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# High pressure study of $\text{Pu}_{0.92}\text{Am}_{0.08}$ binary alloy

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Received 4 March 2008, in final form 14 May 2008

Published 4 June 2008

Online at [stacks.iop.org/JPhysCM/20/275217](http://stacks.iop.org/JPhysCM/20/275217)

## Abstract

The phase transitions (by means of x-ray diffraction) and electrical resistivity of a  $\text{Pu}_{0.92}\text{Am}_{0.08}$  binary alloy were determined under pressure (up to 2 GPa). The evolution of atomic volume with pressure gives detailed information concerning the degree of localization of 5f electronic states and their delocalization process. A quasi-linear  $V = f(P)$  dependence reflects subtle modifications of the electronic structure when  $P$  increases. The electrical resistivity measurements reveal the very high stability of the  $\delta$  phase for pressures less than 0.7 GPa, since no martensitic-like transformation occurs at low temperature. Remarkable electronic behaviours have also been observed. Finally, resistivity curves have shown the temperature dependence of the phase transformations together with unexpected kinetic effects.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Plutonium lies at the borderline between the light actinides (Pa–Np), with itinerant 5f electrons, and the heavy actinides (Am–Cf) with localized 5f states. Due to this peculiar position, Pu exhibits six allotropic solid phases depending on the temperature. The face centred cubic (fcc)  $\delta$  phase, stable between 315 and 457 °C [1], is by far the most studied, especially because of the intermediate behaviour between delocalization and localization of 5f electrons that still remains very challenging for physicists to describe. Alloying Pu with gallium, aluminium, cerium or americium allows the stabilization of this  $\delta$  phase at room temperature.

Americium stabilizes the  $\delta$  phase of Pu at room temperature and pressure over a wide range of concentrations: from 5 at.% up to 75 at.% [2]. Recently, Dormeval *et al* [3, 4] reported the extreme stability of the  $\delta$  phase in Pu–Am alloys that do not exhibit martensitic transformation at low temperature, unlike what happens with other deltagen elements Ga, Al or Ce.

According to a recent x-ray photoemission spectroscopy (XPS) study performed on thin films of Pu–Am alloys by Gouder *et al* [5], the character of plutonium 5f states would not be appreciably modified, with respect to ‘pure’  $\delta$ -Pu, for americium contents less than 33 at.%. This was confirmed by electronic structure calculations [6]. For higher Am contents, only a weak tendency towards Pu 5f localization would be observed.

In order to get a new insight into the  $\delta$  phase stability mechanisms, we initiated a systematic x-ray diffraction (XRD) study of  $\text{Pu}_{1-x}\text{Am}_x$  alloys under high pressures at ambient temperature. Our objectives mainly consist of determining the  $(P, x)$  phase diagram of the Pu–Am system and obtaining the equations of states of the several phases observed. Whereas pure Pu is reported to stay monoclinic up to at least 40 GPa, pure Am exhibits four phase transitions when applying pressure up to 100 GPa, reflecting the progressive delocalization of its 5f orbitals [7]. But no experimental data have been reported concerning the pressure phase diagram of the Pu–Am system that only consists, up to now, of extrapolations from pure Pu and Am data.

To achieve a better understanding of  $\delta$  phase stability and electronic properties of Pu–Am alloys, we decided to

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perform resistivity measurements under high pressures. Our motivation was two-fold. On the one hand this technique can give essential information about the electronic structure of the alloys as a function of pressure (electronic correlations, degree of localization of 5f electrons, . . .). On the other hand, these measurements would allow the observation of structural, electronic and/or magnetic phase transitions as a function of pressure and temperature. In that way we aim to start drawing the  $(P, T, x)$  phase diagram of the Pu–Am binary system.

In the present paper we report the first known experimental determination of phase transitions and electrical resistivity under pressure of a  $\text{Pu}_{0.92}\text{Am}_{0.08}$  binary alloy.

