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# Point contact spectroscopy of $Al_{70}Pd_{30-x}Mn_x$ quasicrystals

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**Abstract**
We report here the electrical resistivity and point contact spectroscopy (PCS) of $Al_{70}Pd_{30-x}Mn_x$ quasicrystals ($x = 7, 9$ and 11). All samples show a negative temperature coefficient of resistivity (TCR) at room temperature and a positive TCR below 100 K giving rise to resistivity maxima. The positive TCR at lower temperature is attributed to spin–orbit scattering. For $x = 11$, we observe an upturn with a sharp rise in the resistivity below 20 K and $\ln T$ dependence of resistivity is observed below 10 K indicating Kondo-like behaviour. In the PCS we are able to see evolution of the point contact regime to the tunnelling-like regime as a function of contact resistance. We see the signature of the Kondo effect in the PCS. In this spectroscopy we observe three regimes showing a $V^n$ dependence where $n \sim 1.7$ at low bias voltages (for $V < 10$ meV) crossing over to $n \sim 0.5$ at higher voltages and to $n \sim 2$ above 60 meV.

## 1. Introduction

Icosahedral quasicrystals (i-QCs) having unique structural and electrical properties [1] are of interest both experimentally and theoretically. Structurally the i-QCs have no translational symmetry like disordered solids but have rotational symmetry like crystalline solids with a forbidden fivefold symmetry. They have a very high electrical resistivity value $\rho$ and a negative temperature coefficient of resistance (TCR, $d\rho/dT < 0$) near room temperature (300 K) in spite of the fact that they are made of purely metallic components. The quasicrystalline alloy shows the presence of a pseudo-gap (minimum of the density of states—DOS) at the Fermi energy $E_F$ due to the nature of the lattice arrangement of the atoms. The Brillouin zone (BZ) of the i-QC system has many faces leading to an almost spherical shape and the diameter of

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the Fermi surface (FS) is also almost the diameter of the BZ, and hence the spherical Fermi surface–Brillouin zone (FS–BZ) interaction leads to a pseudo-gap at the Fermi energy. This is very similar to that observed for divalent disordered liquid metals and metallic glasses where a pseudo-gap opens up due to intraband overlap effects [2]. But the magnitude of the high resistivity value observed cannot be explained by just invoking the concept of a pseudo-gap because the resistivity of i-QCs increases by orders of magnitude as the quality of the quasicrystallinity improves (by annealing or by varying the growth conditions), whereas the reduction in the DOS is only by a factor of a few. This aspect of increase in $\rho$ with the improvement of the quasicrystalline quality also remains an open question. The origin of the negative TCR is still not very clear. In our earlier paper on the Al–Cu–Cr system [3], we attributed the negative TCR to either the weak-localization (WL) effect or the diffraction effect (temperature dependent structure factor). The WL effect for most good i-QCs gives a negative TCR, $\sigma \sim T^n$ with $n = 1$–1.5 [3], which arises predominantly from quantum correction to conductivity [4]. It is still not clear why the WL effect should be valid at high temperatures ($T > 50$ K). We pointed out earlier [3] that another plausibility for negative TCR to arise is through the temperature dependence of the structure factor as is observed in various 'diffraction models' of resistivity [5]. This latter explanation fits naturally in the case of quasicrystals because one generally observes $k_p \approx 2k_f$ where $k_p$ is the reciprocal scattering wavevector associated with the first intense peak in the x-ray structure factor and $2k_f$ is the diameter of the Fermi sphere. This condition of $k_p \approx 2k_f$ also leads to the stability of the quasicrystalline phase. One can thus find a common link of stability and negative TCR. But the issue of negative TCR at higher temperature is still not fully resolved theoretically. Some lacuna of the above models were mentioned earlier by us [3].

