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Ordered Al–Pd–Ru icosahedral quasicrystal and its crystalline approximants and their electrical resistivities

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Abstract. In the Al–Pd–Ru system, a structurally ordered icosahedral phase has been successfully produced near the composition $Al_{73}Pd_{15}Ru_{12}$ by heat treatment at 1273 K for several hours. The x-ray diffraction patterns of the Al–Pd–Ru i-phase are very sharp, indicating that the i-phase is quite stable and that samples of high structural quality are attainable by appropriate heat treatment in this system. Prolonged annealing at 1273 K, however, results in phase transformation into the 1/0 cubic approximant ($a = 1.5$ nm). Also, we found the formation of a 2/1 cubic approximant phase ($a = 2.0$ nm) near the composition $Al_{71}Pd_{19}Ru_{10}$ when samples were annealed at 1173 K for one hour.

The temperature dependence of the resistivity of the i-phase is significantly large and the resistivity ratio R ($R = \rho_{12\,K}/\rho_{300\,K}$) reaches as high as 2.5, comparing well to that seen in the ordered Al–Cu–Ru i-phase. The resistivity and its temperature dependence for the 2/1 approximant phase are quite similar to those for the i-phase, exhibiting a large resistivity ratio $R \sim 1.6$, in contrast with the metallic behaviour of the 1/0 cubic approximant phase. These results indicate that the characteristic length which determines the temperature dependence of the resistivity is somewhere between 1.5 and 2.0 nm and suggest that the long-range quasiperiodicity beyond the length scale is of less significance as far as the electrical properties are concerned.

1. Introduction

High resistivity has been shown to be one of the most striking properties of quasicrystals (QCs) since the discovery of stable i-phase alloys such as i-AlCu(Fe, Ru, Os) [1] and i-AlPd(Mn, Re) [2]. Among them, i-AlPdRe is outstanding, with its extraordinary high values of the resistivity and resistivity ratio ($\rho_{4\,K}/\rho_{300\,K}$) [3–5]. A recent investigation even implies that i-AlPdRe is an insulator at absolute zero near the composition $Al_{70.5}Pd_{21}Re_{8.5}$ [6]. The origin of the metal–insulator transition of i-AlPdRe has been strongly debated in recent years [7–10]; however, it is not yet clear whether the localized states at the Fermi level are intrinsic to QCs or not.

Meanwhile, studies of electrical properties on high-order crystalline approximant phases show that their electronic transport is quite similar to that of QCs when the lattice parameter is large enough. For approximants of the Frank–Kasper-type (FK-type) i-phase, the resistivity of the 1/1 cubic (FK-phase), 2/1 cubic, and (3/2–2/1–2/1) orthorhombic approximant phases has been investigated in the Mg–Zn–(Ga, Al) system [11, 12] as well as that of the 1/1 cubic approximant in the Al–Li–Cu system [13]. The corresponding lattice parameters are $a = 1.41$–1.44 nm, $a = 2.29$–2.30 nm, and $(a, b, c) = (3.69, 2.30, 2.28)$ nm for the Mg–Zn–(Ga, Al)

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system and $a = 1.39$ nm for the Al–Li–Cu system, respectively. The ρ–T dependence of the 2/1 cubic and (3/2–2/1–2/1) orthorhombic approximants has been found to be essentially the same as that of the i-phase, whereas that of the 1/1 cubic phases exhibits positive temperature dependence of the resistivity over the whole temperature range of the measurement. Therefore the results obtained so far on the FK-type approximants which do not contain transition metals imply that those which have approximation degrees of 2/1 or higher exhibit a similar behaviour to the i-phase while those with degrees of 1/1 or lower reveal a metallic behaviour. These results are considered to be an indication that the characteristic length determining the electron transport is somewhere between 1.4 and 2.3 nm. For approximants of the Mackay-icosahedron-(MI-) type i-phase which contain transition metals, the situation is basically similar to the case for the FK-type approximants. The temperature dependence of the resistivity of the 3/2 rhombic approximant ($a = 3.2$ nm) in the Al–Cu–Fe system is identical to that of the corresponding i-phase in the range from 4.2 K to 1000 K, including their magnitudes [14], whereas low-order approximants such as 1/0 cubic ($a = 0.77$ nm) and 1/1 cubic ($a = 1.24$ nm) phases in the Al–Cu–Ru system exhibit a metallic behaviour [15], which is consistent with the trend observed for the FK-type approximants. The exceptions here are the behaviours of 1/1-(Al, Si)CuFe [16] and 1/1-AlMnSi [17], the latter of which shows both positive and negative temperature coefficients of the resistivity (TCR) according to the annealing temperature and exhibits a prominent negative TCR when annealed at high temperature, implying a significant role of transition metals in the case of the MI-type approximants, in addition to those of the degree of approximation and the lattice parameter. However, irrespective of the alloy system, in both FK-type and MI-type approximants, the above results taken together indicate that the complex local structure with a length scale of more than 1.5 nm is mainly responsible for the anomalous properties of i-phases rather than the quasiperiodicity itself.