## 2. Experimental procedure

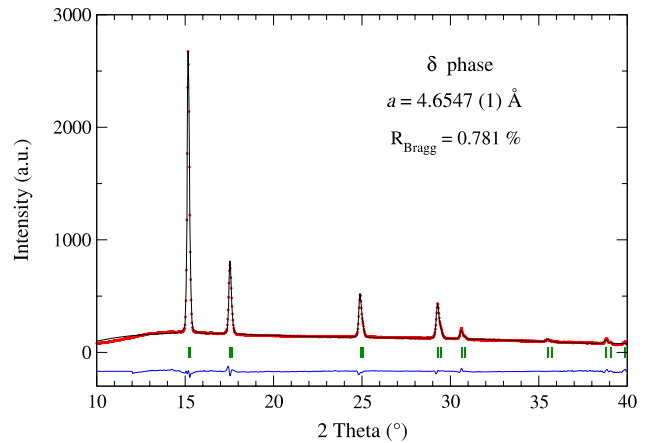
The studied  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy was synthesized at the Institute for Transuranium Elements (ITU) by arc melting from pure Pu and Am metals [4].

### 2.1. High pressure x-ray diffraction

High pressure XRD experiments were carried out on a polycrystalline foil of the alloy loaded in a large aperture ( $80^\circ$ ) diamond anvil cell (DAC) equipped with a boron seat and a gas membrane. We used  $520\ \mu\text{m}$  culet diamonds and a  $290\ \mu\text{m}$  thick rhenium gasket pre-indented to  $90\ \mu\text{m}$  and drilled with a hole of diameter  $270\ \mu\text{m}$ .

A piece of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy was first rolled at room temperature down to a thickness of  $35\ \mu\text{m}$ , then annealed (3 h at  $450^\circ\text{C}$ ) to restore the metallic structure (elimination of both structural defects caused by self-irradiation and stress induced by rolling). Then a micro-sized sample (about  $100 \times 100\ \mu\text{m}^2$ ) was cut from the resulting foil and put in the gasket hole together with four little ruby spheres ( $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ ) used as pressure gauges. The pressure transmitting medium, argon, was loaded at room temperature using a high pressure gas-loading system.

XRD experiments were carried out at CEA, Valduc on a Mo rotating anode, Nonius FR591 diffractometer equipped with a graphite monochromator ( $\lambda\ \text{K}\alpha_1 = 0.7093\ \text{\AA}$ ;  $\lambda\ \text{K}\alpha_2 = 0.71359\ \text{\AA}$ ), in transmission geometry and angular dispersive mode. Pressure was increased *in situ* by tuning the gaseous pressure inside the membrane of the DAC. The sample pressure was measured before and after each diffraction measurement using a PRL (pressure ruby luminescence) system. XRD exposure times ranged from  $\sim 4$  to  $\sim 17$  h to ensure good statistics. The sample was oscillating  $\pm 7^\circ$  around the two rotation axes of the goniometer perpendicular to the incoming x-ray beam. The sample to detector distance ( $\sim 200\ \text{mm}$ ) was determined from the diffraction pattern of a NIST  $\text{LaB}_6$  standard (SRM660). Uncertainty in positioning was less than  $5\ \mu\text{m}$ . The diffraction patterns, recorded on an image plate, were integrated with FIT2D software [8]. The data were then analysed using the FULLPROF program [9]. The relative uncertainty for the cell parameter was  $\Delta a/a \sim 1 \times 10^{-4}$  for the  $\delta$  phase, refined with the whole pattern profile matching method. The other phases observed under pressure during this study were refined using the Rietveld method. We should note



**Figure 1.** Profile refinement of the diffraction pattern of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy recorded at  $P = 0.44(1)$  GPa. The continuous line (on top) is the calculated pattern and the dots are the experimental data. Vertical lines are the calculated  $hkl$  positions, and the bottom trace is the difference plot.

that an XRD pattern of the sample was collected before argon was loaded in order to get a reference at ambient conditions.

