

Reply to “Comment on ‘Extrinsic origin of the insulating behavior of polygrain icosahedral Al-Pd-Re quasicrystals’ ”

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We clarify issues raised in the preceding Comment regarding the viewpoint that the highly porous and oxidized arc-melted polygrain *i*-Al-Pd-Re samples could reveal intrinsic electrical transport properties of this icosahedral family. Flux-grown single-grain *i*-Al-Pd-Re samples of superior structural quality do not show insulatinglike behavior, and their transport properties are on common ground with all other Al-based icosahedral families.

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The preceding Comment has raised two fundamental questions regarding the transport properties of *i*-Al-Pd-Re quasicrystals (QCs).

(A) Are the extremely high R and ρ_{4K} values and the metal-to-insulator transition (MIT) intrinsic properties of the *i*-Al-Pd-Re phase?

(B) Is the “oxidized-bridge” scenario the right explanation for the insulatinglike behavior of polygrain arc-melted *i*-Al-Pd-Re samples?

(A) Regarding the intrinsic properties of *i*-Al-Pd-Re, the following facts should be considered.

(i) Among the Al-rich QC families, insulatinglike behavior and a MIT were so far only reported for the polygrain *i*-Al-Pd-Re samples. These phenomena have neither been observed in single-grain *i*-Al-Pd-Re nor in any other Al-based QC family. Flux-grown single-grain *i*-Al-Pd-Re samples do not show insulatinglike behavior,¹⁻³ and their transport properties, being semimetallic, are on common ground with all other Al-based icosahedral families.

(ii) There can be only one physical picture of the icosahedral *i*-Al-Pd-Re, regardless of its polygrain or single-grain form. In view of that, the reported spectacular differences between the two morphologies of the same material do not seem to have a rational explanation in view of the intrinsic properties of the *i*-Al-Pd-Re phase. A property can only be called *intrinsic* when it is invariant to the change of morphology of the sample; it should exist regardless of the polygrain or single-grain form. This is not the case for *i*-Al-Pd-Re.

(iii) The fact that *i*-Al-Pd-Re is on common ground with other Al-based QCs is supported by comparing it with the structurally isomorphous *i*-Al-Pd-Mn QC, which does not show insulating like phenomena in any of the morphologies. Re (a $5d$ element) is isoelectronic to Mn ($3d$) and the Re $5d$ wave functions are more extended in space than the $3d$ wave functions of Mn. This suggests an even higher electrical conductivity of the Re compound, but this can be partially compensated by the slightly larger distances between the atoms in *i*-Al-Pd-Re (the lattice parameter of *i*-Al-Pd-Re is a_6

$=6.53\text{\AA}$, as compared to $a_6=6.452\text{\AA}$ of *i*-Al-Pd-Mn). There is no intrinsic physical reason why the electronic transport properties should change dramatically upon replacing Mn by Re.

(iv) In the commented paper,¹ we use an arc-melted ingot polygrain *i*-Al-Pd-Re sample supplied to us by S. J. Poon, one of the authors of the Comment. The electrical conductivity of this sample is a power law $T^{1.35}$, its $\rho_{4.2K}=3.1\ \Omega\ \text{cm}$ and $R=154$, which are very typical figures for the best insulating polygrain *i*-Al-Pd-Re. We found that this sample is highly porous and oxidized at the surfaces; in the bridges connecting bulky grains, even 8 at. % of oxygen was detected. The large oxygen contamination is most likely associated with imperfect sample synthesis and annealing conditions. In addition to oxidation, annealing at high temperature also results in corrupted chemical composition of the surface layer due to evaporation of the material (for the *i*-Al-Pd-Mn QCs annealed at $800\ ^\circ\text{C}$, Grushko⁴ has reported that the corrupted surface layer was $0.5\ \text{mm}$ thick). The polygrain *i*-Al-Pd-Re we used was annealed in the first step at $960\ ^\circ\text{C}$, so that the corruption of the “skin” due to evaporation is present as well. The “all-skin-no-meat” bridges of a few μm in length and $1-2\ \mu\text{m}$ in diameter between bulky grains are made of corrupted surface layers and are hence foreign bodies to the *i*-Al-Pd-Re phase. The small volume of the bridges prevents any x-ray diffraction determination of the chemical compounds that actually form the bridges (most likely they also contain the electrically insulating Al_2O_3 oxide). Yet the porous geometry of the polygrain *i*-Al-Pd-Re demands that the conduction electrons inevitably cross these bridges upon long-range transport over the material. The electrical transport will therefore be strongly affected by these extrinsic defects, and one can seriously doubt that intrinsic electrical conductivity is measured in such samples. It is instructive to note that the long-range transport properties (electrical conductivity, thermoelectric power, Hall coefficient), where the electrons travel over macroscopic distances in the material, are in fact the main source of the literature-

reported discrepancy between polygrain and single-grain *i*-Al-Pd-Re.