To understand the behaviour of electronic properties of the i-QCs one needs to understand the behaviour of the DOS at and near $E_F$. Earlier studies have used specific heat and photo-electron spectroscopy (PES) to determine the DOS near the Fermi energy. Most recently, tunnelling spectroscopy (TS) and point contact spectroscopy (PCS) techniques have been used extensively to study various electronic properties of materials [6, 7]. The TS is very sensitive to any gap in the quasi-particle spectrum at $E_F$. This can be clearly seen as a characteristic feature near the zero bias in the conductance $G = \mathrm{d}I/\mathrm{d}V$ versus the bias voltage $V$ curves, where $I$ is the tunnelling current. Compared to any other technique, TS has a very high resolution of the order of $k_B T$ which is less than 1 meV when the experiment is conducted at liquid helium temperatures. Recently a pseudo-gap has been observed in i-AlCuFe [8, 9] and i-AlPdRe [8] using TS. Apart from the DOS information one can obtain magnetic information on the system from TS and PCS [6, 7]. It is well known that the magnetic properties of 3d transition metal (TM) alloys are affected by the local atomic environment. Mn atoms in Al–Pd–Mn alloys have a giant magnetic moment, whereas in other i-QCs with Mn most of the Mn atoms are nonmagnetic [10]. Al–Pd–Mn also exhibits a spin-glass state at low temperature and the spin freezing temperature $T_f$ for $Al_{85-x}Pd_{15}Mn_x$, $12 < x < 16$, lies between 9 and 14 K [11]. At low concentrations of Mn atoms ($Al_{70}Pd_{21}Mn_9$), spin freezing has been observed at very low temperature ($T_f = 0.5$ K) [12]. PCS can be used as a probe to see low energy excitations such as magnons and phonons [7]. At very low bias voltages one can identify signatures of spin-glass and Kondo behaviour. Schematically we have shown in figure 1 how the conductance versus bias voltage behaves in the PCS. This schematic figure is empirical in nature, and is based on available experimental data and not on any theoretical calculation. The figure will be discussed in detail later in this paper. We have tried to see whether spin-glass and Kondo behaviour can be observed using PCS in $Al_{70}Pd_{30-x}Mn_x$. Recently, a point contact measurement [13] on i-QCs AlPdRe, AlCuFe and AlPdMn in the tunnelling regime as a function of temperature was reported. Here, we present the evolution of conductance $G$ as a function of contact resistance.

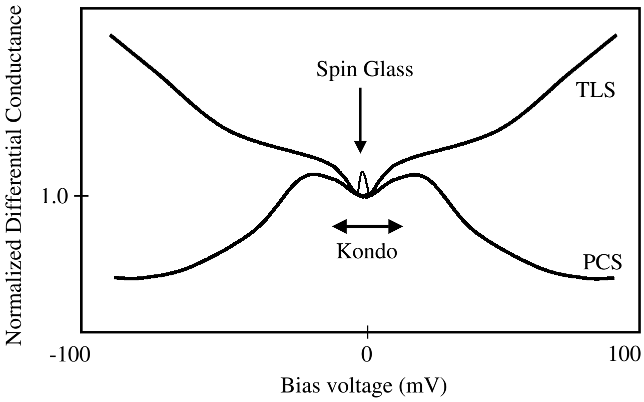


**Figure 1.** Schematic diagram showing the variation of the conductance in the point contact regime (PCS) and the tunnelling-like regime (TLS). The signatures of the spin-glass behaviour and Kondo-like behaviour are shown.

In this present investigation our aim is to address the following issues.

(1) How the resistivity of the present i-QC alloys evolves as one varies the magnetic concentration in the system.
(2) What the effect is of magnetic impurities on PCS.
(3) Whether there is any universal characteristic feature of i-QCs in the $I$–$V$ characteristics in the point contact for low and high contact resistance.

## 2. Experimental details

The $Al_{70}Pd_{30-x}Mn_x$ ($x = 7, 9$ and 11) alloys were prepared from high purity (99.999%) constituent elements by induction melting in pure Ar atmosphere. The QCs were made from the alloy ingots by the melt spinning technique using a rotating copper wheel. The samples were obtained in a strip form of thickness $\sim$25 $\mu$m and 2–3 mm in width. The structural and microstructural characterization of the alloy strips were carried out by transmission electron microscopy (TEM) and x-ray diffraction (XRD). The resistances of the alloy strips were measured by a low frequency ($\sim$20 Hz) ac four-probe method. The leads of the samples were attached by silver paste. The measuring current was $\sim$1 mA. The precision for measurement was $\sim\pm$20 ppm whereas the absolute accuracy limited by sample geometry is $\sim$15%. The resistivity measurements were carried out in a bath type $He^4$ cryostat to cover the temperature range of 4.2–300 K. The point contact measurements were made at 4.2 K with a electrochemically etched gold tip. The details of the experiment are given elsewhere [14].

