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Linear increase of the conductivity with the concentration of local defects in AlPdMn quasicrystals

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We find a linear relation between the conductivity σ and the Mn spin concentration x in pure AlPdMn single grains of high structural quality. We associate the vanishing concentration of Mn spins (down to 4×10^{-5} moments) to local defects in the Mn atoms local environments. Both σ and x are set by the nominal composition and can be reversibly tuned by careful heat treatments. We deduce that low σ characteristics of perfect AlPdMn quasicrystals can only be observed for concentrations of magnetic Mn lower than $x<5\times10^{-4}$, i.e., for defects more than about 30 Å apart. In addition, we show that a Kondo-like effect explains the low-temperature σ upturn, also linear with x.

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The physical origin of the low conductivity of Al-based quasicrystals (QC) containing transition metals is still a controversially debated question. The main feature is conductivity values orders of magnitude lower than crystalline alloys and some quasicrystalline alloys can even undergo a puzzling metal-insulator transition.[1,2]

A promising way to understand the electronic properties characteristic of QC's is the study of the conductivity dependence when the quasiperiodic potential is perturbed by defects. This is the same challenge as for the residual resistivity decades ago in standard metals. But in quasicrystals, it is the conductivity that increases with the amount of defects,[1] which is not the least peculiarity of this class of materials. However, up to now, such a quantitative study could not be carried out, because it requires to detect a vanishing concentration of local defects (a few tens of ppm) out of reach of structural studies.

Here we present a study of the conductivity σ and magnetism of *i*-AlPdMn pure samples of extremely high structural quality (single grains). In this compound, almost all the Mn atoms are in a zero-spin state.[3] We find a linear relation between σ (both its value and the magnitude of the low-temperature upturn) and the concentration of residual magnetic moments. In addition, we explain the low-T σ upturn by a Kondo-like effect. We argue that Mn spins arise from defects in the local environment of Mn atoms. It follows that σ increases *linearly* with the concentration of magnetically probed defects. Thus, a *quantitative* correlation between transport properties in QC's and a vanishing concentration of such defects is shown.

In the dilute regime of magnetism, it is required to measure pure samples to avoid any possible grain-boundary contribution. So we studied only large single grains that we grew by the Czochralski method. Early studies on melt-spun ribbons have shown that a finely tuned composition around $Al_{70.5}Pd_{22}Mn_{7.5}$ is crucial to obtain the lowest σ, where the typical QC resistivity is observed.[4] Since pure single grains cannot be grown at that composition, we chose the closest available ones. Parallelepipedic bars ($8\times1.5\times0.5$ mm^3) were cut in the core of two single grains by spark erosion: three adjacent bars (A, A', A'') in an $Al_{70.5}Pd_{21}Mn_{8.5}$ single grain and two (B, B') in an $Al_{70.3}Pd_{21.5}Mn_{7.9}$ single grain. Due to composition gradients, albeit tiny, along the growth direction, we cut the bars perpendicularly to this axis and have measured the composition by inductively coupled plasma emission spectrometry on samples cut next to them. The bars were initially annealed 3 days at 800 °C.

We could tune both σ and the Mn spin concentration by applying successively various thermal treatments in the order I to VI to any given bar. For treatment I to IV, a first 3 h step at 800 °C results in a single-phased *i* state, as observed by high-resolution x-ray diffraction.[5] Subsequently, we cooled down the samples at the following rates. I at 150 °C/mn, II at 10 °C/hour, III again at 150 °C/mn, IV is intermediate between I and II. Step I was skip for samples A', B, and B'. Treatments V and VI are low-T annealing (500 °C) for 2 and 30 h, respectively, right after a rapid cooling III (IV skip). The rapid cooling rate (I, III) locks the *i* state, whereas for the slow one (II) a superlattice ordered *i* phase either F2 or F2M develops for some compositions.[5,6] In contrast the plateau annealing of V and VI might be too low for a transformation into F2M.[6] Resistivity was measured with four probes and the sample shape factor (yielding $\Delta\rho/\rho=3\%$) estimated from sample weight and density (5.1 g/cm^3). Due to the small sample size (20–30 mg) and the low moment concentration, we measured the magnetization using a superconducting quantum interference device magnetometer of high sensitivity (10^{-8} emu). Magnetization measurements and synchrotron radiation revealed no parasitic phase, magnetic or otherwise.

Figure 1 shows the temperature dependence of $\sigma(T)$ and $\chi_p(T)$, measured after each thermal treatment. The susceptibility is $\chi_p(T)=M/H-\chi_0$, where M is the magnetization measured in a field $H=0.1$ T and χ_0 is deduced by extrapolation of M/H for $1/T\rightarrow0$ using a polynomial fit. The magnitude and the T dependence of σ are comparable to those of the most resistive polygrained (melt-spun) samples.[4] Note that the bars A, A', A'' cut adjacentely in the same single grain exhibit close σ and χ_p values when they are in the same annealed state.

