Conductivity of icosahedral Al-Pd-Re at ultralow temperatures

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(Received 8 February 1999; revised manuscript received 4 June 1999)

The low-temperature electrical conductivity $\sigma(T)$ has been studied for four samples of icosahedral $Al_{70.5}Pd_{21.0}Re_{8.5}$ in the form of annealed ingots. The resistance ratios $R=\rho(4\,\mathrm{K})/\rho(295\,\mathrm{K})$ were in the range 70–180. The overall temperature dependence of the conductivity below 1 K is stronger than for previously reported results and the conductivity is lower. Two samples were measured down to 15 mK and two down to 0.1 mK. For the latter samples $\sigma(T)$ attained constant finite values at the lowest temperatures. A variable-range-hopping mechanism is discussed. It is concluded that the conjecture for a metal-insulator transition in i-AlPdRe remains unresolved and that measurements must include temperatures below 15 mK on samples of higher residual resistance ratios to settle this problem. [S0163-1829(99)08039-X]

Icosahedral (i)-AlPdRe displays the highest resistivities of all known quasicrystals with values of ρ at 4.2 K in excess of 1 Ω cm.[1,2] In addition, this alloy also has the strongest temperature dependence of the resistivity, and values of the resistance ratio $R[=\rho(4\,\mathrm{K})/\rho(295\,\mathrm{K})]$ up to 200 and above have been reported.[3,4] However, in spite of the general consensus that these properties are insulatinglike, the fundamental questions remain unresolved if and how a metal-insulator transition may occur. Proposed descriptions are controversial. One striking example is the interpretation of the low-temperature conductivity $\sigma(T)$ of i-AlPdRe in terms of variable-range-hopping (VRH) mechanisms.[5,6]

In $Al_{70.5}Pd_{21}Re_{8.5-x}Mn_x$ it was found[5] that VRH of the Efros-Shklovskii type, including Coulomb interactions, and with $\sigma\approx\sigma_0\exp[-(T_0/T)^{1/2}]$, could describe data for $x\geqslant 2$ between 0.45 and 10 K. For $x=0$, however, this was no longer the case. Instead a Mott VRH with

$$\sigma\approx\sigma_0\exp[-(T_0/T)^{1/4}] \qquad (1)$$

was found to describe the temperature dependence of $\sigma(T)$, with T_0 of order 10^3 K, provided a small and constant $\sigma(0)$ was admitted in the observed σ. This effect was ascribed to precipitated defects in the sample or to possible defects in the quasicrystalline state. On the other hand, Eq. (1), without $\sigma(0)$, was found to describe $\sigma(T)$ in the temperature range from 20–600 mK for $Al_{70.5}Pd_{21.0}Re_{8.5}$, albeit in this case T_0 was of order 1 mK.[6] These results are remarkably different for an alloy of the same nominal composition with a six order of magnitude variation in purported T_0, let alone the questions of the origin of the finite $\sigma(0)$ in Ref. 5 and the validity of Eq. (1) at temperatures much greater than T_0 in Ref. 6.

It should be emphasized that these results were obtained in samples which were phase pure in standard x-ray diffraction and of similar R values of order 100. Although the overall strong temperature dependence of $\rho(T)$ is thus similar, there can apparently be important sample differences. The phase diagram and relevant microstructural details are not known for i-AlPdRe, however, and these differences can at present not be specified. It is not clear, for instance, if they are due to small concentration variations, with a possible solid solution range in the icosahedral phase, or if they are due to precipitates or some special type of defects. In this situation the R value may nevertheless serve as a useful sample characterizing parameter, ordering i-AlPdRe samples within a wide range of different results according to what is presumably the foremost transport anomaly of the icosahedral phase.

In the present paper we further investigate the problem of the very-low-temperature conductivity of i-AlPdRe and report results of $\sigma(T)$ for samples with R values in the range 70–180 at temperatures down to 0.1 mK. Ingots were made by arc-melting pressed pellets of high purity elemental powders of the nominal composition $Al_{70.5}Pd_{21.0}Re_{8.5}$. Samples were subsequently annealed at 940 °C for 12 h and 600–650 °C for a few hours. These procedures have been found to enhance the the compositional homogeneity of the samples, as characterized by the R ratios.[4] Bar-shaped samples of typical dimensions $1\times1\times5\ \mathrm{mm}^3$ were cut from the ingots. Standard x-ray diffraction showed a single icosahedral phase. Scanning electron microscopy (SEM) investigations of some samples revealed the presence of a secondary phase of Al and Re only.[7] The SEM pictures showed a substantial amount of needle-shaped voids in the structure. A micrograph has recently been published.[7] The influence of this microstructure on the measurements of ρ was estimated in a model to be described below.