## 3. Results

### *3.1. X-ray diffraction and TEM*

XRD patterns obtained from the as-quenched alloy strips of $Al_{70}Pd_{30-x}Mn_x$ ($x = 7, 9$ and 11) are shown in figure 2. The x-ray powder diffraction pattern for all the compositions of the alloy could be indexed by all odd or all even numbers indicating that the icosahedral quasilattice is F-type (FCI) icosahedral phase without any other crystalline or quasicrystalline phase. The TEM measurements on these samples revealed a typical fivefold symmetry in the electron diffraction

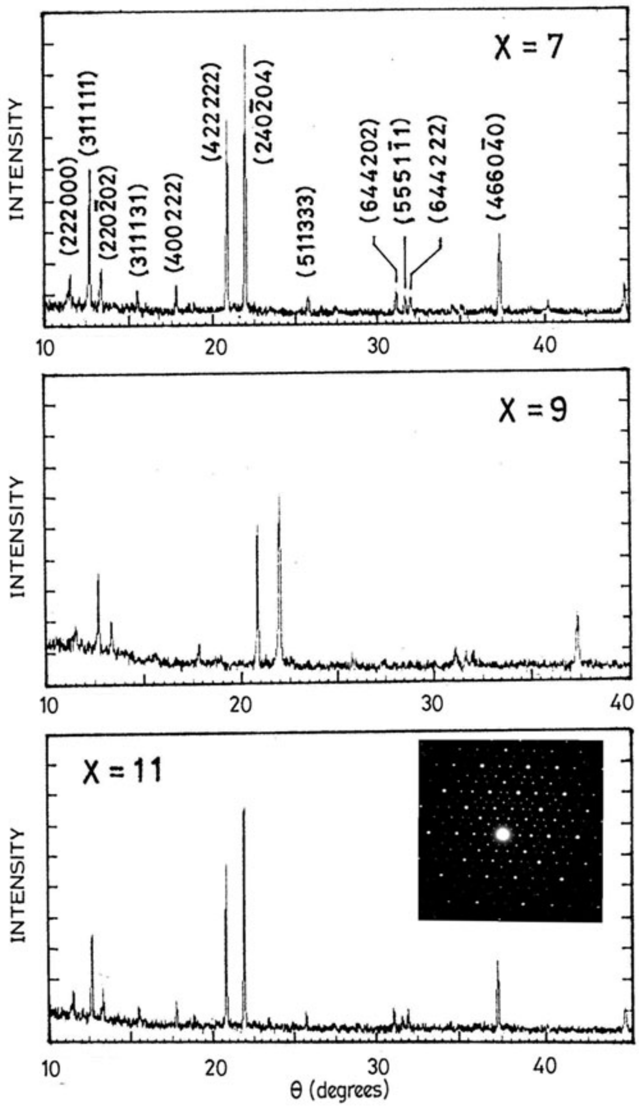


**Figure 2.** XRD of $Al_{70}Pd_{30-x}Mn_x$ for $x = 7$, 9 and 11. The inset of $x = 11$ shows the electron diffraction spots with the fivefold symmetry.

pattern as shown in the inset of figure 2 for $x = 11$, which confirms the quasicrystallinity of the samples. We also observe very sharp spots which implies the absence of phason strain in the samples. However the quality of the quasicrystallinity can be known from the absolute resistivity value and the temperature dependence of the resistivity as mentioned in our earlier work [3].

### *3.2. Resistivity*

In figure 3 we show the temperature dependence of the resistivity $\rho(T)$ of the samples. All the compositions show negative TCR for $T > 100$ K like other conventional quasicrystals.

