Enhanced Insulatorlike Electron Transport Behavior of Thermally Tuned Quasicrystalline States of Al-Pd-Re Alloys

F. S. Pierce, Q. Guo, and S. J. Poon
Department of Physics, University of Virginia, Charlottesville, Virginia 22901
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Low temperature annealing of insulatinglike AlPdRe icosahedral-quasicrystalline (iqc) samples has led to unexpected large changes in their transport properties, with resistivities at 0.45 K increasing from ~ 1 to $> 10\ \Omega$ cm, but their electronic structure is apparently unaffected. These findings, which add evidence for quasiperiodic order effects on electronic properties, as well as the unusual low-T (< 4.2 K) conductivity trend noted in the thermally tuned samples, underline fundamental differences between iqc and conventional materials that exhibit electron localization.

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Recent reports of transport studies of icosahedral-quasicrystalline (iqc) samples of AlPdRe that are thermally ordered at comparable high temperatures of 850–910 °C show a wide range of resistivities ρ, varying from $\rho(4.2\ \text{K}) \sim 0.3\ \Omega$ cm [1] to $\sim 0.13\ \Omega$ cm [2] to $\sim 0.025\ \Omega$ cm [3]. While the large disparity in transport properties can be attributed to the degree of metallic-phase inclusion emphasized earlier [4], the highest ρ values reported [1,2] are noted to be comparable to those of doped semiconductors in the barely insulating regime of the metal-insulator transition (MIT) [5]. It was pointed out that the low-T behavior of conductivity was unconventional with respect to crystalline alloys near the MIT, and the density of states at the Fermi level as well as the Hall number were semimetalliclike [1]. These preliminary results on AlPdRe i-alloys, which were not seen in ordered metallic iqc's studied previously [4], were expected to provide a new basis for understanding quasiperiodicity effects on electronic properties. In this Letter we report observation of some striking changes in the transport properties of previously noted insulatinglike AlPdRe i-alloys upon further annealing at lower temperatures of 600–700 °C, namely, the samples become much more insulatinglike. Such observation on quasicrystals is unprecedented. Through the study of trends in electronic properties measured by transport and specific heat on thermally tuned samples characterized by x-ray diffraction, the importance of qc ordering effects is discussed.

$Al_{70.5}Pd_{21}Re_{8.5}$ ingots were made by melting appropriate combinations and quantities of high-purity elements sequentially, under argon in an arc furnace. The procedure was carried out to mitigate the problem of ingot inhomogeneity in alloying aluminum with high melting point refractory metals, details of which will be given elsewhere [6]. Composition of our alloys was chosen based on its high probability of yielding samples of very good phase purity and thus reproducibility of large $\rho(4.2\ \text{K})/\rho(295\ \text{K})$ ratio (~ 20) when annealed at ~ 930–950 °C. Samples for measurements, in dimensions of $\sim 1 \times 1.5 \times 5$ mm, were annealed under highly purified conditions at ~ 940 °C for 12 h. Some samples were given further annealing at lower temperatures ~ 600–850 °C for up to ~ 10 h. All heat-treated samples were rapidly quenched in chilled water. X-ray diffraction, performed using a SCINTAG diffractometer with a resolution of $< \sim 0.13°$ (Cu K_α), shows no apparent change in shape for all the diffraction peaks [1] as a function of annealing temperature. Especially for the three low-angle peaks as shown in the inset of Fig. 1, the absence of peak broadening or splitting upon annealing at 600 °C [7] contrasts sharply with those noticeable changes observed that indicate structural phase transformation in the diffraction patterns of low-temperature-annealed i-AlCuFe [8,9]. Although high resolution diffraction measurements need to be performed to determine the exact nature of the transformation, to our instrumental resolution, it appears that the i-AlPdRe samples retain their quasicrystallinity upon being annealed at various temperatures. Conductivity, Hall effect, and specific heat measurements were performed as described earlier [6,10].

