Reinterpretation of the zero-temperature conductivity in icosahedral AlPdRe

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(Received 17 May 2016; revised manuscript received 16 June 2016; published 13 July 2016)

The zero-temperature conductivity $\sigma(0)$ of icosahedral (i)-AlPdRe has been found to be simply related to the resistance ratio $R = \rho_{4.2\,\mathrm{K}}/\rho_{295\,\mathrm{K}}$ by a power law, $\sigma(0) \sim R^{-1.74}$, over four orders of magnitude in $\sigma(0)$. This relation includes metallic single grain samples, and polygrain samples of different morphologies which are metallic for small R values, and insulatinglike at large R. Electronic transport properties of single grain i-AlPdRe samples are thus found to be on common ground with polygrain i-AlPdRe. The relation between R and $\sigma(0)$ can be qualitatively understood from published band-structure calculations on quasicrystalline approximants.

DOI: 10.1103/PhysRevB.94.024202

I. BACKGROUND

Electrical transport properties of icosahedral (i)-AlPdRe remains an area of surprises and controversies. One outstanding problem is the strong variation of the resistivity ρ and its temperature dependence. For different i-AlPdRe samples, ρ at 295 K varies from roughly 1 to 15 mΩ cm, while $\rho_{4.2\,\mathrm{K}}$ may vary between different samples by a factor of $\sim$1000 for polygrain samples of the same nominal composition [1]. The parameter $R = \rho_{4.2\,\mathrm{K}}/\rho_{295\,\mathrm{K}}$, which has a negligible experimental error, is conveniently used for sorting these different quasicrystals. Single grain samples have much lower resistivities and R values [2–4], which are more in line with other quasicrystals. The results for $\rho_{4.2\,\mathrm{K}}$ in polygrain i-AlPdRe have therefore been strongly contested. Suggestions of extrinsic sources, such as grain boundary scattering, impurity phases, intergranular tunneling, or oxygen bridges between grains, have been advanced [3–7], and have rapidly proliferated [8–11]. Objections to the proposals of extrinsic effects were consequently raised [12–16].

Preparation of polygrain i-AlPdRe usually follows one of two major routes: (i) melting in an arc furnace, followed by various annealings and water quenching after the last step, giving *ingot samples*, or (ii) melting in an arc furnace, followed by melt spinning and various anneals, with cooling in an oven after the last step, giving *ribbon samples*. The microstructures of these samples differ. In ingots there are needle-shaped voids with bridges between the grains, while in ribbon samples the structure is more homogeneous and bridges are absent [17]. The proposals or discussions of the extrinsic properties [3–11] have all been limited to ingot samples, neglecting the similar high resistivities in the ribbon samples. It is also well known from groups making polycrystalline i-AlPdRe samples that oxygen bridges cannot account for high resistivities. ρ in i-AlPdRe does not increase with oxygen impurities, rather, it decreases [12]. These objections and further arguments [13–16] suggest that extrinsic effects can be ruled out as the origin of high resistivities. A main difference between samples of similar composition is the different annealings used in sample preparation.

A second major problem is that high R samples show variable range hopping (VRH) in the conductivity and in the magnetoresistance [18–21], indicating insulating behavior and a metal-insulator transition (MIT) at a lower R value, while, on the other hand, such samples nevertheless display a zero-temperature conductivity $\sigma(0) > 0$. For samples with the largest R value this was deduced from measurements at very low temperatures [22,23]. A nonzero $\sigma(0)$ contradicts the standard definition of an insulator, i.e., $\sigma(0) = 0$ at $T = 0$ K, and this result has also been controversial, particularly for large R samples.

The VRH-like behavior of samples with R of order 100 showed a steep decrease of $\sigma(T)$ below 600 mK down to 20 mK [19], and it was conjectured that $\sigma(0) = 0$. The tendency of a saturation of $\sigma(T)$ below about 20 mK was assigned to inadequate thermal contact between the sample and sample holder. Measurements to much lower temperatures [22,23] were also implied to involve cooling problems [16,24]. Thermal contact is a well-known concern at ultralow temperatures. A nonzero $\sigma(0)$ in samples with $R > 100$ [22,23] was hence carefully tested [25].

In this paper it will be shown that the sometimes problematic parameters R and $\sigma(0)$ of i-AlPdRe are intimately related by a simple power law, valid over four orders of magnitude in $\sigma(0)$. Single grain samples and polygrain ingots and ribbon samples are included in this relation. A qualitative explanation is discussed in terms of the strong sensitivity of electronic properties to details in the atomic site occupancy, which Krajčí and Hafner [26,27] have found from band-structure calculations in quasicrystalline approximants.

II. THE RELATION BETWEEN R AND $\sigma(0)$

Data for $\sigma(0)$ and R were collected from the literature. A few compilations of data for $\sigma(0)$ could not be used for the present purpose [28,29]. $\sigma(T)$ was then fitted at too high temperatures to an assumed expression for the conductivity, which did not take into account the decrease in $d\sigma(T)/dT$ when it was extrapolated to $T = 0$ K. If used to evaluate $\sigma(0)$, it therefore becomes greatly underestimated. However, data obtained by extrapolation from 400 mK were included [30], since R was limited to the region $R \lesssim 16$.