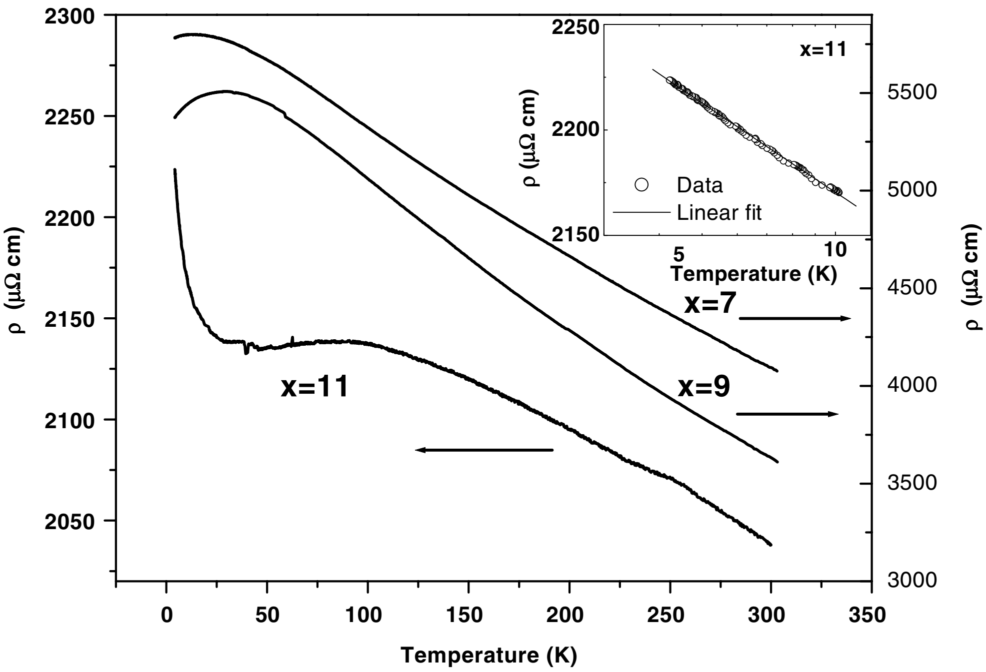


**Figure 3.** The resistivity of the $x = 7, 9$ and 11 samples showing the negative TCR at room temperature, the maxima in the resistivity and the upturn for the $x = 11$ sample. Inset: ln $T$ dependence of resistivity of the $x = 11$ sample below $T \sim 10$ K.

All of them show a maximum in $\rho$ for $T < 100$ K and at lower temperatures these show interesting features in $\rho(T)$ as a function of Mn concentration. We observe that for $x = 11$, $\rho$ increases steeply below 20 K with a minimum at about 40 K. This sudden increase in $\rho$ is not observed for the other two lower concentration samples ($x = 7$ and 9) for temperatures down to 4.2 K. The maximum in $\rho$ shifts towards a higher temperature $T_{\max} \sim 13$, 29 and 84 K for $x = 7, 9$ and 11 respectively as $x$ increases. The absolute value of $\rho$ (300 K) decreases with increase in Mn concentration.

### *3.3. Point contact spectroscopy*

In figure 4 we show the normalized conductance $G(V)/G(V = 0) = (\mathrm{d}I/\mathrm{d}V)/(\mathrm{d}I/\mathrm{d}V)_{V=0}$ for a 20 Ω junction at 4.2 K for $x = 7, 9$ and 11. The curves have been vertically shifted for the sake of clarity. All the samples show a sharp decrease in conductance near zero bias showing a *zero-bias anomaly* (ZBA). It can be seen that the magnitude of the dip in the conductance increases as the Mn concentration increases. In figures 5 and 6 we have shown the normalized conductance for $x = 9$ and 11 as a function of contact resistance showing the evolution of normalized conductance from point contact to tunnelling-like behaviour. The conductance features are very similar to that shown in figure 1 where we have shown schematically the evolution of normalized conductance as a function of contact resistance from the point contact to the tunnelling-like regime (TLS). We call this a tunnelling-like regime, because $\mathrm{d}I/\mathrm{d}V$ increases as a function of bias voltage which is the signature of $\mathrm{d}I/\mathrm{d}V - V$ characteristics for conventional tunnel junctions. We will come back to this point in the discussion section.

