

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

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In a recent paper, Dolinšek *et al.* [Phys. Rev. B **74**, 134201 (2006)] suggested that the insulating behavior of icosahedral (*i*) Al-Pd-Re is of extrinsic origin. Large resistivities and insulatinglike properties of high resistivity samples were conjectured to result from the porous structure and the observed enhanced oxygen concentration in between the quasicrystal grains in some *i*-Al-Pd-Re samples. We point out that these hypotheses are incompatible with published work on the structure and properties of *i*-Al-Pd-Re.

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Recently, Dolinšek *et al.* have investigated the structure of some icosahedral (*i*) Al-Pd-Re quasicrystals.¹ A polygrain sample, which was arc-melted, subsequently annealed, and then quenched in water, was compared with large single grain samples obtained by slow cooling from a prealloyed melt. It was found that there was oxygen enrichment up to a factor of 4 in between the grains of a quenched polygrain sample compared to the average oxygen concentration of slowly cooled single grain samples. Dolinšek *et al.* ascribed the much larger resistivity ρ in polygrain samples to the porous structure of their sample. It was suggested that *i*-Al-Pd-Re is on common grounds with other Al-based quasicrystals, and the conjecture advanced was that the strong temperature dependence of ρ in polygrain *i*-Al-Pd-Re is an extrinsic effect occurring by some conduction mechanism of the material in between grains (such as tunneling or variable range hopping).

The observation of oxygen enrichment in rapidly quenched polygrain *i*-Al-Pd-Re is interesting. However, the conclusions drawn from the results and comparisons with other quasicrystals are not supported by experiments. In contrast, published work contradicts the statements of Dolinšek *et al.* We discuss several points below under the two main issues raised in Ref. 1, i.e., morphology and oxygen concentration.

*Differences in morphology do not account for the large $\rho(4.2\text{ K})$ in *i*-Al-Pd-Re*

Polygrain (*i*)-Al-Pd-Re samples can be prepared as (I) ingot samples or (II) melt-spun samples. In method I, arc-melted ingots are annealed and rapidly quenched. In method II, samples are melt-spun, followed by annealings and slow cooling in an oven. The only polygrain sample used in Ref. 1 was one of type I. The microstructure of these two types of samples have been compared.² Samples prepared by method II were found to be homogeneous, with some secondary phases of order 5% on the surface of the samples. Samples from method I had needle shaped voids of volume of about 30%, giving a porous structure with scanning electron microscope pictures resembling that shown in Ref. 1 for the polygrained sample.

The low temperature resistivity ρ of homogeneous polygrain Al-Pd-Re samples is similar to that of the porous samples.³ However, when data for *i*-Al-Pd-Re samples were

displayed as $\rho(4.2\text{ K})$ vs the average temperature dependence $R = \rho(4.2\text{ K})/\rho(295\text{ K})$, it was found that ingot samples fell consistently above melt-spun samples. The conductivity of ingot samples was, therefore, modeled according to theories for conduction in inhomogeneous media as described in Ref. 3. The estimated volume of voids of 30% gave a reduction of conductivity of about 50%. When this correction was applied, the relation between $\rho(4.2\text{ K})$ and R was found to be approximately the same for melt-spun and ingot samples. Hence, pores are not a general explanation for the large $\rho(4.2\text{ K})$.

A consistent relation between the estimated zero temperature conductivity $\sigma(0)$ and R has later been established, which covers more than 2 orders of magnitude in $\sigma(0)$ and includes ingots and melt-spun samples.⁴ For low R samples, estimates of $\sigma(0)$ can be made from measurements in the liquid ⁴He region. Including such results for melt-spun² and single grain^{5,6} samples, the relation between $\sigma(0)$ and R was extended over almost 4 orders of magnitude in $\sigma(0)$.^{7,8} This result is a strong empirical support that intrinsic electronic properties are measured.