In the Al–Pd–Ru system, we have found that a structurally ordered i-phase can be produced by subsequent heat treatment of melt-spun samples. An interesting question arising here is that of whether this QC also exhibits the high resistivity and large resistivity ratio R which are commonly seen for ordered QCs of high structural perfection. In addition, formation of 1/0 cubic approximant phases has been reported in this system [18], and also a 2/1 cubic approximant phase has been found by the present authors. Therefore it is also of great interest to investigate the electrical resistivity of these approximant phases in comparison with that of the i-phase on the basis of the same alloy system, and to gain further insights into the role of the long periodicity as regards the electrical properties of QCs.

In this paper we first focus on the formation region and stability of the Al–Pd–Ru QC and its crystalline approximants. Then we present the temperature dependence of the resistivity of the icosahedral, and 1/0 and 2/1 cubic approximant phases. The composition dependence of the resistivity is also discussed.

2. Experimental procedure

Ingots of various compositions typically around $Al_{73}Pd_{15}Ru_{12}$ were prepared under an argon atmosphere with an arc-melting furnace. Thin ribbons (15 μm thick) were produced by melt spinning the alloys and then annealed at temperatures between 1173 and 1273 K for one to twelve hours in vacuum or in an argon atmosphere in a sealed quartz tube. The phases of the samples were studied by powder x-ray diffraction with Cu Kα radiation and transmission electron microscopy. For samples of single phase the electrical resistivity was measured as a function of temperature from 12 to 300 K by the four-probe method.

3. Results and discussion

3.1. Formation of the i-phase and its crystalline approximants

In figure 1, we present x-ray diffraction spectra of $Al_{75.5}Pd_{14}Ru_{10.5}$ annealed at 1273 K for various lengths of time ranging from 0 to 24 hours as typical examples. The spectrum of the as-spun sample consists of peaks from both icosahedral and second phases. The broad peaks indicate the presence of a large amount of structural disorder in the as-spun sample. As shown in the figure, a single i-phase is obtained when the sample is annealed at 1273 K for two to eight hours. The structure of the i-phase is well ordered chemically, as shown by the intensity of the (1/2)(311111) superlattice peak near $2\theta = 26^\circ$, and has a high degree of structural perfection, illustrated by the narrow linewidths. Further annealing at 1273 K, however, causes phase transformation into the 1/0 cubic approximant phase, which is presumably a stable phase for this particular composition at 1273 K. Although the present i-AlPdRu is considered to be a metastable phase, it is clearly seen that the quality of the i-phase was significantly improved and second phases present in as-spun samples totally disappeared upon heat treatment at 1273 K for a couple of hours. This fact indicates that a structurally well-ordered i-phase suitable for the resistivity measurement is attainable in the Al–Pd–Ru system by appropriate heat treatment.

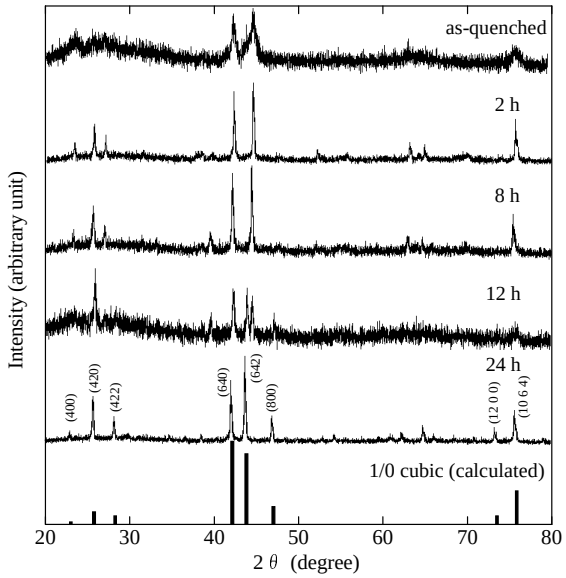

Figure 1. X-ray diffraction patterns for $Al_{75.5}Pd_{14}Ru_{10.5}$ annealed at 1273 K for 0 to 24 hours. At the bottom, a pattern for the 1/0 approximant phase calculated using the projection method is shown.