(v) The problem of degradation of the *i*-Al-Pd-Re material upon annealing was also described by Fisher and co-workers,² who showed that annealing at 900 °C *outside* the melt resulted in partial decomposition of the material (samples only survived annealing at this temperature when held *inside* the melt prior to decanting). Properly annealed flux-grown single-grain *i*-Al-Pd-Re samples are of superior quality to the polygrain samples; porosity, oxidation, and secondary phases are absent.

(vi) In Ref. 1, we compare the *i*-Al-Pd-Re material in the extreme limits of the highest (arc-melted polygrain sample) and the lowest (flux-grown single grain) R and $\rho_{4\text{ K}}$ values. Another polygrain form of the material, melt-spun ribbons produced by arc melting followed by melt spinning and finally annealing, remains to be discussed. The ribbons generally show R and $\rho_{4\text{ K}}$ values intermediate to the arc-melted and single-grain samples, but the extreme values of the arc-melted samples are not reached. The reported R and $\rho_{4\text{ K}}$ values of the ribbons of nominally the same composition scatter by as much as a factor 50 (R values being typically between 2 and 100), so that their structural quality may vary a lot between samples. It is not clear which R value should be taken as intrinsic to the *i*-Al-Pd-Re phase. We are not aware of any quantitative study of the structural assessment of the ribbons (oxidation and possible degradation of the ribbons upon annealing), which is necessary to discuss the ribbons side by side with the other two morphologies of the material.

(vii) There is no deeper theoretical background for understanding the role of the R parameter in the electrical transport of *i*-Al-Pd-Re and the associated empirical relation between R and the estimated zero-temperature conductivity $\sigma(0)$ (see the discussion of this issue on p. 024116-3 of Ref. 5 of this Reply). There is no common agreement on the critical R value where the MIT occurs. In addition, the R - $\sigma(0)$ relation is also suggested to serve as a measure of the structural quality of *i*-Al-Pd-Re samples and other Al-rich QCs, where higher R and lower $\sigma(0)$ values are supposed to denote higher quality of the samples. This is expressed in the Comment by the statement that “*further improvement of cleanliness was required for the arc-melting process that samples with R values up to 280 could be produced.*” Since the highly porous and oxidized arc-melted samples show the highest R and the lowest $\sigma(0)$ values, whereas single-grain samples of superior structural quality show consistently low R and high $\sigma(0)$, the validity of this phenomenological argument needs reconsideration. Flux-grown single-grain samples are the “cleanest” (no secondary phases, porosity, and oxidation), yet they show the lowest R values, thus contradicting that high R could be predominantly a consequence of the samples’ cleanliness. In view of the above, it is not clear how the R - $\sigma(0)$ relation could give *strong empirical support that intrinsic electronic properties are measured.*

The above points (i)–(vii) show the problems encountered when intrinsic transport properties try to be inferred from measurements on polygrain *i*-Al-Pd-Re samples.