Results on thermal relaxation processes in AlPdRe i-alloys utilizing the dependence of resistivity on annealing temperature and time, which constitutes a topic in itself, will be given elsewhere [11]. For our analysis of qc effects on electronic properties, it will suffice to state several key findings on annealing that are relevant. Starting with samples preannealed at ~ 940 °C for 12 h to ensure their phase purity, there is a rather well-defined narrow temperature region ~ 700–750 °C below which further annealing can lead to a large increase in $\rho(4.2\ \text{K})$ and $\rho(4.2\ \text{K})/\rho(295\ \text{K})$ ratio r within the convenient laboratory time scale of less than several hours for $T(\text{anneal}) > 600$ °C. The maximum r obtained, defined by the saturation in r [$r(\text{sat})$] versus annealing time, remains rather constant (~ 100) between ~ 600 and 700 °C, but above ~ 750 °C it shows a rapid drop toward the 940 °C value. As a result, $r(\text{sat})$ for samples treated between ~ 800 and 950 °C has a similar value ~ 20. For convenience in discussion, we will heretofore label the i-alloys by two "qc states" and focus study of electronic properties on samples annealed at 600–650 °C, in view of our findings. Figure 1 displays the large effects on

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ρ as well as $\rho(T)$ for i-$Al_{70.5}Pd_{21}Re_{8.5}$ annealed at 600 °C for 2 h, long enough to saturate r at 600 °C. The average value of ρ(295 K) for samples cooled from 940 °C was 12 000 $\mu\Omega$ cm with a standard deviation of 2500 $\mu\Omega$ cm. ρ(295 K) was enhanced by the 600 °C anneal to 16 000 $\mu\Omega$ cm with a standard deviation of 4000 $\mu\Omega$ cm. ρ(4.2 K) is seen to be enhanced 5 times, and ρ(0.45 K) 10 times relative to those of the 940 °C sample; ρ also rises more rapidly at low T in the 600 °C sample, with ρ at 0.45 K equal to ~1000 times its room-temperature value. The value ρ(4.2 K) ~ 1.5 Ω cm is comparable to those seen in doped semiçonductors well inside the insulating region of the MIT [5]. These results are unprecedented in structurally ordered aluminum-based metallic systems. It should be mentioned that our results have been reproduced in over 100 samples, obtained from more than 20 ingots. Another finding from our annealing study is that the effects on ρ are essentially reversible when the samples are cycled between two T(anneal)'s [11].

To shed light on the nature of electronic states as well as the conduction mechanism in view of the apparent divergence in ρ at low T (Fig. 1), we analyze the conductivity (σ) behavior below ~4.2 K for i-phase samples stabilized in the two qc states introduced above. $\sigma(T)$'s for some of these samples, grouped according to their T(anneal) and thus qc state, are depicted in Fig. 2. For the 600 °C samples, it is clear that $\sigma(0)$ extrapolates to very nearly zero [< 0.008 $(\Omega\,\mathrm{cm})^{-1}$] and that $\sigma(T) \sim T$. In comparison, $\sigma(T)$ for the 940 °C samples exhibits an increasingly negative curvature at decreasing temperature. This suggests fitting $\sigma(T)$ to a power-law expression, as shown in Fig. 2 and inset. One obtains $\sigma(T) \sim T^{\beta}$, possibly with an intercept ≤ 0.01 $(\Omega\,\mathrm{cm})^{-1}$ at $T = 0$, and

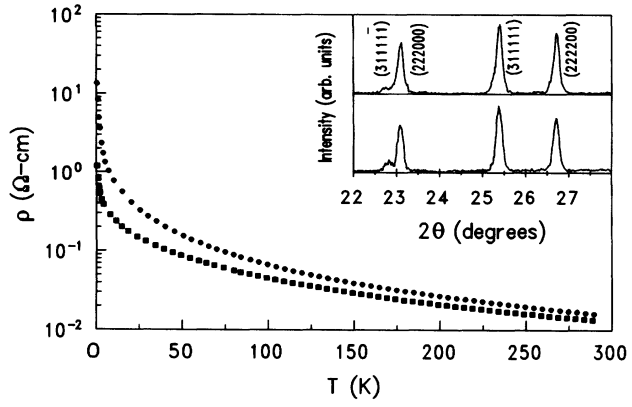

FIG. 1. Resistivity versus temperature and x-ray diffraction patterns (inset) for $Al_{70.5}Pd_{21}Re_{8.5}$ (■) annealed at 940 °C for 12 h, without additional annealing ρ(295 K) = 12 000 $\mu\Omega$ cm, lower x-ray pattern and (●) with an additional anneal at 600 °C for 2 h, ρ(295 K) = 16 000 $\mu\Omega$ cm, upper x-ray pattern. Trend of x-ray patterns is described in text. Peaks are labeled by the 6D indexing scheme according to Ref. [7].