### 2.2. High pressure electrical resistivity

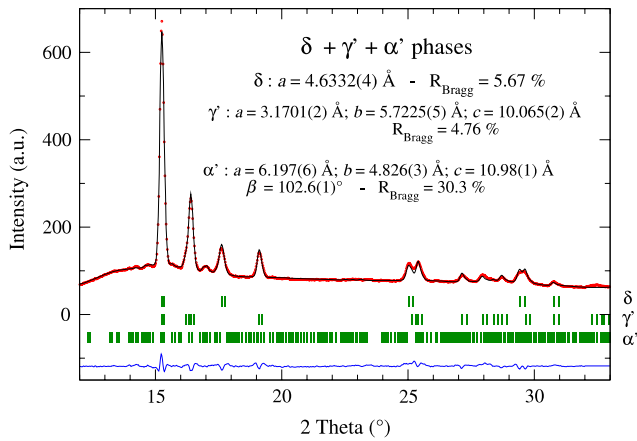
For the high pressure resistivity measurements, performed at the ITU, another small piece ( $1.80 \times 0.20\ \text{mm}^2$ ) was cut from the foil, and then loaded, with a small piece of lead, in a high pressure cell developed at ITU and dedicated to resistivity measurements. This pressure device is a piston–cylinder system made of non-magnetic CuBe. It consists of two tungsten carbide anvils ( $3.5\ \text{mm}$  diameter), a pyrophyllite gasket ( $2\ \text{mm}$  inner diameter) and steatite discs as the solid pressure transmitting medium. The DC (direct current) resistance is measured using a standard four-probe technique with Pt wires. The temperature is determined by a Pt thermometer above  $20\ \text{K}$ , and by a germanium sensor below. The pressure is increased at room temperature, then measured at low temperature using the superconducting transition temperature of lead [10]. Experiments were performed at temperatures down to  $T = 1.5\ \text{K}$  using a pumped  $^4\text{He}$  cryostat.

The self-heating effect appeared negligible in the considered temperature range, the mass of the sample being very low ( $m \sim 193\ \mu\text{g}$ ). No appreciable effect of defect accumulation on the low temperature resistivity was observed during the experiments ( $\sim 1$ – $2$  days at each pressure).

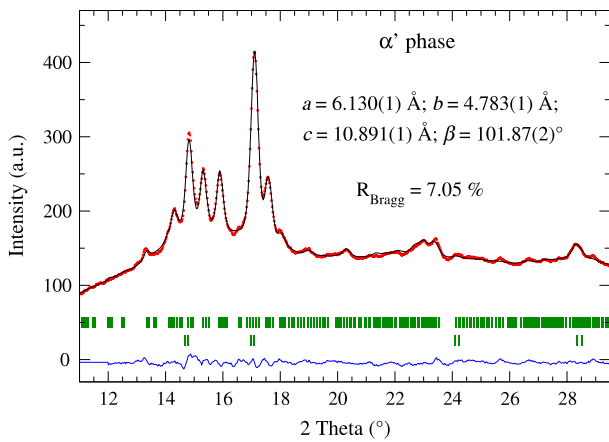
## 3. Results and discussion

### 3.1. High pressure XRD study at room temperature

Figures 1–3 represent the evolution of the XRD patterns of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy under pressure. When increasing pressure the  $\delta$ -Pu fcc form (space group  $Fm\bar{3}m$ , figure 4), which is stable at ambient pressure first starts to convert at  $P_s = 0.70(5)$  GPa to a face-centred orthorhombic structure (S.G.  $Fddd$ ) similar to  $\gamma$ -Pu and Am III structures (figure 4). The corresponding phase will be referred to in the following as the