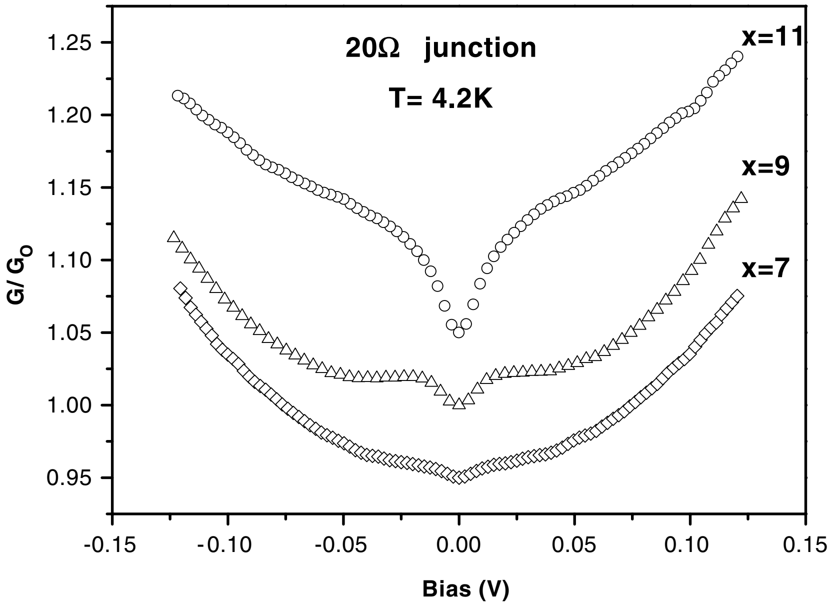


**Figure 4.** The point contact conductance spectra for the 20 Ω junction at 4.2 K for $x = 7$, 9 and 11, showing the ZBA.

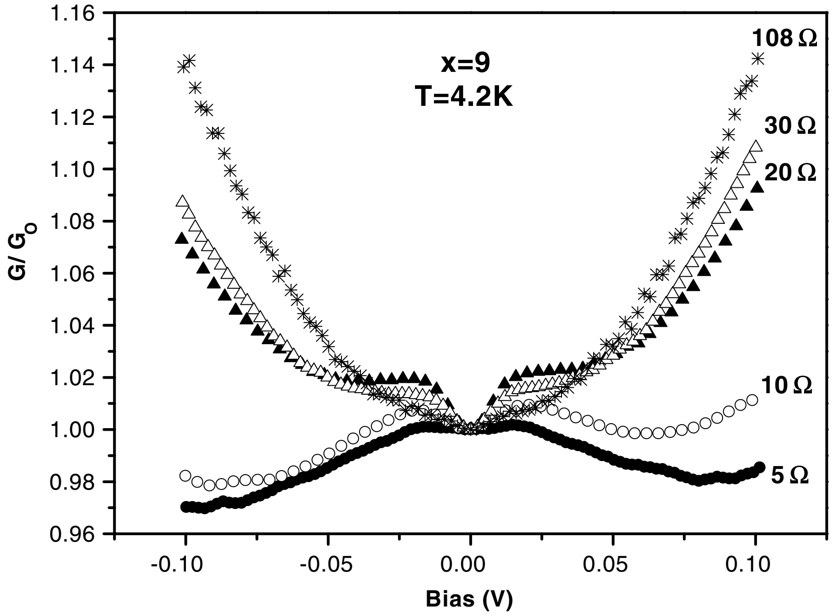


**Figure 5.** The evolution of the conductance spectra for the $x = 9$ sample, showing the evolution from the point contact regime to the tunnelling-like regime as a function of junction resistance.

For $x = 7$ we could not vary the contact resisitance for a reason not clear to us, but the high resistivity of the sample may be one of the reasons for not being able to control the contact resistance with the present experimental technique.