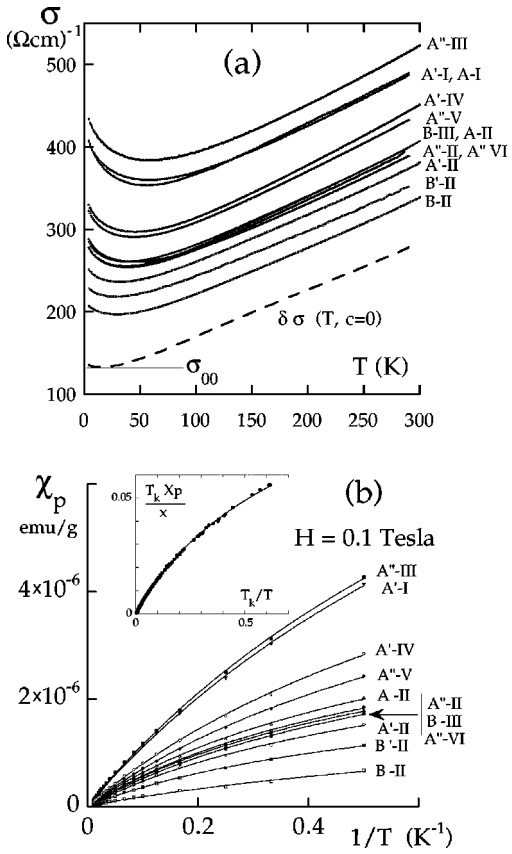

FIG. 1. Temperature dependence of the electrical conductivity σ (from 4 to 300 K) and susceptibility χ_p (from 2 to 150 K) of the same samples in the same annealed state. Inset: all the χ_p data are reported in a $\chi_p T_K/x$ vs T_K/T diagram. The Kondo fits for the χ_p are represented by solid curves.

The heat treatment leads to reversible results. Treatment III performed after the slow cooling II restores the σ and χ_p values of treatment I. For bar A', a subsequent intermediate treatment (IV) results in σ and χ_p values in between these obtained with I and II. Note that the low-T annealing VI (after III) gives similar σ and χ_p values as the slow cooling II. The sensitivity of the magnetization to temperature scans is in line with previous exploring studies.[7,8]

The first key result of Fig. 1 is that above a temperature $T_L \sim 100$ K, $\sigma(T)$ increases with T and the curves are all *parallel* with one another. This is known as the inverse Matthiessen rule: $\sigma(T)=\sigma_0+\Delta\sigma(T)$.[9] This is the same trend but for the resistivity of dilute metallic alloys. In contrast with the magnitude of the T-independent term σ_0, $\Delta\sigma(T)$ is almost the same for the more resistive icosahedral i-AlCuFe, i-AlCuRu, i-AlPdMn, and noninsulating i-AlPdRe samples, whatever their annealing state.[2,9]

The second result is that the more magnetic the samples, the more conductive.

The third one is that all samples lie in the very dilute regime for the spin concentration x, for we find $x \sim 10^{-4}$. In a first attempt, as $\chi_p(T)$ is not linear in $1/T$ in contrast with pure paramagnets, we fitted the χ_p data from 2 K up to 100 K with a Curie-Weiss law: $\chi_p = C/(T+\theta)$. Here, C is the Curie constant: $C = xNS(S+1)(g\mu_B)^2/3k_B$ where N is the total number of atoms. Taking $S=2.5$,[3,10] we find $x=6.3\times10^{-5}$ for sample A''-II as an example. We checked by measuring in a field ten times smaller that the negative curvature of the $\chi_p(1/T)$ was not a high-field induced curvature effect. Similar curvatures were reported previously for other i-AlPdMn samples, 12–50 times more magnetic than our less magnetic one[10] and analyzed by a Kondo effect, due to the progressive screening of the localized moment by the conduction electrons as T decreases. It results in a susceptibility χ_p/C given by a function of T and of a Kondo temperature T_K: $\chi_p = Cf(T/T_K)/T_K$, where f is found to be almost independent on S in the n-channel Kondo model (for $n=2S$).[11] We analyzed our $\chi_p(1/T)$ in the same way. Using the exact result: $f(0)=0.41072$ and the numerical results for $\chi_p(T)/\chi_p(0)$,[11] we estimated x and T_K for each sample, by taking $S=2.5$. It allows to superpose all the data on a single curve in the $\chi_p T_K/x$ vs T_K/T diagram shown in Fig. 1(b). We find T_K to decrease from 1.2 to 0.6 K as x increases from 3.7 to 19.3×10^{-5}, in agreement with the value of T_K: 0.7 K, reported in Ref. 10 for other i-AlPdMn samples.