(B) Following the finite quality of the investigated

polygrain *i*-Al-Pd-Re sample (porosity and oxidation), the “oxidized-bridge” scenario of the high- R and $-\rho_{4\text{ K}}$ phenomenon appears an obvious possibility. Another issue to consider is the possible strong concentration dependence of the resistivity—i.e., the possibility of a resonant increase of the resistivity at a particular sharp Al-Pd-Re concentration. Krajić and Hafner⁵ have predicted theoretically the appearance of topologically induced semiconductivity for the composition $\text{Al}_{70.7}\text{Pd}_{20.6}\text{Re}_{8.6}$, which was assigned to a specific distribution of Al and transition metals on the chains in the B20-type structure. This structure is a 0/1 approximant to the *i*-Al-Pd-Re phase and, due to isomorphism, also to *i*-Al-Pd-Mn. Since the prediction is based purely on topological considerations, the result⁵ should be equally valid for both *i*-Al-Pd-Re and *i*-Al-Pd-Mn. This raises the question why semiconducting like behavior was so far only reported for (polygrain) *i*-Al-Pd-Re and not also for *i*-Al-Pd-Mn? In Ref. 5 it is also suggested that the large difference in the resistivities of the polygrain and single-grain *i*-Al-Pd-Re samples studied in Ref. 1 could be due to their compositional difference and the associated difference in the electron concentration (the composition of the polygrain sample $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ is closer to the above theoretical concentration⁵ than the composition of the single-grain sample $\text{Al}_{73.5}\text{Pd}_{17.1}\text{Re}_{9.4}$). While it is correct to assume that the composition difference brings some difference in the resistivities of the two samples, the extremely large (resonant like) increase of the resistivity of the polygrain sample is unlikely to be of that origin. This follows from the resistivity measurements by Guo *et al.*,³ who have studied single-grain *i*-Al-Pd-Re samples with concentrations in the range $\text{Al}_{71.7\pm 0.9}\text{Pd}_{19.4\pm 1.6}\text{Re}_{8.9\pm 0.9}$, which within the experimental limits includes also the concentration of our polygrain sample and the theoretical concentration of Ref. 5. The resistivities of the Guo samples³ ($\rho_{300\text{ K}}=2\text{--}4\text{ m}\Omega\text{ cm}$, $\rho_{2\text{ K}}=3\text{--}6\text{ m}\Omega\text{ cm}$, and $R<2$) are practically identical to that of our single-grain sample ($\rho_{300\text{ K}}=1.9\text{ m}\Omega\text{ cm}$, $\rho_{4\text{ K}}=2.7\text{ m}\Omega\text{ cm}$, and $R=1.4$), showing no resonant increase close to the theoretically predicted semiconducting concentration.⁵ Here again the extrinsic origin of the high R and $\rho_{4\text{ K}}$ phenomenon in polygrain arc-melted *i*-Al-Pd-Re offers reasonable explanation of the discrepancy between the polygrain and single-grain samples.

Assuming weakly insulating (Al-oxide) junctions between icosahedral grains does not contradict the insulator-metal transition induced by neutron irradiation (Ref. 18 of the preceding Comment) in the porous arc-melted *i*-Al-Pd-Re samples (only such were studied in Ref. 18). Due to the reported loss of the icosahedral volume upon irradiation (the intensity and the number of observable x-ray peaks have decreased with increasing dose and a broad background amorphouslike intensity is evident for angles below 30° in the x-ray spectrum of Fig. 1 of Ref. 18), another effect appears plausible. Irradiation damage results in partial amorphization of the material (both within the bridges and the icosahedral islands) with increased electrical conductivity, resulting in a decreased R upon an increased irradiation dose. To further test this hypothesis, it is desirable to repeat the neutron irradiation experiment on a single-grain *i*-Al-Pd-Re sample, where structural problems of the arc-melted material (porosity, oxidation, secondary phases) are absent.

To summarize, the arguments in the preceding Comment are based exclusively on the previous work on polygrain *i*-Al-Pd-Re material, whereas the work on single grains, available only after 2000,¹⁻³ is ignored. Yet a careful comparison of the physical properties of the polygrain and single-grain samples is the clue to resolve the apparent (non)exceptionality of *i*-Al-Pd-Re. The right questions to discuss, but avoided in the Comment, are (1) why the insulating effects are not present in the superior-quality single-grain *i*-Al-Pd-Re QCs and (2) on what basis could *i*-Al-Pd-Re QCs be intrinsically different from all other

icosahedral Al-rich QC families? Currently there is no rational answer to these questions by considering intrinsic properties of the material.

A minor issue to mention is that in Ref. 13 of the Comment, only one *i*-Al-Pd-Re sample was studied by NMR (the other two were *i*-Al-Pd-Mn and *i*-Al-Cu-Fe). Nothing like a *strong sensitivity of the deep pseudogap to small concentration variations* is reported in that paper. The reported semi-conductinglike behavior of the arc-melted ingot sample investigated in Ref. 13 cannot be associated with the intrinsic properties of this material.

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