In figure 2 we show an x-ray diffraction spectrum taken for $Al_{69}Pd_{21}Ru_{10}$ annealed at 1173 K for one hour as an example. As is shown, the spectrum agrees quite well with the pattern of the 2/1 rational approximant phase calculated using the projection method. The present paper shows the formation of the 2/1 approximant phase in the Al–Pd–Ru system for the first time.

Figure 3 presents the formation range of the i-phase, and 1/0 and 2/1 cubic approximant phases. Note that the results for the i-phase and the 1/0 approximant phase are obtained at 1273 K and those for the 2/1 approximant at 1173 K. As shown in the figure, the i-phase is

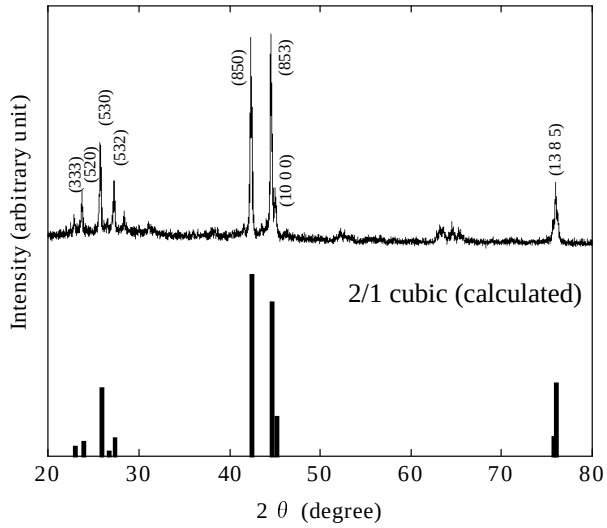

Figure 2. An x-ray diffraction pattern for $Al_{69}Pd_{21}Ru_{10}$ annealed at 1173 K for one hour. At the bottom, a calculated pattern for the 2/1 approximant phase is shown.

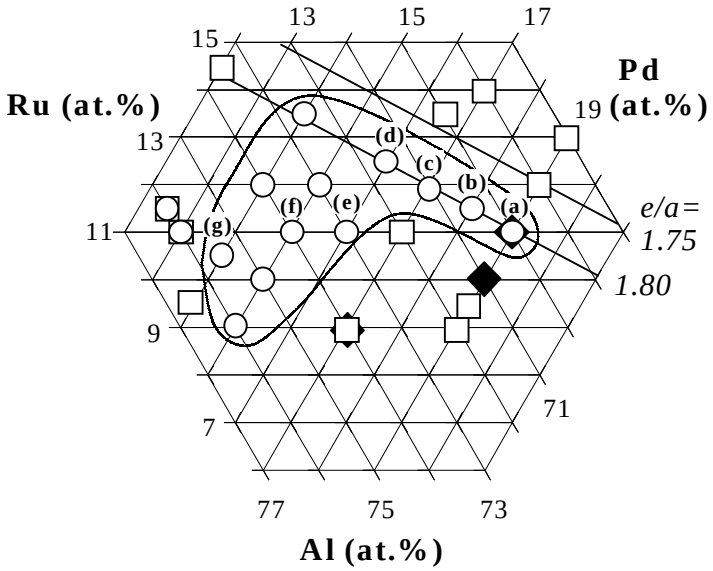

Figure 3. The formation region of the i-phase (open circles) and 1/0 cubic approximant phase (open squares) for the samples heated at 1273 K for one hour and the 2/1 cubic approximant phase (solid squares) heated at 1173 K for one hour. (a) to (g) correspond to the samples (a) to (g) in figure 4.