A larger $\rho(4.2\text{ K})$ in polygrain icosahedral samples than in single grains is not unique for *i*-Al-Pd-Re as suggested in Ref. 1. In polygrain *i*-Al-Pd-Mn samples, $\rho(4.2\text{ K})$ reaches about 10 m Ω cm,⁹ while in high quality single grain materials, values in the range 2–4 m Ω cm have been reported.^{10,11} The difference is in the same direction as for *i*-Al-Pd-Re, but much smaller. However, *i*-Al-Pd-Mn is the alloy system where the most perfect icosahedral quasicrystals can be prepared. There is no porous structure in single grains nor in polygrain samples.

The reason for the difference in ρ between single grain and polygrain samples in icosahedral quasicrystals is not understood. There are other investigations, such as tunneling spectroscopy¹² and NMR measurements,¹³ which indicate that *i*-Al-Pd-Re exhibits semiconductorlike properties. A strong sensitivity of the deep pseudogap to small concentration variations was inferred from the NMR results.¹³ Possibly the compositions of polygrain and single grain samples could be different, resulting in a strong effect on the electronic transport properties.

This problem is yet another one of the many challenging problems of quasicrystals. However, from the brief discussion above, it is evident that the reason cannot be associated

with a porous structure in some of the samples in one of the two alloy systems displaying this effect.

Increased oxygen concentration promotes a more metallic state, not an insulator

The proposition in Ref. 1 that the modest increase of oxygen concentration of up to 8% in grain boundaries of quenched ingots of *i*-Al-Pd-Re produces the large R values, is not accompanied by any details on how this would occur. According to the picture advanced, this amount of oxygen, expected to be located on the surface of the bridges between grains, could apparently produce a change in R from 1.4 in the single grain to 154 for the polygrain sample. The metal-insulator transition occurs at about $R=20$,¹⁴ and this would imply a change of state from a quite weakly electronically disordered metal to a sample deep into the insulating state. The consistent variation of several sample properties with R , ubiquitously observed in *i*-Al-Pd-Re, is also difficult to visualize from different oxygen arrangements and enrichments. Since only one polygrain sample was studied in Ref. 1, the R dependence is hidden when electronic properties are compared with a single grain sample.

Let alone this speculative nature of the mechanism proposed in Ref. 1, the idea that a more insulating state is favored by oxygen impurities is refuted by experimental observations.

Firstly, for several years after the first electronic transport studies of *i*-Al-Pd-Re,^{15,16} the R values were generally limited to below 100. It was not until the realization that further improvement of cleanliness was required for the arc-melting process¹⁷ that samples with R values up to 280 could be produced. Thus, oxygen does not promote large R values, it counteracts them.

Some details of the sample preparation illustrate this point. In view of the high melting temperature of Re, which is significantly higher than that of Al, powder mixtures of the elements were used in order to maximize the melting reaction of Al and Re. Powders of the elements were thoroughly mixed and pressed to form a pellet, followed by melting in an arc furnace. The furnace was evacuated by using a roughing pump, and then backfilled with argon gas to atmospheric pressure before melting. The final pressure during the pump down was recorded. A strong correlation between the achieved final pressure and the measured transport properties was observed. When the final pressure only reached 200 mTorr or higher, $\rho(295\text{ K})$ was found to be $\approx 3\text{--}8\text{ m}\Omega\text{ cm}$, with R values of 1.1–1.5. However, if a final pressure of 15–20 mTorr was attained, $\rho(295\text{ K})$ increased to 10 m $\Omega\text{ cm}$ or larger, and R also increased to >50 .

Secondly, an *i*-Al-Pd-Re sample can be monitored through an insulator-metal transition by high energy neutron irradiation.¹⁸ There is no change of oxygen concentration expected in this process. These experiments instead show a concomitant decrease of ρ and R with a decrease of the amplitude of the x-ray scattering peaks, thus relating changing transport properties to changes of the icosahedral phase.

In conclusion, the conjecture of Ref. 1 that the insulating behavior observed in some quenched polygrain *i*-Al-Pd-Re samples would be of extrinsic origin is unfounded. Experimental results instead indicate that measured electronic properties are intrinsic to the icosahedral phase. Support for this statement is found, e.g., from the extended relation between R and residual conductivity $\sigma(0)$,^{4,7} and by the observation that one single sample can be monitored through an insulator-metal transition by neutron irradiation and then by low temperature annealings be transformed in the opposite direction, with an increasing R for a limited range of R values.^{8,18}

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