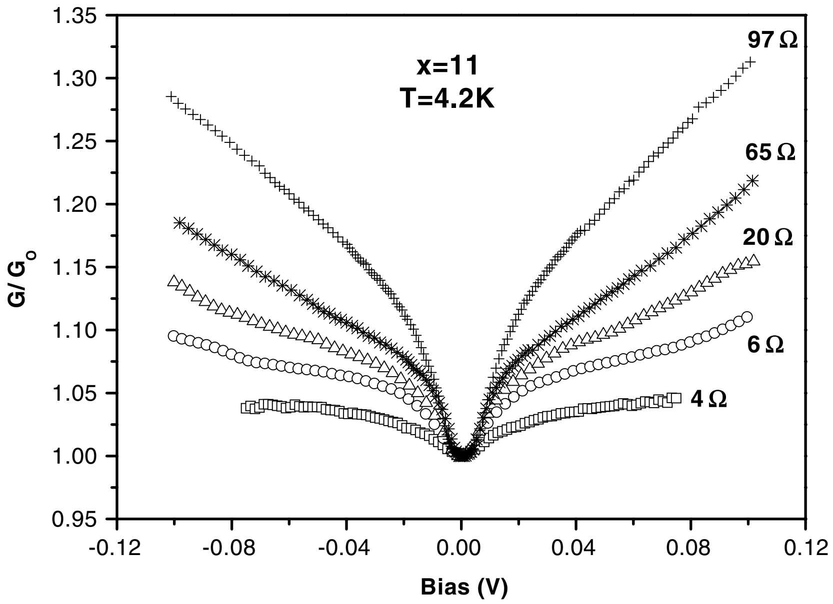


**Figure 6.** The evolution of the conductance spectra for the $x = 11$ sample as a function of junction resistance.

## 4. Discussion

From the x-ray and electron diffraction patterns and also from the values of the resistivity of the samples we can conclusively say that the samples are of good quality and are of single quasicrystalline phase. At present a consensus has been reached that a good quasicrystalline sample will show a negative TCR at room temperature. At low temperature one generally observes for a sample containing magnetic constituents a maximum in resisitivity which has been explained by invoking antilocalization effects due to strong spin–orbit interactions and in such cases one generally observes a positive magnetoresistance [3]. In the present samples also we observe resisitivity maxima as one lowers the temperature. The maximum in the resistivity shifts towards higher temperature as the Mn concentration increases and this can be attributed to the onset of spin–orbit interaction or spin scattering at higher temperature for greater Mn concentration. For $x = 11$ we observe that as one lowers the temperature further there is a steep rise in the resistivity value and the temperature dependence of the resistivity $\rho(T)$ follows a $\ln T$ dependence below $T \sim 10$ K (as shown in the inset of figure 3). We attribute this to magnetic scattering, i.e., the Kondo effect as reported earlier by us [15]. We will present more evidence for this Kondo behaviour from the PCS data. Our values of resistivity (2000–5500 $\mu\Omega$ cm) fall within the range observed earlier for this material (1000–10 000 $\mu\Omega$ cm) [16]. The resistivity of the system decreases as the Mn concentration increases. This has been observed in the earlier studies [16, 17] but no explanation was provided for this observation. However, this observation indicates that as the system becomes more magnetic the alloy becomes less resistive, or in other words the metallicity of the system increases. This is an important observation and more systematic studies have to be carried out to understand the increase of metallicity with the increase in the magnetic constituent. Qualitatively one can give an explanation for this behaviour. It has been observed that the resistivity of quasicrystalline alloys increases as the quality of the quasicrystal improves. The disorder/impurities in quasicrystalline alloys unlike in other metallic alloys destroy the electron localization effect (which is the cause of the high resistivity as well as the negative TCR observed in QCs) and hence the resistivity decreases as the impurities or disorder increases. In our case, the Mn atoms may act as impurities and hence can produce the same effect as above, decreasing the resistivity as the Mn concentration increases.

To understand the magnetic behaviour of the system under study we have used the PCS technique. In PCS, the resultant current–voltage characteristics is a convolution of the sample and the tip properties. Obtaining $I$–$V$ characteristics using a tip and sample of the same material (break junction method) is the most appropriate way to determine the various mechanisms. If this cannot be done, it is important to use a noble metal like Au or Pt as the tip, which have been well characterized. In the present investigation we have used Au as the tip.