found to form over a relatively wide composition range with 14–19 at.% Pd and 9–13 at.% Ru and their region is surrounded by that of the 1/0 cubic approximant phase which is considered to be the equilibrium phase for the compositions studied. In figure 3, lines of constant e/a (electrons per atom) ratio are also drawn, where the effective valencies of Al, Pd, and Ru are assumed to be 3.0, 0, -2.66, respectively [19]. It is seen that the e/a ratio plays an essential

role in stabilizing the i-phase also in the case of the Al–Pd–Ru system, as first demonstrated by Tsai *et al* [20], and that the i-phase region is somewhat extended along the $e/a = 1.80$ line to lower Al concentration. The 2/1 approximant phase was found to form at 1173 K near the composition $Al_{71}Pd_{19}Ru_{10}$ with Pd-rich concentration, and transforms into the 1/0 approximant when heated to 1273 K. It should be noted that due to the formation of the i-phase, and 2/1 and 1/0 approximant phases in the Al–Pd–Ru system, it becomes possible to make a direct comparison of the electrical properties among these phases and to investigate the role of the approximation degree or the lattice parameter on the electronic transport on the basis of the same alloy system.

3.2. Electrical resistivity

Figures 4(a) and 4(b) illustrate the temperature dependence of the resistivity of i-AlPdRu phases of various compositions annealed at 1273 K for one hour. It is clearly seen that the trend of the resistivity variation with temperature is very similar to that of conventional stable i-phases such as i-AlCu(Fe, Ru) [21, 22]. The resistivity increases with decreasing temperature in all of the samples investigated, and the higher the resistivity, the stronger the temperature coefficient. As shown in figure 4(a), very high resistivities are measured ranging from $\rho_{12\,K} = 1200\ \mu\Omega$ cm in $Al_{75.5}Pd_{14}Ru_{10.5}$ up to 24 000 $\mu\Omega$ cm in $Al_{70}Pd_{19}Ru_{11}$. These resistivity values are in the same range as those seen in stable QCs of high structural perfection like i-AlCuFe and i-AlCuRu. The resistivity ratio R ($R = \rho_{12\,K}/\rho_{300\,K}$) ranges from 1.2 to 2.5 (figure 4(b)), which is quite large and compares well to that of the i-AlCuRu. Furthermore, strong dependence of ρ on the nominal composition, which is a feature common to stable QCs, is also observed. The nominal compositions of the samples subjected to the resistivity measurement are depicted in figure 3. High resistivities and large resistivity ratios were observed in the composition region where the e/a ratio is 1.8, and increasing the e/a ratio leads to substantial decrease in the resistivity and its temperature dependence (see figure 4). In addition there is also a trend for substitution of the transition elements palladium and rhenium for aluminium also to raise the resistivity and its ratio at a constant value of e/a ($e/a = 1.8$). These trends are in good accordance with the results for i-AlPdRe [23]. The present results confirm that high resistivity, large resistivity variation, and its sensitive composition dependence are common features of structurally ordered i-phases and thus are intrinsic properties of Al-based i-phases.

Figures 5(a) and 5(b) present the temperature dependence of the resistivity of 1/0 and 2/1 cubic approximant phases in the Al–Pd–Ru system. The lattice parameters of the 1/0 and 2/1 cubic approximant phases are 1.5 and 2.0 nm, respectively. Note that unusual electronic behaviour is also seen in these approximant phases. For instance, as shown in figure 5(a), quite high resistivities are observed in the 2/1 cubic approximant phase, ranging from $\rho_{12\,K} = 3700$ to 10 000 $\mu\Omega$ cm, which are comparable with resistivities of the Al–Pd–Ru i-phases. The resistivity ratio is also large for the 2/1 approximant and varies from $\rho_{12\,K}/\rho_{300\,K} = 1.3$ to 1.6 (figure 5(b)), which is in the same range as those of the i-phase. These results indicate that the local atomic structure common to the i-phase and the approximant is of more importance for the high resistivity of the ordered Al–Pd–Ru QC than the quasiperiodicity itself.

In the case of the 1/0 cubic approximant, the resistivity at 12 K is about 600 $\mu\Omega$ cm (figure 5(a)) and the temperature variation is very small compared with that of the i-phase and the 2/1 approximant (figure 5(b)). This overall tendency is consistent with the general expectation that the higher the degree of the approximation to the QC, the larger the resistivity and its negative temperature coefficient. According to Shibuya *et al* [24], for both FK and MI types of approximant, their electrical properties can be classified solely according to the lattice parameter; approximants with a lattice parameter larger than 2.0 nm, which corresponds to