Data for $\log \sigma(0)$ vs $\log R$ for i-AlPdRe are shown in Fig. 1. Sources are as follows: The eight solid circles at low R are single grain samples [2–4], and include six samples of varying Re concentration [3], the eight open up triangles are polygrain ribbon samples with R in the range 2–110 [17,23,31], and the six open down triangles are polygrain ingot samples [22,23]. The six samples with open circles are the ribbon samples with $\sigma(0)$ extrapolated from 400 mK [30]. All these polygrain

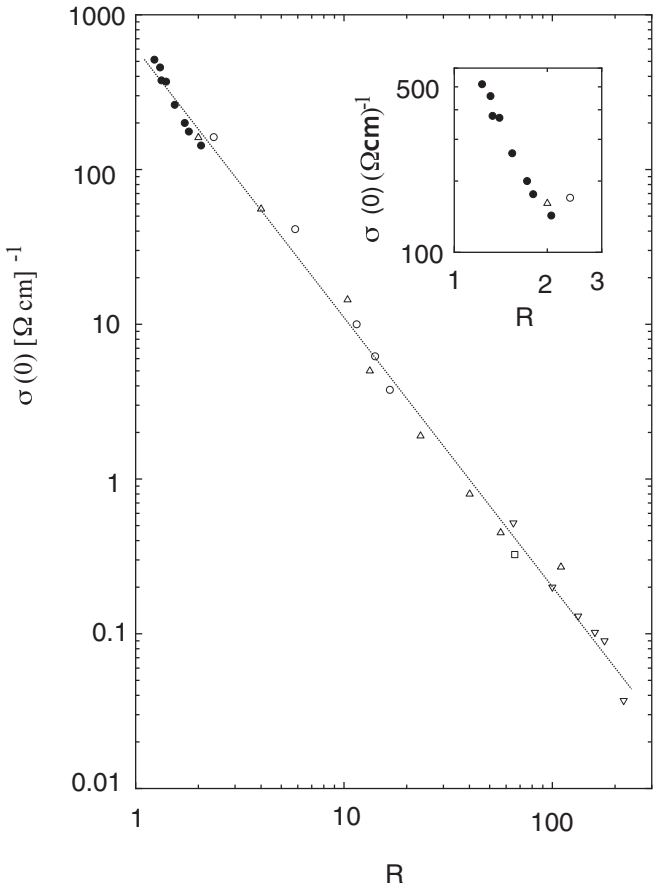

FIG. 1. $\sigma(0)$ vs R for i-AlPdRe. Solid symbols: Single grain samples of varying Re concentration. Open symbols: Polygrain samples, usually with 8.5 at. % Re in the form of open up triangles, (ribbons), open down triangles (ingots), and open circles (ribbons, extrapolated from 400 mK). An open square is a polygrain sample with 7.5 at. % Re. Data sources are given in the text. The straight line is a fit of Eq. (1). The inset shows the low R region on a scale where data are resolved.

samples have the nominal composition $Al_{70.5}Pd_{21}Re_{8.5}$. Only one reliable estimate has been found for a 7.5 at. % Re sample at 20 mK, a sufficiently low temperature for this sample [32]. This i-$Al_{70}Pd_{22.5}Re_{7.5}$ sample is shown in Fig. 1 by an open square at $R = 66$ and $\sigma(0) = 0.325\ (\Omega\,\mathrm{cm})^{-1}$.

It has been questioned how good a parameter is R to represent a description of the varying properties of i-AlPdRe [16]. However, in ingot and ribbon samples of similar R values up to about 60 the normalized resistivity $\rho(T)/\rho(295\ \mathrm{K})$ was found to be accurately similar from 4.2 to 300 K [15]. On the other hand, for lower temperatures it is well known that this is not always the case [15,16]. For example, great differences in $d\sigma/dT$ between the ribbon and ingot samples have been observed from 20 mK to 1 K [22,23]. Nevertheless, $\rho(T)$ saturates below 20 mK for both types of samples and extrapolated values of $\sigma(0)$ fit into the relation in Fig. 1. The differences in curve form in $\sigma(T)$ at low temperatures thus do not seem to affect the correlation between $\sigma(0)$ and R.

The straight line in Fig. 1 is an empirical fit. It has the equation

$$\sigma(0) = 610R^{-1.74}, \tag{1}$$

with σ in $(\Omega\,\mathrm{cm})^{-1}$.

Data for $\sigma(0)$ have been displayed previously in the form $\log\sigma(0)$ vs R [33]. These data included only one single grain sample. The much compressed low R region in such a plot led to the erroneous conclusion that there was a change of slope in $\log\sigma(0)$ vs R at about $R \approx 20$. It is now seen that all data, including also single grain samples, obey one single power law over the full range of R values for i-AlPdRe.

