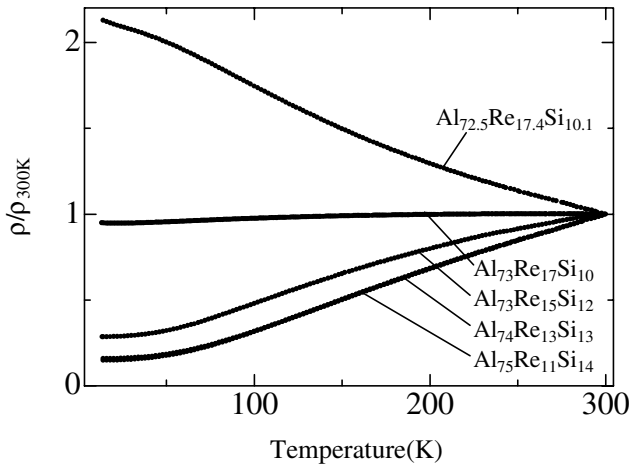

FIG. 4. Temperature dependences of the resistance ratio $\rho/\rho_{300\ \mathrm{K}}$ for α-AlReSi with changing the Re concentration from 11 at. % to 17.4 at. %.

In order to make the point clear, we then studied the resistance ratio for samples by varying only Al/Si ratios at fixed Re concentrations of 16 and 17 at. %. The results are presented in Figs. 6(a) and 6(b), respectively. Although the resistivity behavior varies with the concentration of Si, we see a distinct difference between the alloys with only one at.% difference of Re. For 16 at. % Re and 17 at. % Re, 8% and 2% of the 12 atomic sites of the TM icosahedron are occupied by Al or Si atoms, respectively. Here it is noted that for 16 at. % Re the TM cluster is composed of 11 Re and 1 Al/Si atoms on average, which is equivalent with removing one Re atom from the icosahedron. From the figures, first it is seen that the resistance ratio depends on Al/Si ratio to some extent. This trend may be explained in terms of the band structure effect with a shift of the Fermi level since the number of the valence electrons is different between Al and Si. However, we will not go into any detail for this behavior since our current interest is in its dependence on the Re concentration. At 16 at. % Re the temperature coefficient of the resistivity (TCR) is found to be weakly positive with considerably large values of the $\rho_{300\ \mathrm{K}}$ ranging from 780 $\mu\Omega$ cm in $Al_{74}Re_{16}Si_{10}$ to 1760 $\mu\Omega$ cm in $Al_{75}Re_{16}Si_9$, showing a barely metallic behavior. Meanwhile at 17 at. % Re, or when the TM cluster is almost fully occupied by Re atoms, large negative TCR's have been observed with the $\rho_{300\ \mathrm{K}}$ ranging from 1600 $\mu\Omega$ cm

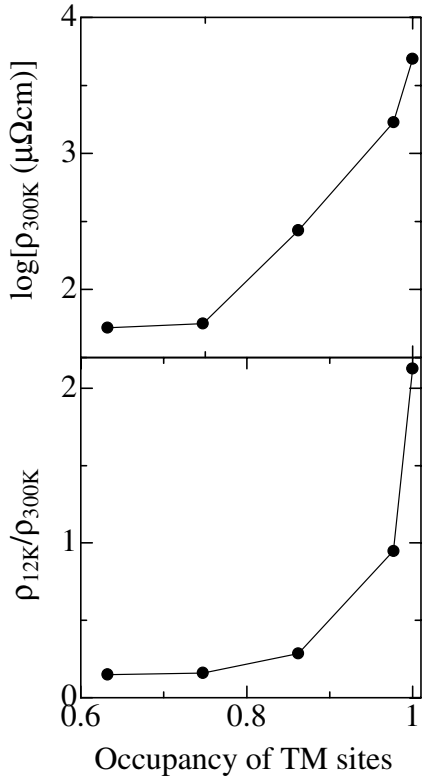

FIG. 5. The resistance ratio $\rho_{12\ \mathrm{K}}/\rho_{300\ \mathrm{K}}$ and $\rho_{300\ \mathrm{K}}$ as a function of the occupancy of the TM sites in the icosahedral clusters.