Contacts for the electrical measurements were prepared by silver paint without further annealing. The low-temperature resistance measurements were made in a dilution refrigerator down to 15 mK and at the EC Ultra Low Temperature Facility (Bayreuth, Germany). The sample was attached to a silver sheet covered by a thin layer of varnish, and screwed into a sample holder also made of silver. A temperature of 0.1 mK was reached after demagnetization to 25 mT in the nuclear demagnetization cryostat.[8] This cryostat is situated in an electromagnetically shielded room. The experiments are shared between different projects and run for several months. Long-waiting times at low temperatures and different measurements on heating and cooling cycles of the cryostat were therefore part of the experiment.

Thermometry at ultralow temperatures must be carefully considered. At the lowest measurement temperatures the current was increased by a factor of 10 without influencing the results, indicating that Joule heating of the samples did not occur. Other sources of heat leaks and noise might arise from external heat leaks in the cryostat, intrinsic heat leaks of the samples, and electronic noise from the outside or from instruments at the cryostat. Noise from external sources and instruments and external heat leaks would be shared between many experiments in the cryostat. Experience from experiments which are known be very noise sensitive indicates that this is not an important factor in the present case.[9] Internal heat leaks are sample dependent and little is known about quasicrystals at these temperatures. However, such leaks would be expected to be time dependent and to disappear after a few weeks. Reproducible measurements of the resistance were made over longer time periods, indicating that such effects are not present.

The problem of thermal contact between sample and sample holder is also important. Quasicrystals are brittle, and mechanical pressure to improve the thermal contact had to be avoided in order not to risk breaking samples. This point is therefore the most difficult one in the present experiments. With the sample at a few mK, the current level was increased until a sufficient temperature rise was obtained that a changing sample resistance could be observed. When then decreasing the current, the resistance decreased to its original value indicating adequate cooling. Furthermore, measurements down to 7 mK were made in two experiments, one in which the samples were cooled by the mixing chamber in zero field, one in which they were cooled by the nuclear stage at 25 mT. These are two completely different systems, and the agreement between the results (see Fig. 4), support that cooling was adequate at least down to the base temperature of the dilution refrigerator. We conclude that the thermometry appears to be reliable down to at least a few mK. At lower temperatures, however, deviations between the sample temperature and thermometer cannot be excluded.

To relate the scale of the observations to be discussed to the overall temperature dependence of the resistivity, $\rho(T)/\rho(285\,\mathrm{K})$ is shown in Fig. 1. $\rho(T)$ varies by 2–3 orders of magnitude from 10 mK to 300 K. On this scale the normalized $\rho(T)$ resembles previous results both for similarly prepared as well as for melt-spun and subsequently annealed samples.[7] At low temperatures $\rho(T)$ changes less dramatically. Yet it can be seen from Fig. 1 that the temperature dependence is sizable, and $\rho(10\text{ mK})/\rho(4.2\text{ K})$ is in the range 3–6.

$\sigma(T)/\sigma(1\text{ K})$ at $T\leqslant 1$ K is compared in Fig. 2 with results from Ref. 6. To our knowledge there are no further published

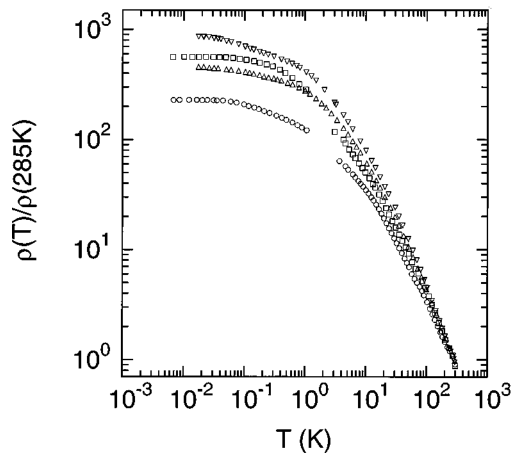

FIG. 1. Overview of the temperature dependence of $\rho(T)$ for the presently studied samples. The values of R $[=\rho(4\,\mathrm{K})/\rho(285\,\mathrm{K})]$ are as follows: ○, 65; △, 133; □, 100; and ▽, 178.