III. DISCUSSION

A. Extended relation between $\sigma(0)$ and R

Some conclusions following from Fig. 1 are pointed out. First, all major forms of bulk i-AlPdRe samples are included, covering extended regions of $\sigma(0)$ and R. The samples have been prepared in different laboratories, from elements of varying impurity concentrations, and have been elaborated in different ways, resulting in varying morphologies. This suggests that $\sigma(0)$ is an intrinsic, temperature-independent property of these quasicrystals. There are three major groups in Fig. 1 with different preparation techniques, i.e., ribbon and ingot polygrain samples and single grain samples which all follow Eq. (1) [34]. In particular, and in contrast to previous assertions [4,5], this result indicates that transport properties of single grain samples are on common grounds with all bulk i-AlPdRe samples.

Second, the relation in Fig. 1 is also smooth around $R \approx 20$, indicating that $\sigma(0)$ does not depend on the MIT, nor on the drastic change in major contributions to the conductivity at the MIT, from weak localization and electron-electron interactions at low R [17], to variable range hopping at large R [20].

Finally, it has long been expected that the concentration of Re is the most sensitive part of the i-AlPdRe composition, but clear evidence has apparently not been published. The present correlation qualitatively supports this conjecture, since in Fig. 1 the Re concentration is larger for the eight single grain samples [2–4] than for all polygrain samples. Indications for the sensitivity of transport properties to the Re concentration have also been been obtained in unpublished results by Mori and co-workers [35]. In a spark plasma sintering method the Re concentration was varied in small steps from 8 to 9 at. %. Results are shown in Fig. 2. The reduced resistance ratio $\rho_{15\ \mathrm{K}}/\rho_{300\ \mathrm{K}}$ is quite sensitive to changes in the Re concentration and may vary by a factor of order ≈10 for an increase of the Re concentration by a few tenths of 1 at. %.

B. Origin of $\sigma(0)$

The close relationship between $\sigma(0)$ and R suggests a common origin of the variations in these parameters. The most significant difference between the polygrain samples is the various annealing procedures, and it is well known that judiciously chosen annealing procedures in one sample can considerably increase the R value [36]. An increasing R value is believed to reflect improved quasicrystalline order. Direct experimental evidence has been obtained from an experiment

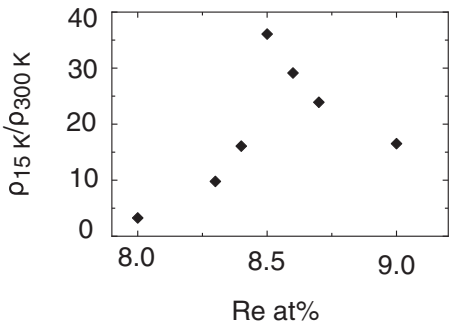

FIG. 2. $\rho_{15\,\mathrm{K}}/\rho_{295\,\mathrm{K}}$ vs Re concentration in i-$Al_{70.5}Pd_{21.5-x}Re_{8.0+x}$ with x in the range 0–1. Unpublished results by Mori *et al.* [35].

in the reverse direction, where successively increased doses of high energy neutron irradiation of one i-AlPdRe sample was found to decrease R and decrease x-ray peak heights, indicating decreasing long range icosahedral order [37]. For the polygrain samples one is thus led to conjecture that R measures the approach to a perfect quasicrystal, while $\sigma(0)$ measures a deviation from a perfect quasicrystal. For the single grain samples it is likely that the decisive factor is the larger Re content.

Linked changes in R and $\sigma(0)$ are consistent with the model developed by Krajčí and Hafner [26,27] from band-structure calculations of approximants to i-AlPdRe. They found that a semiconducting gap is opened by hybridization between Al(s,p) states and transition metal d orbitals, and is located at or in the vicinity of the Fermi level. It was suggested that in the quasicrystalline limit i-AlPdRe is an insulator. This was supported, e.g., by calculations in a series of transition metals alloyed with Al, where a hierarchy of quasicrystalline approximants could be selected. These approximants had slightly varying electron per atom ratios and the Fermi level was nevertheless always in the gap. Chemical site disorder, e.g., substitutional Al/Pd defects, leads to localized states in the band gap. These states exhibit a weak dispersion with a nonzero bandwidth causing $\sigma(0) > 0$. The interactions of the localized states are expected to decrease with decreasing disorder, leading to a decreasing $\sigma(0)$.

It was also shown in this work [26,27] that the position of the Fermi level in the gap is very sensitive to details of the atomic ordering and also to varying Re concentration. For example, switching of atoms between nearby sites could result in a shift of the Fermi level in the direction from the energy gap and into the conduction band and metallic behavior.

Based on the Krajčí-Hafner picture [26,27], one can thus suggest that for single grain samples ($R \lesssim 2$), the relation in Fig. 1 is mainly due to changes in the Re concentration, while for optimal Re concentration and $R \geqslant 2$, it is the shifting site occupancy caused by the varying annealing procedures which leads to a decreased $\sigma(0)$ and an increased R value.

ACKNOWLEDGMENT

The author is grateful to Dr. R. Tamura for his kind permission to reproduce Fig. 2.

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could be observed. When decreasing the current, ρ returned to its original value, indicating adequate cooling. Several samples were measured in the completely different system of a dilution refrigerator to 7 mK. These results overlapped with those from the NDC.

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