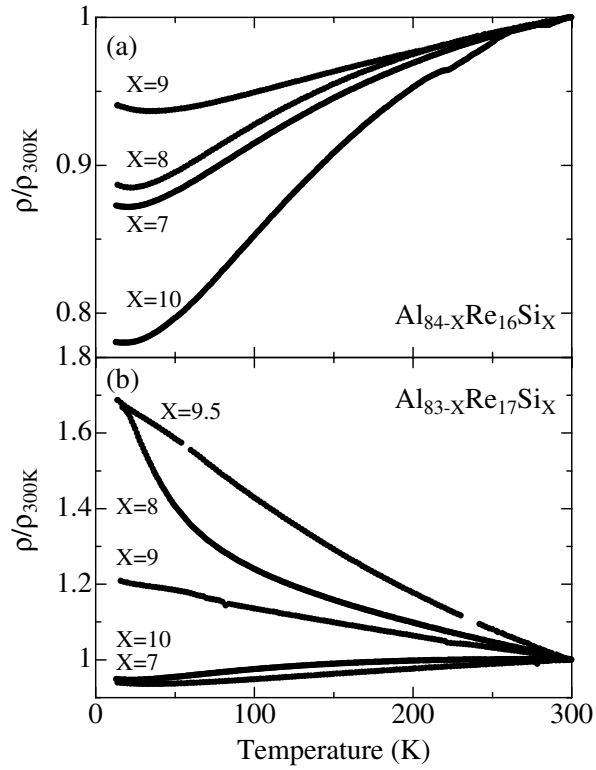

FIG. 6. Temperature dependences of the resistance ratio $\rho/\rho_{300\,\mathrm{K}}$ for α-AlReSi with varying the Al/Si ratio at fixed Re concentration of (a) 16 at. % and (b) 17 at. %.

in $Al_{76}Re_{17}Si_7$ to 3000 $\mu\Omega$ cm in $Al_{74}Re_{17}Si_9$. The resistance ratio even reaches to $\rho_{12\,\mathrm{K}}/\rho_{300\,\mathrm{K}} = 1.7$ for $Al_{75}Re_{17}Si_8$ and $Al_{73.5}Re_{17}Si_{9.5}$, thus exhibiting a peculiar nonmetallic character. It is noteworthy here that for all the studied samples a negative TCR has been observed only at the Re concentration more than 17 at. % and the highest resistivity and resistance ratio was obtained for 17.4 at. % Re. The sensitiveness of the resistivity to the Re concentration, or to the substitution of Al/Si atoms in the TM icosahedron, indicates that the icosahedral clusters exclusively made of Re atoms have a strong influence upon electron confinement, or electron localization. In this view, removing a Re atom from the icosahedron significantly destroys the localization tendency. The present result is in good agreement with the *ab initio* calculation which shows that the strongest confinement in clusters occurs when the clusters have the icosahedral symmetry. Since there is a close similarity in the local atomic structure between approximants and i-phases, the same situation may also occur in case of the i-phase.

In conclusion, first we have synthesized α-AlReSi and showed that it is a $(1/1, 1/1, 1/1)$ rational approximant phase which possesses a primitive cubic lattice with $a =$ 12.9 Å. Next, we have studied the resistivity of the new alloy and found that it shows anomalous high resistance ratio ($\rho_{12\,\mathrm{K}}/\rho_{300\,\mathrm{K}} = 2.1$) for the low order approximant phase, comparable to those seen in the stable i-phases. Since there is no long-range quasiperiodicity in the approximant, such anomalous behavior is mainly due to the local quasiperiodic order. In order to understand the role of transition atoms on the transport, we then studied the resistance ratio of the α-AlReSi with varying the Re concentration and found that the highest resistivity and resistance ratio are observed at the Re concentration close to 17.4 at. % where the icosahedron is fully occupied by the Re atoms. The resistance ratio rapidly decreases when the Re concentration is lowered. The present experimental result showing that the strongest localization effect occurs when the icosahedral clusters are fully occupied by transition atoms is in good agreement with the *ab initio* calculation, and it indicates the formation of the virtual bound states, or electron confinement, in clusters.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

[1] H. Akiyama, Y. Honda, T. Hashimoto, K. Edagawa, and S. Takeuchi, Jpn. J. Appl. Phys. **32**, L1003 (1993).
[2] F. S. Pierce, S. J. Poon, and Q. Guo, Science **261**, 737 (1993).
[3] C. Berger, T. Grenet, P. Lindqvist, P. Lanco, J. C. Grieco, G. Fourcaudot, and F. Cyrot-Lackmann, Solid State Commun. **87**, 977 (1993).
[4] J. Delahaye, J. P. Brison, and C. Berger, Phys. Rev. Lett. **81**, 4204 (1998).
[5] C. Berger, in *From Quasicrystals To More Complex Systems,* edited by F. Axel, F. Denoyer, and J. P. Gazeau (EDP Science, Springer-Verlag, 2000), p. 49.
[6] S. J. Poon, Adv. Phys. **4**, 303 (1992).
[7] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991).
[8] B. D. Biggs, S. J. Poon, and N. R. Munirathnam, Phys. Rev. Lett. **65**, 2700 (1990).
[9] P. Lanco, T. Klein, C. Berger, F. Cyrot-Lackmann, G. Fourcaudot, and A. Sulpice, Europhys. Lett. **18**, 227 (1992).
[10] G. Trambly de Laissardiere and D. Mayou, Phys. Rev. B **55**, 2890 (1997).
[11] T. Fujiwara and T. Yokokawa, Phys. Rev. Lett. **66**, 333 (1991).
[12] J. Hafner and M. Crajci, Phys. Rev. Lett. **68**, 2321 (1992).
[13] *Ternary Alloys,* edited by G. Petzow and G. Effenbrg (VCH Verlagsgesellschaft, Germany, 1993), Vol. 8, p. 165.
[14] M. Cooper and K. Robinson, Acta Crystallogr. **20**, 614 (1966).
[15] B. D. Biggs, F. S. Pierce, and S. J. Poon, Europhys. Lett. **19**, 415 (1992).