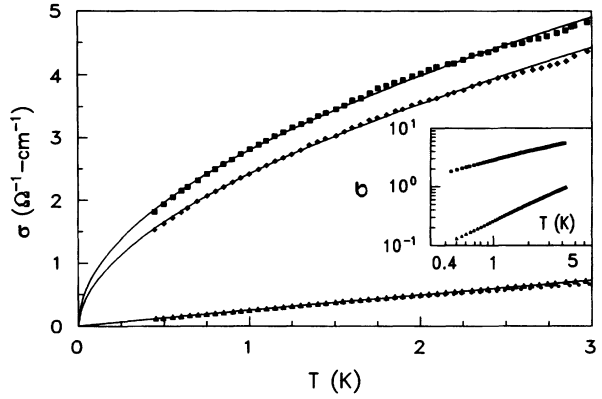

FIG. 2. Low temperature σ for annealed $Al_{70.5}Pd_{21}Re_{8.5}$ samples. Lines are drawn to show power law dependence corresponding to the slope of the log-log plot for $T < 3$ K (inset). (■) $\sigma \sim T^{0.55}$, (◆) $\sigma \sim T^{0.51}$, for samples annealed at 940 °C for 12 h. (●) and (▲) samples with additional annealing at 600 °C for 2 h, showing $\sigma \sim T$ (data overlap for these two samples below 2 K).

the conductivity exponent $\beta \sim 0.5$–0.6. Thus, results on the 940 °C samples are similar to those observed in the $Al_{70}Pd_{20}Re_{10}$ samples [1]. We have also looked at samples annealed at intermediate temperature as well as time, that is, those not in a well-defined qc state. Their conductivity exponents are found to lie between 0.5 and 1. Given the insulatinglike σ values and $\sigma(T) \gg \sigma(0)$, these conductivity exponents are clearly unknown in the study of MIT in conventional alloys [5,12].

To further explore electron transport process in the qc states, results from Hall effect measurements are shown in Fig. 3. While the strong temperature and composition dependence of the Hall coefficient (R_H) in semimetallic iqc has been discussed in terms of electronic structure effects [4,13,14], R_H in the present qc's is much larger in magnitude and in the case of the 600 °C samples varies more rapidly with temperature than previously noted.

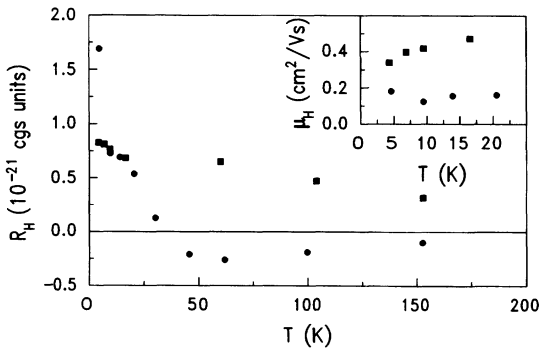

FIG. 3. Hall coefficient and Hall mobility (inset) for $Al_{70.5}Pd_{21}Re_{8.5}$ annealed at 940 °C for 12 h (■), and annealed at 940 °C for 12 h, followed by an additional anneal at 600 °C for 2 h (●).

Thus, it is unlikely that these results can be explained solely on band structure grounds. From data taken on several samples in each of the two qc states, $R_H(4.2\ \mathrm{K})$ values for the 940 and 600 °C samples are found to be at least 3 and 10 times larger, respectively, than previously measured in other iqc systems [13]. For clarity, only one sample in each qc state is shown. However, their results are found to be characteristic of the state. It gives a Hall number $n_H \sim 8 \times 10^{19}\ \mathrm{cm}^{-3}$ for the 940 °C samples and $\sim 3 \times 10^{19}\ \mathrm{cm}^{-3}$ for the 600 °C samples, a much reduced free-carrier density at 4.2 K compared with previous iqc's. However, at higher temperature (> 100 K), n_H tends to the value $\sim 2\text{–}3 \times 10^{20}\ \mathrm{cm}^{-3}$, comparable to the semimetallic qc's. Since $\sigma(T)$ varies most rapidly below ~20 K, we plotted the Hall mobility $\mu_H \sim \sigma/n_H$ at low T in the inset to Fig. 3. It is seen that μ_H varies by ~50% from 4.2 to ~20 K, a variation much smaller than in σ, particularly for the 600 °C sample. This implies that the rapid decrease in n_H, the free-carrier density, is largely responsible for the insulatinglike σ trend at low T. This finding lends support to the notion of carrier localization at low temperature, consistent with recent optical conductivity measurements [15]. Meanwhile, it is also noted that μ_H for the 940 °C sample is about twice that for the 600 °C annealed sample, consistent with its higher conductivity. Future measurement will extend below 4.2 K to examine the Hall number exponent.