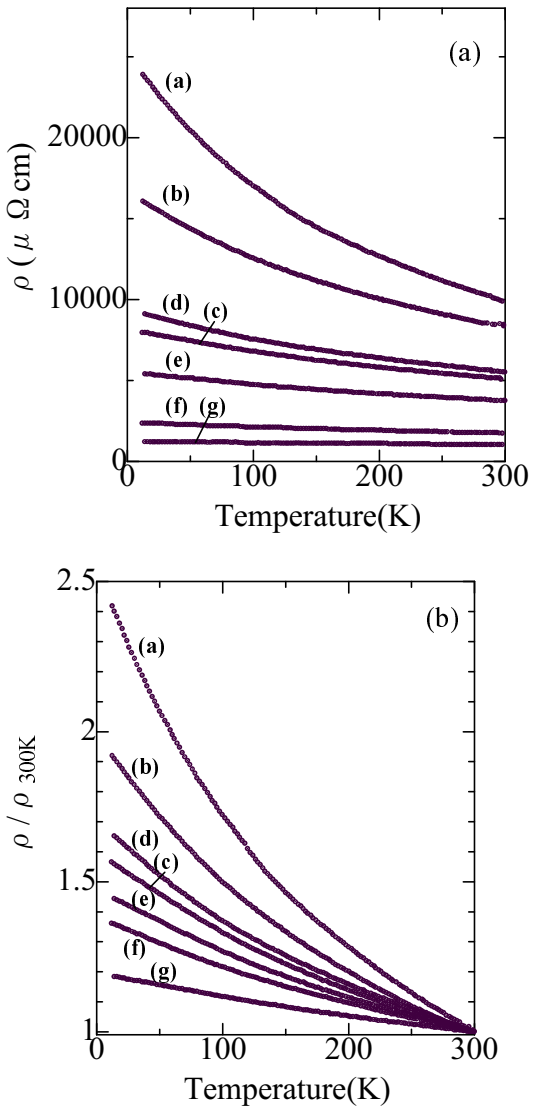

Figure 4. The temperature dependence of (a) the resistivity and (b) the resistivity ratio $\rho_{12\,\mathrm{K}}/\rho_{300\,\mathrm{K}}$ for the i-AlPdRu samples annealed at 1273 K for one hour. (a) $Al_{70}Pd_{19}Ru_{11}$, (b) $Al_{70.5}Pd_{18}Ru_{11.5}$, (c) $Al_{71}Pd_{17}Ru_{12}$, (d) $Al_{71.5}Pd_{16}Ru_{12.5}$, (e) $Al_{73}Pd_{15}Ru_{12}$, (f) $Al_{74}Pd_{15}Ru_{11}$, (g) $Al_{75.5}Pd_{14}Ru_{10.5}$.

2/1 approximants or higher ones, such as 2/1-, (3/2–2/1–2/1)-MgZn(Ga, Al) and 3/2-AlCuFe, are similar to those of the QCs [11, 12, 14], whereas approximants with a lattice parameter smaller than 1.5 nm, which corresponds to 1/1 approximants or lower ones, such as 1/1-MgZn(Ga, Al), 1/1-AlLiCu, and 1/0- and 1/1-AlCuRu, reveal metallic behaviour [11–13, 15], except for the cases of 1/1-(Al, Si)CuFe [16] and 1/1-AlMnSi [17]. Therefore, the present results are in good agreement with the previously reported ones and clearly confirm that the lattice parameter is a key parameter when describing and classifying the electronic transport of approximants. Since our results show that the temperature dependence of the resistivity is marginally metallic for the 1/0 approximant which has a lattice parameter twice as large