results for $\sigma(T)$ of i-AlPdRe down to temperatures less than 40 mK. The samples of Ref. 6 were melt-spun followed by annealing at different temperatures. For simplicity, the present samples and those of Ref. 6 will be denoted as ingots and melt-spun, respectively, although it is likely the annealing conditions which are most important for the different sample properties. It is seen in Fig. 2 that $\sigma(T)$ depends more strongly on temperatures below 1 K for the ingot samples than for melt-spun ones. The same conclusion is valid also when higher temperatures are considered as illustrated in the inset for $\sigma(20\text{ mK})/\sigma(295\text{ K})$. The conductivity ratio displays a clear trend of decreasing with increasing R for both sets of samples. It can be noted that for the $R=178$ sample, $\rho(20\text{ mK})/\rho(295)$ K reaches 1000.

The steep decrease of $\sigma(T)/\sigma(1\text{ K})$ at low T for the melt-spun samples in Fig. 2 raises the question if $\sigma(T)$ of these samples reaches lower values of the conductivity than the ingot samples. Due to the difficulties to obtain absolute values for the resistivity this question is not straightforward.

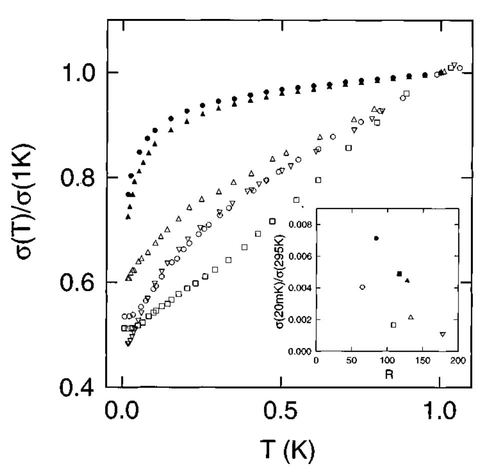

FIG. 2. The normalized conductivity, $\sigma(T)/\sigma(1\text{ K})$ below 1 K. The open symbols are the samples from Fig. 1 with the same legend. The filled symbols are data from Ref. 6 for i-AlPdRe samples of the same nominal composition with $R=84$ (●) and 128 (▲). The inset shows $\sigma(20\,\mathrm{mK})/\sigma(295\,\mathrm{K})$ vs R. ■ is a sample with $R=117$ from Ref. 6.

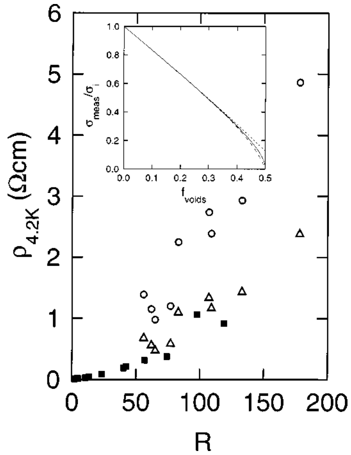

FIG. 3. ρ(4.2 K) vs R. The filled squares (melt-spun samples) and open circles (ingots) are data from Ref. 7 and present results, showing a larger resistivity for the ingot samples at comparable R:s. The inset shows the influence of voids of volume fraction f_{voids} on the ratio of the measured conductivity σ_{meas} and the conductivity of the icosahedral phase σ_i, calculated from a model described in text. The dashed curves are upper and lower Hashin-Shtrikman bounds and the full curve a mean-field calculation. Correcting for this effect gives the open triangles in the main panel, in fair agreement with the results for the melt-spun samples which do not contain voids.

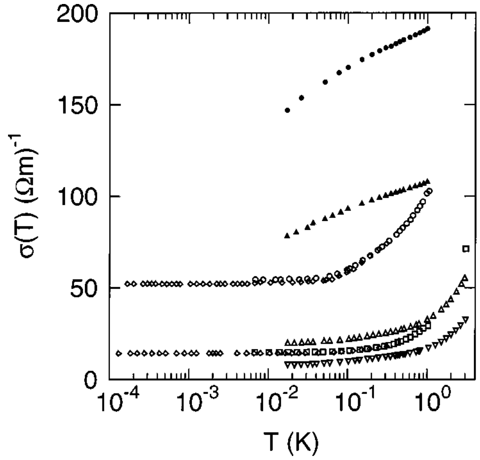

FIG. 4. $\sigma(T)$ vs T on logarithmic T scale to include all data below 1 K. The filled symbols are melt-spun samples, the open symbols ingot samples. The filled symbols and the open circles, squares, up triangles, and down triangles correspond to the data in Figs. 1 and 2 measured in zero field. The measurements below 7 mK were made in 25 mT (open rhomboids). In the region of overlap (7–300 mK) the results coincide within instrumental scatter.