Typical results of the 20 Ω junction are presented in figure 4 for $x = 7$, 9 and 11. Figures 5 and 6 show the evolution of the $\mathrm{d}I/\mathrm{d}V - V$ characteristics as a function of junction resistance for the $x = 9$ and 11 samples respectively. We see that all the curves (except for the very low resistance junctions for the $x = 9$ sample) show a tunnel-like behaviour (i.e. increase in the conductance as a function of the bias voltage). The resistivities of our samples are very high, indicating that $l_e$ (the elastic mean free path) at 4.2 K is very small. This falls in the Maxwell or thermal regime ($l_e < d$, $d$ being the diameter of the contact) of PCS [7] and the point contact resistance in this regime is given by $R_{PC} = \rho/d$, where $\rho$ is the electrical resistivity. The contact resistance $R_{PC}$ falls in the range 5–110 Ω corresponding to a contact diameter $d \sim$ 10–0.1 $\mu$m respectively. Hence we are still in the point contact regime of the spectroscopy even though we observe an increase in $\mathrm{d}I/\mathrm{d}V$ as a function of the bias voltage. Hence we would like to call this regime a tunnelling-like regime. In the presence of magnetic impurity scattering the PCS should show a ZBA which can be either a minimum or a maximum at zero bias depending on whether it is a Kondo system or a spin-glass system respectively, as pointed out in earlier reports [18–22]. This is shown schematically in figure 1. In figure 1 PCS represents the point contact regime and TLS represents the tunnelling-like regime (which is observed for high contact resistance and/or high resistivity samples).

From figure 4 we see that all the samples show a minimum in the conductivity at zero bias. The ZBA is an indication of the magnetic nature of the samples showing the signature of a Kondo system. It is clear that the strength of the magnetism increases as the Mn concentration ($x$) increases, since the dip is more pronounced as the concentration $x$ increases. Comparing figures 5 and 6 we can see that the $x = 9$ sample shows a clear evolution from the PCS to TLS as the junction resistance increases. The $x = 11$ sample does not show typical PCS curves (decrease in conductance as a function of bias voltage) even at low junction values. This may be due to the fact that at 4.2 K the $\mathrm{d}\rho/\mathrm{d}T$ is negative and also a very high value indicating that the sample is tending towards a highly insulating state. For the $x = 9$ sample, $\mathrm{d}\rho/\mathrm{d}T$ is positive at 4.2 K and hence we are still able to see typical PCS data on this sample at low junction resistances.

To find the exact power law dependence of the conductance we have selected, for each concentration $x$, point contact spectra having similar contact diameter '$d$' $\sim$ 3 $\mu$m and these are represented in a log–log plot as in figure 7. We observe three distinct regions for samples $x = 7$ and 9 and two regions for the $x = 11$ sample. The conductance varies as $V^n$, where $n \sim 1.7$ for region (a), $n \sim 0.5$ for the region (b) and $n \sim 2.0$ for region (c) (for $x = 11$ we can only see the beginning of region (c)). In earlier studies of TS on QCs it has been reported that the $V^n$, $n \sim 2$, dependence observed at zero bias is a signature of enhancement of the pseudo-gap [8, 9], and also a cross-over from $n \sim 2$ to $n \sim 0.5$ as the bias voltage increases has been reported. We also observe a similar cross-over from $n \sim 1.7$ (region (a)) to $n \sim 0.5$ (region (b)). Thus we would like to point out that $V^2$-like dependence is observed both in the