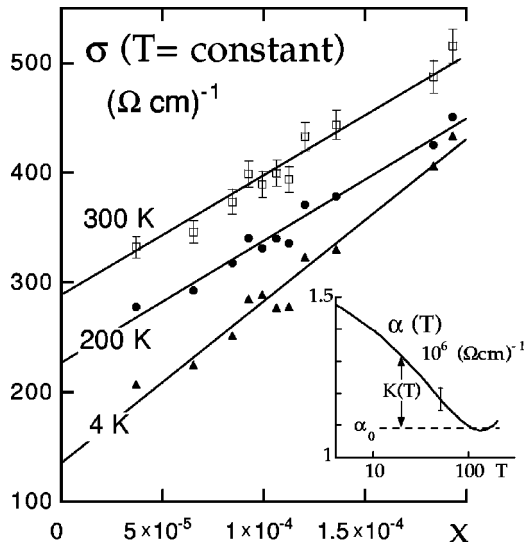

FIG. 2. Conductivity at constant temperature T vs the concentration x of magnetic Mn. Inset: magnetic contribution to the conductivity, α vs $\ln(T)$ as defined by Eq. (1).

Figure 2 shows the direct relation between σ and the Mn magnetism. In the plot $\sigma(T=\text{constant})$ vs x, the σ values of all the samples are aligned on a straight concentration line for each temperature. Thus, σ is driven by the Mn spin concentration x:

$$\sigma(T) = x\alpha(T) + \delta\sigma(T) \tag{1}$$

For a set of temperatures T, we have estimated both $\alpha(T)$ (shown in the inset of Fig. 2) and $\delta\sigma(T)$ [dotted line in Fig. 1(a)] from the linear fit of the $\sigma(T)$ vs x curves.

The first result of Eq. (1) is the existence of a contribution $\delta\sigma(T)$ that is the same for all samples, even below T_L.

The second result is that the sample dependent part of σ is directly proportional to the concentration of magnetic moments. The term $\alpha(T)$ can be split between an almost T-independent contribution: $\alpha_0 = \alpha(T > T_L)$ observed above

T_L and a strong negative temperature-dependent $K(T)$ term that occurs below T_L (see Fig. 2) so that

$$\sigma(T) = \delta\sigma(T) + x\alpha_0 + xK(T). \quad (2)$$

The term $xK(T)$, which reflects the large upturn below T_L, is simply proportional to the spin concentration. Thus, we believe that the dominant effect is not a strong spin-orbit effect on weakly localized electrons as claimed previously.[12] We propose that it is due to the same spin effect (Kondo type) that explains the $\chi_p(T)$ behavior. Similarly as in the case of χ_p, it is a one-spin effect since $xK(T)$ is proportional to the moment concentration. Also, the $\ln(T)$ type dependence of $\sigma(T)$ over one T decade (see Fig. 2) is characteristic of a Kondo effect. For very dilute alloys, the $\ln(T)$ dependence applies for $\rho(T)$.[11] But it may apply for σ when quantum interferences at the origin of a lowered σ are broken due to the spin flip of the conduction electrons by the Kondo spins, as it is the case for the weak localization.[13] We note that a more detailed analysis should take into account a possible $K(T)$ dependence on T_K.

We now turn to the origin of the term $x\alpha_0$. Because it is almost T independent, we discard interpretation related to direct interactions between the Mn spins and the spins of the conduction electrons. As a consequence, it is a residual conductivity of nonmagnetic origin, which, however, increases *linearly* with the number of magnetic Mn. Thus, we attribute this term to the presence of a vanishing concentration of local ''defects'' detected by the Mn magnetism. Our argument, which agrees with recent theoretical results,[14] is the following. The zero-spin state of almost all the Mn atoms implies that it is the fundamental state of Mn in this type of structure. Conversely, the fewness of magnetic Mn's (down to 3.7×10^{-5} times the number of atoms, i.e., 4.5×10^{-4} of the total number of Mn atoms) suggests the occurrence of magnetism to be due to variations in the local environments. We expect the Mn atoms to be sensitive to most of these fluctuations since Mn are about one every 12 atoms, and magnetism is predicted to be sensitive up to middle range order.[14] We call ''defects'' any local departure from perfect local environments, which does not imply necessarily topological defects. Indeed they can be point defects such as vacancies but also chemical substitution of an atomic species by another one, for instance, to accommodate a departure from an ideal composition, or local change accounting for subtle phase difference (like ico vs F2M).