ρ(4 K) is known to be almost linearly correlated with R in i-$Al_{70.5}Pd_{21.0}Re_{8.5}$.[10] However, when comparing melt-spun samples with ingots, the latter samples were found to have larger ρ(4 K) at comparable R than melt-spun samples.[7] This is likely due to the presence of the needle-shaped voids mentioned above, absent in the melt-spun samples.[7] The volume fraction of voids in the ingots was estimated to be ~30% both by a computer-based analysis of their area observed at the surface in scanning tunneling microscope, and also by the ratio of the estimated and calculated densities.

The conductivity of the ingot samples was modeled in the following way. The conductivity of a grain with volume fraction f of voids was calculated for current parallel and perpendicular to the needle-shaped voids. The sample was considered to be a single-phase macroscopically isotropic material, and the resulting conductivity was calculated both by applying Hashin-Shtrikman upper and lower bounds[11] and by an effective-medium theory where the grains were supposed not to deviate strongly from spheres embedded in a matrix of the resulting conductivity.[12]

The calculated reduction of the measured conductivity, σ_{meas}, is shown in the inset of Fig. 3 as a function of f. For $f=30\%$ the three estimates agree and one finds $\sigma_{\mathrm{meas}}(f=0.3)=49\%$ of the conductivity of the icosahedral phase. The main panel in Fig. 3 shows the results from Ref. 7 and present results, before and after applying this correction factor for the ingot samples. The corrected ρ(4 K) is seen to correspond fairly well to the results for the melt-spun samples. This agreement supports our procedures and the low-temperature results for $\sigma(T)$ of the ingot and melt-spun samples can now be compared.

These results are shown in Fig. 4. $\sigma(T)$ for the melt-spun samples was calculated from data given in Ref. 6. In spite of the stronger temperature dependence of $\sigma(T)$ at low T for the melt-spun samples, it is seen that their conductivities remain larger than for the ingots at all measurement temperatures below 1 K. With decreasing temperatures from high temperature, $\sigma(T)$ of the melt-spun samples displays a plateau around 1 K before the low-temperature drop.[13] For the present $R=65$ and 100 samples, in contrast, σ is constant below about 30 mK down to the lowest measuring temperature. In particular, this saturation region occurs well above the temperature region where possible concerns about the thermometry could be relevant as discussed above. For the $R=133$ and 178 ingot samples there is still a temperature dependence of $\sigma(T)$ around 20 mK, although the slope is reduced at least for the $R=178$ sample. This is more clearly seen in Fig. 2. Figure 4 therefore suggests that for the melt-spun samples and the present $R=133$ and 178 samples, measurements down to 20 mK are insufficient to resolve if $\sigma(T)$ saturates.

We now discuss if variable-range-hopping (VRH) behavior can describe the data. The Efros-Shklovskii treatment of VRH takes electron-electron interactions into account in contrast to Mott VRH.[14] One must ask which picture should be applicable in an insulating regime of the present $Al_{70.5}Pd_{21.0}Re_{8.5}$ samples. From recent studies of the magnetoresistance in terms of quantum interference effects in samples of intermediate resistivities, it was concluded that the Hartree term of the electron interactions was strongly reduced already at $R=23$,[15] which supports that a Mott VRH should be applicable in the present samples also if they are insulators close to a metal-insulator (MI) transition.