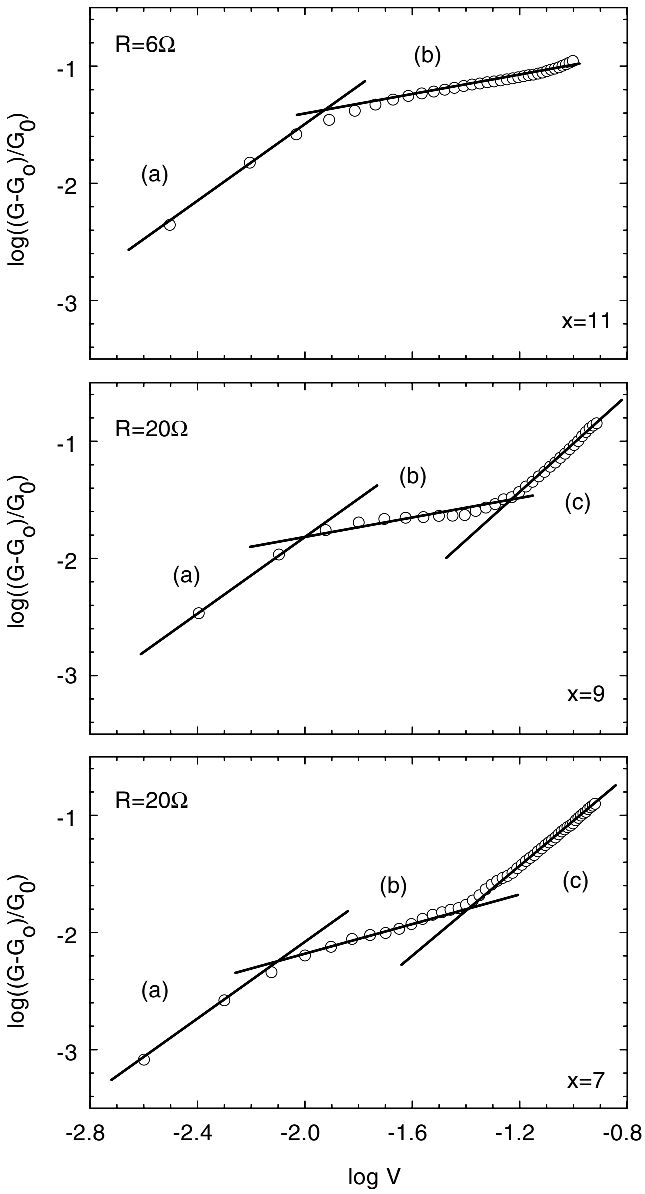


**Figure 7.** The plot of logarithmic values of the normalized conductance and bias voltage, indicating the $V^n$ dependence, where $n \sim 1.7$ for region (a), $n \sim 0.4$ for region (b) and $n \sim 2.0$ for region (c) for the three samples (see text for details).

PCS and the TS near zero bias both of which probe the DOS at Fermi level. This $V^2$-like dependence observed at such low bias voltages is not predicted by the theory of Altshuler and Aronov [4] and is found to be specific to quasi-crystals and approximant phases [8, 9]. In our case we observe the $V^2$-like dependence at very low bias voltages, and taking a clue from the $\ln T$ dependence of resistivity for the $x = 11$ sample we attribute this $V^2$-like dependence to the magnetic scattering typical of a Kondo behaviour. A similar dip in the conductance $\mathrm{d}I/\mathrm{d}V$

at zero bias has been observed in typical Kondo systems like Cu:Mn, Cu:Fe, [21] etc, but a quantitative voltage dependence of $dI/dV$ has not been pointed out.

## 5. Conclusions

We observe high resistivity values of the alloys $Al_{70}Pd_{30-x}Mn_x$ ($x = 7, 9$ and 11). The samples show resistivity maxima which shift towards higher temperatures as Mn concentration increases. The resistivity maximum has been attributed to the magnetic contribution (spin–orbit interaction). The $x = 11$ sample shows an upturn in the resistivity at a temperature below $T \sim 20$ K, and has a $\ln T$ dependence below 10 K. This is a signature of 'Kondo-like' behaviour. We were not able to see this upturn for the $x = 7$ and 9 samples until $T \sim 4.2$ K. For the first time we have observed, using PCS, the evolution from the point contact regime to the tunnelling-like regime as a function of the junction resistance for a quasicrystalline sample. In the tunnelling-like regime, we have observed near zero bias $V^n$ dependence, where $n$ crosses over from ∼1.7 to ∼0.5 as a function of the bias voltage. We have attributed the $V^2$-like dependence at zero bias as the signature of a Kondo effect. The $V^2$ dependence seems to be a generic behaviour of the QCs containing magnetic impurities.

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