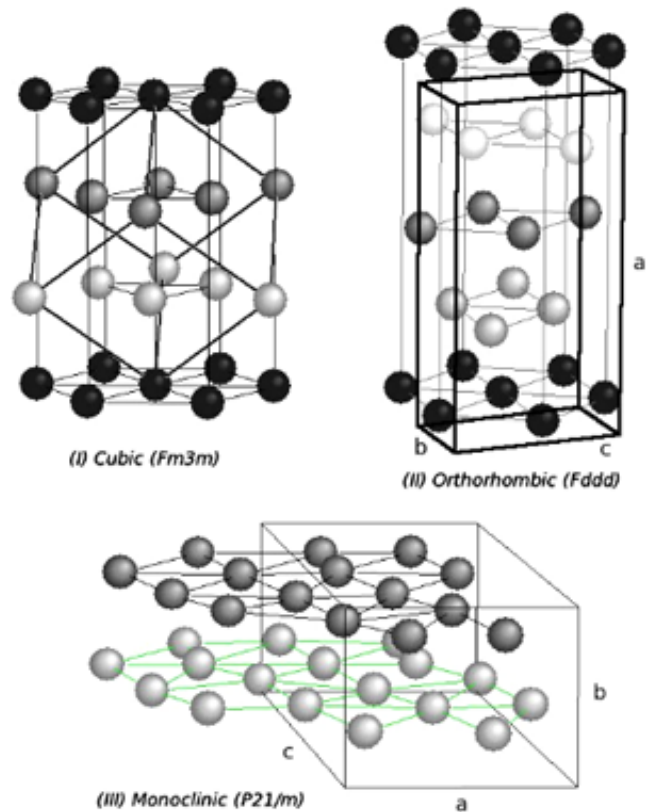
**Figure 2.** Profile refinement of the diffraction pattern of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy recorded at  $P = 0.85(1)$  GPa, showing the presence of the three phases. The high  $R_{\text{Bragg}}$  value for the  $\alpha'$  phase results from the very small amount of this phase at this pressure.



**Figure 3.** Profile refinement of the diffraction pattern of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy recorded at  $P = 1.78(2)$  GPa.

$\gamma'$  phase, the prime standing for *expanded*, since substitutional Am atoms are embedded in the structure. It should be noted that traces of a similar expanded  $\gamma'$  phase were already found to appear under pressure in Pu–Ga alloys with low Ga contents (below 2 at.%) during the  $\delta \rightarrow \alpha'$  transformation [11–13], but these were generally reported to disappear very rapidly at room temperature.

The stability domain of the  $\gamma'$  phase appears to be very narrow. Pure  $\gamma'$ - $\text{Pu}_{0.92}\text{Am}_{0.08}$  was never observed, and the orthorhombic structure rapidly transformed to a monoclinic form (S.G.  $P2_1/m$ ) with increasing pressure, thus adopting the same structure as that known for pure  $\alpha$ -Pu (figure 4). This phase will be referred to in the following as the expanded  $\alpha'$  phase. Thus, between  $P_s = 0.70(5)$  GPa and  $P_e = 1.30(5)$  GPa, two or three phases coexist in the sample (figure 2). The phase transformation is complete above  $P_e = 1.30(5)$  GPa where the monoclinic  $\alpha'$  phase is the only phase observed. It is worth noting that after decompression of the cell down to ambient pressure the alloy remained in the  $\alpha'$  phase. This hysteresis indicates that a martensitic character of the  $\delta \rightarrow \alpha'$  transformation is likely.

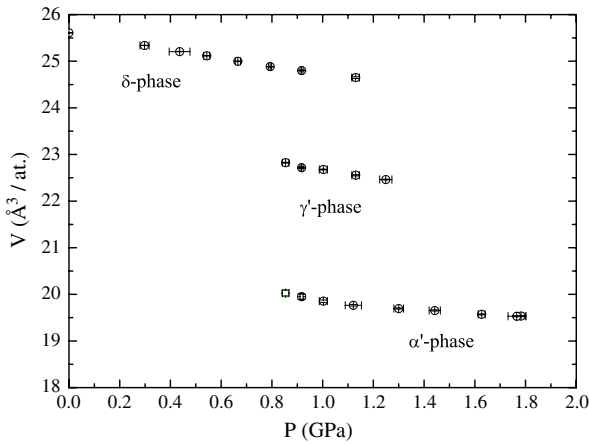


**Figure 4.** Crystallographic structures observed with  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy between 0 and 2 GPa: (I)  $\delta$ -phase; (II)  $\gamma'$ -phase; (III)  $\alpha'$ -phase.