However, Eq. (1) cannot describe the data. Only if a constant residual is admitted as in Ref. 5, an acceptable description could be obtained at temperatures between 20 mK and 1 K. These results are shown in Fig. 5 for the $R=133$ and 178 samples. Similar results were obtained for the $R=65$ sample with T_0 of about 30 K and a somewhat larger $\sigma(0)$. For the $R=100$ sample, however, T_0 was of order ~100 K. The origin of a finite $\sigma(0)$ is not known. A metallic impurity phase at small concentrations could perhaps form a percolat-

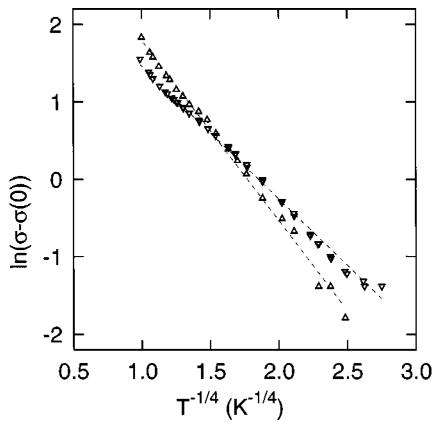

FIG. 5. $\ln[\sigma-\sigma(0)]$ vs $T^{-1/4}$ between 1 K and 20 mK for two of the present samples: $\triangle$, $R=133$ and ∇, $R=178$. It was necessary to assume a finite $\sigma(0)$ in Eq. (1) to describe data in this way. Results for the parameters were then for $R=133$: $\sigma(0)=9.65\,\Omega\,\mathrm{m}^{-1}$, $\sigma_0=62.6\,\Omega\,\mathrm{m}^{-1}$, $T_0=29.6\,\mathrm{K}$, and for $R=178$: $\sigma(0)=3.81\,\Omega\,\mathrm{m}^{-1}$, $\sigma_0=24\,\Omega\,\mathrm{m}^{-1}$, $T_0=8.7\,\mathrm{K}$.

ing network, e.g., in the grain boundaries, which might contribute to $\sigma(T)$ at low temperatures. Our attempts to model such a contribution with reasonable parameters in a two-phase model have failed, however. Furthermore, this remains speculative in the absence of any structural information on such grain boundary impurities.

The present results for T_0 are considerably smaller than the results of Ref. 5 and much larger than those of Ref. 6. If a VRH conductivity is applicable well above T_0, one could speculate that the small T_0 and corresponding large coherence lengths in Ref. 6 indicate that these samples are quite close to a MI transition while, assuming that $\sigma(0)$ can be ascribed to an impurity effect, the present samples and the $Al_{70.5}Pd_{21.0}Re_{8.5}$ samples of Ref. 5 would be more insulatinglike.

It should be emphasized that a discussion on the possibility of a VRH conductivity in quasicrystals remains tentative. It is not clear that VRH would be the relevant conduction mechanism, and the attempts so far can rather be seen as a first attempt to analyze the insulatinglike properties of these samples. The results are not clarifying on several points. E.g., the proximity to a MI transition can apparently not be monitored by the R value alone. The melt-spun sample in Fig. 4 with the highest R value is close to our $R=133$ sample, and the temperature behavior of $\sigma(T)$ is quite different. Furthermore, the apparent T_0 is, e.g., larger for the $R=133$ sample than for the $R=178$ sample, while the converse would be expected from the observed larger σ and smaller R values.

These attempts to understand $\sigma(T)$ of i-AlPdRe underline a number of problems. Firstly, the strong difference in temperature dependence of $\sigma(T)$ below 1 K in melt-spun and ingot samples is remarkable in view of the overall similar R values, and is not understood. Secondly, it appears that measurements must be taken to lower temperatures to determine if saturation of $\sigma(T)$ at low temperatures is a general property of i-AlPdRe or is limited to samples of not too high resistivities. Thirdly, although saturation of $\sigma(T)$ at a finite value does not rule out an insulating matrix, the nature of a possible nonintrinsic $\sigma(0)$ must be understood. It would thus seem that either a reasonable model for $\sigma(0)$ or a consistent trend in T_0 with increasing ρ and R would considerably strengthen the conjecture of a metal-insulator transition. A way to circumvent the need for very-low-temperature measurements could of course be to study samples with even larger ρ and R values, where one would expect a larger T_0 to give a more easily accessible temperature range for the analysis of an insulating behavior.

C. Berger and R. König are heartily thanked for fruitful discussions. We are grateful to P. Ågren and D. Haviland for the loan of and help with the dilution refrigerator. The measurements in Bayreuth were performed within the EC Ultra Low Temperature Facility Program. We gratefully acknowledge the help received from R. König. A grant from KTH has made possible a research visit of one of us (M.R.) to the University of Virginia. This work has been supported by research grants from the Swedish Natural Science Research Council and the U.S. National Science Foundation Grant No. DMR 97-00584.

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