This is supported by the following experimental facts. First, both x and σ are very sensitive to the chemical composition. This suggests that low values of σ and x can be obtained only from a finely tuned average composition to enable the best local chemical order. But, even for an optimized composition, some local chemical fluctuations might occur. Then, we expect the electronic properties to depend primarily on the concentration of such residual ''defects.'' Striking enough, the data for any given bar, that is at a constant composition, obey Eq. (1) whatever the cooling. In other words, for each temperature, σ increases linearly with magnetically probed local ''defects.'' We propose the following scenario: such defects present at high T (800 °C) can be frozen by a rapid cooling (process I and III), yielding a more conductive and magnetic state than for a sample either slowly cooled or annealed at 500 °C, where defects can be more (II, VI) or less (IV, V) relaxed. The reversibility of the magnetic and transport properties observed for the successive treatments I, II, III, can most probably be accounted for by a reproducible concentration of ''defects'' occurring at a given temperature. We outline that the decreasing number of ''defects'' (by about a factor 2) obtained by a type II slow cooling could be also associated to the local atomic arrangements leading to the superlattice ordering of the F2M phase or to the precursor F2 state.[6] This is presently under investigation.[15]

A this step, we stress that Eq. (2) reduces to the inverse Matthiessen rule: $\sigma(T) = \sigma_0 + \Delta\sigma(T)$ down to low temperatures in the lack of Kondo-like spin effect, i.e., for $K(T) = 0$. Thus the dependence of σ_0 on the composition and annealing observed for other QC's, such as *i*-AlCuFe,[1] could also be due to a change in local arrangements, unfortunately undetectable to the level of the present study.

Now, we show that QC's follow the same conductivity trend as standard amorphous alloys when the mean distance $\langle r \rangle$ between magnetically probed ''defects'' is smaller than 30 Å. In early works, both σ and M have been measured for *i*-AlPdMn single grains[16,17] and melt-spun ribbons,[4,17] more concentrated in Mn (9–11 at %). Their spin concentration x ranges from 7 to 50 times that of sample A''-II. As in amorphous alloys, their conductivity depends weakly on T, varies little with x and saturates at a value of the order of 800–1000 $(\Omega\text{cm})^{-1}$. It is precisely the value expected for the conductivity of a typical amorphous metal once normalized to the density of states of *i*-AlPdMn, which is 1/3 to 1/4 the estimated free electron value.[17] Here, the $\sigma = 1000$ $(\Omega\text{cm})^{-1}$ saturation value is reached for $x = 5\times10^{-4}$ ($\langle r \rangle = 30$ Å) from a crude linear extrapolation of the σ $(x, T = 300$ K) curve of Fig. 2.

Finally, let us discuss the possible microscopic origin of the different contributions to σ. From Eq. (2) and following Ref. 1, it is tempting to write $\sigma(T)$ as a function of $1/\tau$, where τ stands for the various scattering electronic times. It is in line with the weak localization hypothesis, where the electronic coherent interference pattern is destroyed at a rate $1/\tau_\phi$, arising from phonons, Kondo spins, ... These effects, clearly identified in *i*-AlPdMn,[18] may account in part for the T dependence of σ. However, the σ increase with defects calls for an additional interpretation, which should take into account the role of transition metals (TM). These are known to strongly scatter sp electrons, affect the density of states[19] and yield unusual high resistivity in QC's. At three dimension, an icosahedral cluster of second neighbors TM atoms plugged into an Al jellium results in a resonance effect in the density of state.[20] It follows an electronic confinement, with electrons trapped for an unusually long time in cluster-induced states. A TM atom removal off the cluster reduces significantly the resonance effect.[21] This confinement effect pertains to the conductivity results on α AlMnSi and α AlReSi approximants known to contain such TM icosahedra.[22,23] The icosahedral symmetry of the Mn atomic positions in *i*-AlPdMn[24] should imply the same type of con-

finement. Thus the conductivity term α_0 could originate from local ''defects'' in the Mn arrangement, which free the confined electrons. Consequently, the number of free-like electrons, or the time of nonconfinement, should increase with the amount of such ''defects'' in the dilute limit. Clearly in *i*-AlPdMn there remain sufficient nonfully confined electrons at $T=0$, even for vanishing magnetically detected defects, to contribute to the nonzero σ_{00} term (see Fig. 1).

In summary, we have shown a linear relation between the conductivity σ and the concentration of magnetic moments, which can be finely tuned by the sample composition and heat treatments. This strong sample dependence of the properties explains the large range of σ values [$\sigma_{300\ \mathrm{K}} = 300$–$1000\ (\Omega\mathrm{cm})^{-1}$] in the literature, that we relate to defects probed by Mn magnetism. Indeed, we show that systematic measurements on the very same samples in the same annealed state, can turn the sample dependent magnetization into a probe of local defects down to very low concentration. From this study, we conclude that a low σ is characteristic of perfect AlPdMn QC, and this can be observed only for a defect concentration lower than 500 ppm, i.e., defects more than about 30 Å apart. This distance turns out to be comparable to the size of few clusters in QC's. The low σ value is in agreement with recent theoretical results supporting an electronic confinement induced by specific local icosahedral environments,[20] this confinement being destroyed by local defects.

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