In view of the large reduction in $\sigma(T)$ due to low temperature annealing, one wonders if the band structures of the two qc states are significantly different. Specific-heat measurement provides information about the electronic density of states at the Fermi level. Figure 4 shows specific-heat data from the 940 and 650 °C samples plotted in the form C/T vs T^2, which are fitted to the standard expression $C = \gamma T + \beta T^3 + \delta T^5$. It gives $\gamma = 0.1$ mJ/g atom K^2, $\theta_D = 425$ K for the 940 °C sample, and $\gamma = 0.11$ mJ/g atom K^2, $\theta_D = 450$ K for the 650 °C sample. These γ values are comparable to those of semimetallic i-AlCuRu alloys with σ 2 orders of magnitude greater [4]; they are also compatible with the semimetallic n_H in the more delocalized state at $T > 100$ K reported above. These points, together with the rather surprising finding of almost the same γ for the two distinctive qc states, give clear evidence that the small σ value and its large reduction upon additional low temperature treatment is not of band structure origin. Meanwhile, the factor of 2 difference in γ between presently 8 at.% and previously [1] 10 at.% rhenium alloys may be accounted for by the strong compositional dependence in properties alluded to earlier [4,13].

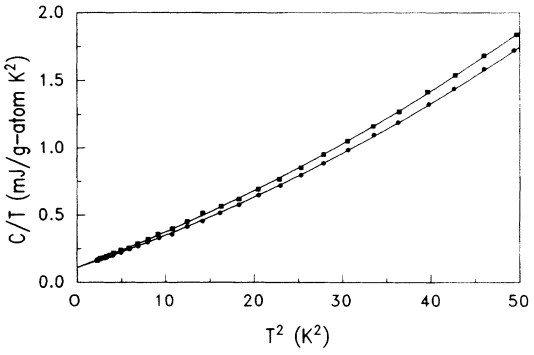

FIG. 4. Specific heat data for $Al_{70.5}Pd_{21}Re_{8.5}$. Solid lines are fits to the standard form $C = \gamma T + \beta T^3 + \delta T^5$. (■) Sample annealed at 940 °C for 12 h. $\gamma = 0.1$ mJ/g atom K^2, $\beta = 0.026$ mJ/g atom K^4, and $\delta = 1.9 \times 10^{-4}$ mJ/g atom K^6. (●) Sample annealed at 940 °C for 12 h followed by an additional anneal at 650 °C for 3 h. $\gamma = 0.11$ mJ/g atom K^2, $\beta = 0.022$ mJ/g atom K^4, and $\delta = 2.2 \times 10^{-4}$ mJ/g atom K^6.

Since the reports of barely metallic iqc's [4,16], there have been several proposals to understand the anomalous electron transport observed, ranging from hopping of eigenstates between structural units [17–19], to anomalous wave propagation of critical states [20], to band structure effects [4,14], with high structural order as their common basis. In putting forth a credible theory to explain our findings, one would have to bear in mind the important facts that $\sigma(0) \to 0$, $\sigma(\text{low } T) \sim T^\beta$ with $0.5 < \beta \leq 1$, n_H in the delocalized regime and γ exhibit semimetallic and self-consistent values, and improved qc order rather than reducing γ clearly leads to a much enhanced insulatinglike behavior. Improved qc order in low-T(anneal) samples showing very good i-phase x-ray diffraction patterns is favored on entropic grounds [21]. Further assessment of qc order in our samples, of course, awaits high-resolution x-ray diffraction study. Indirect evidence of improved qc order may also be inferred from the ~6% increase in Debye temperature in the low-T(anneal) samples. Conversely, the softening of phonon modes in a lattice is normally attributed to disorder. As far as the theories go, the requirement of high qc order and finding of semimetallic γ do not contradict them. Meanwhile several theories either explicitly [18,20] or implicitly [17] suggest that $\sigma(0) \to 0$, but the value of the conductivity exponent is either known only in 2D qc [20], or in disagreement with the present result [17,18]. As a final note, it should be pointed out that in view of the importance of qc order, the nature of eigenstates should be specific to quasiperiodicity. One should then contemplate the notion of critical states originally studied in 2D quasilattice [22] and its implications on transport in qc [20]. It is quite clear that the picture of Anderson localization in disordered systems is not relevant in quasicrystals. Present experimental results should provide a new basis for further experimental and theoretical investigation.

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