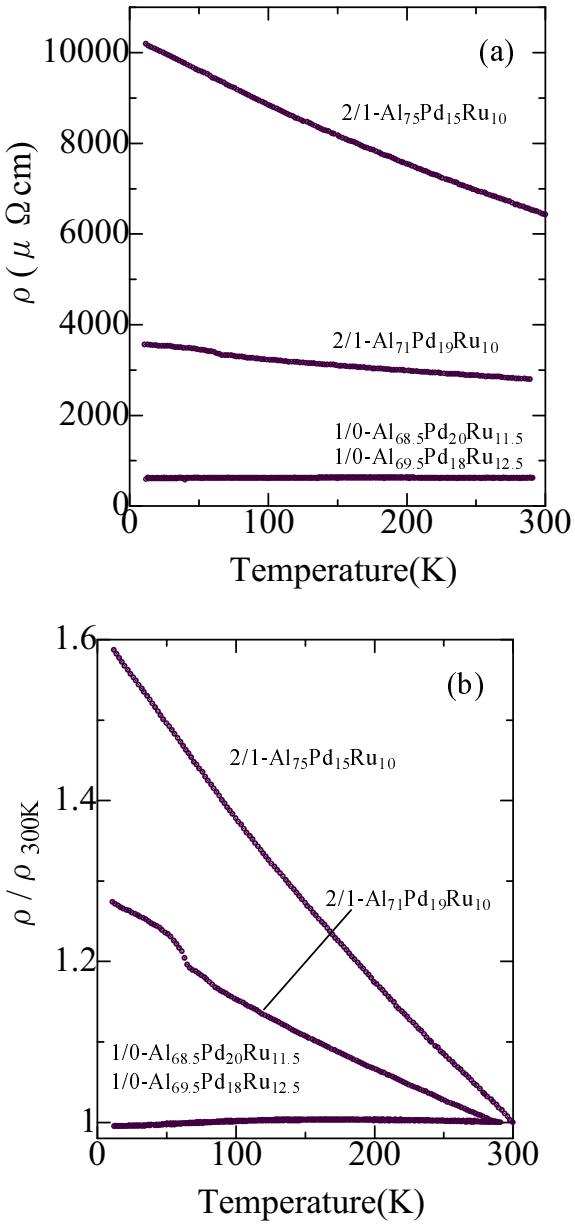

Figure 5. The temperature dependence of (a) the resistivity and (b) the resistivity ratio $\rho_{12\,\mathrm{K}}/\rho_{300\,\mathrm{K}}$ for the 2/1 and 1/0 cubic approximant phases.

as that of the conventional 1/0 approximant due to its ordered structure, it may follow that the characteristic length which determines the temperature coefficient of the resistivity is somewhere between 1.5 and 2.0 nm. In order to exploit the nature of the transport of approximants and to gain further insights into the underlying physics behind the behaviours of the approximants, we would need to proceed to a more detailed investigation, by considering the specific local environment including the basic atom clusters, the role of transition metals,

the effect of chemical ordering, etc. In any case, improving the sample quality by reducing both topological and chemical disorder, as has been frequently done for i-phases, would be of significant importance.

4. Conclusions

In this paper, formation regions of the i-phase and its crystalline approximant phases in the Al–Pd–Ru system have been investigated. As a result, we have found that a structurally ordered i-phase can be produced by appropriate heat treatment in the Al–Pd–Ru system. Although the Al–Pd–Ru i-phase is considered to be metastable, the stability of the i-phase is quite high and the quality of the i-phase can be improved by annealing for a couple of hours at a temperature as high as 1273 K. Prolonged annealing of the i-phase at 1273 K causes phase transformation into the 1/0 cubic approximant phase. In addition, we have found the formation of a 2/1 cubic approximant phase near the composition $Al_{71}Pd_{19}Ru_{10}$ for the first time in the Al–Pd–Ru system.

We observed very high resistivity values in the well-ordered Al–Pd–Ru i-phase. The resistivity ranges from $\rho_{12\,K} = 1200$ to 24 000 $\mu\Omega$ cm and the resistivity ratio $\rho_{12\,K}/\rho_{300\,K}$ reaches as high as $\sim$2.5; these values compare well with the results reported for the Al–Cu–Ru i-phase. The present results thus confirm that high resistivity is a common feature of structurally ordered i-phases irrespective of their thermal stability. For the 2/1 cubic approximant phase, a large resistivity as well as a large resistivity ratio $\rho_{12\,K}/\rho_{300\,K}$ are observed. In fact, the i-phase and the 2/1 approximant are almost indistinguishable as far as the electronic transport is concerned, implying that the long-range quasiperiodicity itself is not the main origin of the high resistivity of the Al–Pd–Ru i-phase, and that the complex local atomic structure common to the i-phase and the approximants plays a more important role in the electronic transport, depending on the lattice parameter. The resistivity of the 1/0 cubic approximant is almost temperature independent, in contrast to that of the other two phases, and the temperature coefficient is weakly positive. These results are consistent with the general trend, seen in both FK and MI types of approximant, for 2/1 or higher-order approximants to exhibit a similar behaviour to QCs while 1/1 or lower-order approximants exhibit a metallic behaviour, and confirm the general expectation that the higher the degree of approximation to the QC, the larger the resistivity and its negative temperature coefficient. Moreover, our results suggest that the characteristic length determining the temperature variation of the resistivity is somewhere between 1.5 and 2.0 nm.

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