The fact that the  $\gamma'$  phase was never observed as pure (between 0.8 and 1.2 GPa, the three  $\delta + \gamma' + \alpha'$  phases even coexist) is quite intriguing. This  $\gamma'$  phase may thus be a metastable structural intermediate phase during the  $\delta \rightarrow \alpha'$  transformation. This result also raises the questions about the exact nature of this structural transformation and its martensitic character. It would be very instructive to perform long time exposures of this alloy at constant pressures between 0.7 and 1.3 GPa in order to check if the respective amounts of  $\delta$ ,  $\gamma'$  and  $\alpha'$  phases evolve significantly with time.

The three structures can be described as stacks of more or less distorted hexagonal atomic planes. The structural sequence observed when increasing the pressure could thus be seen as a succession of distortions and slips of hexagonal planes. First, the  $\delta \rightarrow \gamma'$  transformation consists mainly of the relative contraction of intraplanar bonds along the corresponding [100] direction of the orthorhombic lattice. Whereas the fcc structure is characterized by six equal interatomic distances within perfect hexagonal planes, the  $\gamma'$  structure has four ‘large’ and two ‘short’ equal bonds within its distorted hexagonal planes. Finally, when passing from the  $\gamma'$  to the  $\alpha'$  structure, these six distances become different while the planes are sliding: the distortion is very important and symmetry is drastically lowered [14].

Figure 5 shows the evolution of atomic volume with pressure. A particularly large total contraction of about 20% is observed when passing from the  $\delta$  phase to the  $\alpha'$  phase. To make a comparison, densification under pressure of a Pu–2 at.% Ga alloy involves a contraction of about 18%, which



**Figure 5.** Atomic volume versus pressure curve for  $\text{Pu}_{0.92}\text{Am}_{0.08}$  obtained when increasing  $P$  up to 2 GPa.

is still greater than the 17% contraction observed during the  $\gamma \rightarrow \alpha$  transformation of pure cerium [15]. The structural transition  $\delta \rightarrow \gamma'$  involves a contraction of atomic volume of about 8.3%, whereas the  $\gamma' \rightarrow \alpha'$  transition is accompanied by a contraction of about 12.5%. These structural transitions thus imply large negative stresses within the sample. These ‘negative pressures’ may locally slow down (or even stop) the transformation processes, since the latter are pressure-induced. Therefore we can suppose the existence of relaxation times relative to these stresses, and of a kinetic factor influencing the respective amounts of the several considered phases in the pressure range 0.7–1.3 GPa.

In  $\alpha$ -Pu, 5f states are assumed to be fully itinerant and the electronic structure to be dominated by narrow 5f bands with a large density of states, responsible of the stabilization of the low symmetry structure [16]. On the other hand, 5f electrons in  $\delta$ -Pu are neither fully itinerant nor localized. The theoretical model proposed by Cooper [17], which is in fact an adaptation of Anderson’s disorder-induced localization model [18], appears here to be very interesting for qualitatively interpreting these results. Cooper considers the existence of two plutonium sites randomly distributed on the fcc lattice: (i) the ‘para’ sites, where 5f states are fluctuating between  $5f^4$  and  $5f^5$  configurations through their hybridization with conduction states; (ii) the ‘ortho’ sites where the only configuration is  $5f^5$  (totally localized states). The  $\delta$  phase would be stabilized by the entropy gained by the random distribution of these sites. Cooper’s model allows a quite trivial description of progressive localization of 5f states through the  $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta$  sequence observed in pure Pu with increasing temperature. Hence, in the  $\gamma$  phase, the relative number of ‘para’ sites would be larger than in the  $\delta$  phase. Americium atoms, whose 5f electrons are fully localized, inserted in pure  $\alpha$ -Pu, may be considered as impurity atoms whose presence involves a break in the periodicity of the electronic potential. Americium sites, randomly distributed, may then be seen as ‘scattering centres’ for itinerant  $\alpha$ -Pu 5f states, thus favouring the localization of the latter, following the Anderson mechanism [18], and stabilizing the  $\delta$  phase.

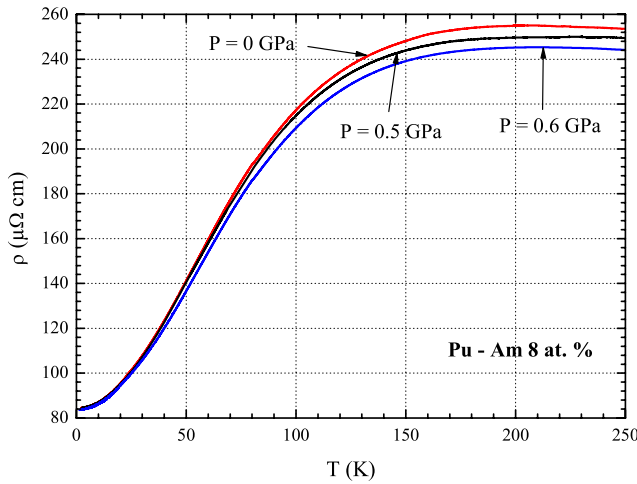
Application of pressure on this  $\delta$  phase stabilized Pu–Am alloy decreases the interatomic distances, and thus tends

to force 5f states to delocalize through hybridization with itinerant s, p, d states. It appears from the present study that this delocalization probably occurs in two steps, each step corresponding to an important increase of the involvement of 5f states in bonding, associated with a structural transformation and volume contraction. The first step would be characterized by the  $\delta \rightarrow \gamma'$  transition, and could mean a sudden increase in the number of ‘para’ sites to the detriment of the number of ‘ortho’ sites, the resulting entropy difference thus favouring stabilization of the  $\gamma'$  phase. In the second step, 5f electrons would finally become fully itinerant, and the  $\alpha'$  phase becomes stable.

The experimental (pressure, atomic volume) data obtained from this XRD study allow the refinement of the isothermal equation of state (at 300 K) for the  $\delta$  phase only. Considering the Vinet formulation at the second order of truncation [19], the following parameters are obtained:  $V_0 = 25.60(1) \text{ \AA}^3/\text{at}$ ;  $B_0 = 30(2) \text{ GPa}$ ;  $B' = -1(6) (\chi = 0.16)$ . The value of the isothermal bulk modulus  $B_0$  is very close to the value previously reported for  $\delta$ -stabilized Pu–2 at.% Ga [13]. Given the narrow pressure stability domain for the  $\delta$  phase, a large uncertainty is associated with  $B'$ . However, the value for  $B'$  is undoubtedly very close to zero, i.e. the pressure–volume relation is almost linear. This kind of behaviour, not frequently observed, is generally associated with a very low or negative thermal expansion of the material [20]. Hence thermal expansion measurements will have to be performed on this alloy. The most relevant models to explain such phenomena are based on the description of two electronic states, each being associated with different volumes. For instance, in Invar alloys, competition between an itinerant magnetic state (large volume) and an itinerant non-magnetic state (small volume) is evoked [21, 22]. This kind of description seems promising here, for instance with regard to the Cooper model. When applying pressure on the  $\delta$ -Pu<sub>0.92</sub>Am<sub>0.08</sub> alloy, the number of ‘para’ sites (characterized by a lower volume) would progressively increase, to the detriment of the number of ‘ortho’ sites: the strengthening of the hybridization of 5f states with s, p, d bands under pressure would thus tend to increase compressibility noticeably with respect to the ‘normal’ compressibility behaviour. Since the importance of this phenomenon would increase with  $P$ , an abnormally low value is observed for  $B'$ . Let us mention here that an Invar-type model was also previously applied by Lawson *et al* to describe the negative thermal expansion of some Pu–Ga alloys [23].

Another ‘two states’ model was proposed by Eriksson *et al* to explain negative thermal expansion of the  $\delta$  phase of pure Pu [24]. Eriksson considers the existence in  $\delta$ -Pu of localized and delocalized 5f states ( $\sim 1$  for 5 states), but not on separate sites, the potential periodicity thus being unaffected (contrary to what happens in the Cooper model). So increasing temperature (or increasing pressure) would stabilize electronic configurations with more delocalized 5f states (of lower volume), like in the  $\epsilon$  phase: there would be fluctuations between  $\delta$ -phase and  $\epsilon$ -phase configurations. But very recently, using dynamical mean field theory, Shim *et al* have found that the ground state (i.e. at 0 K) in  $\delta$ -Pu is in fact a quantum superposition of two atomic valence





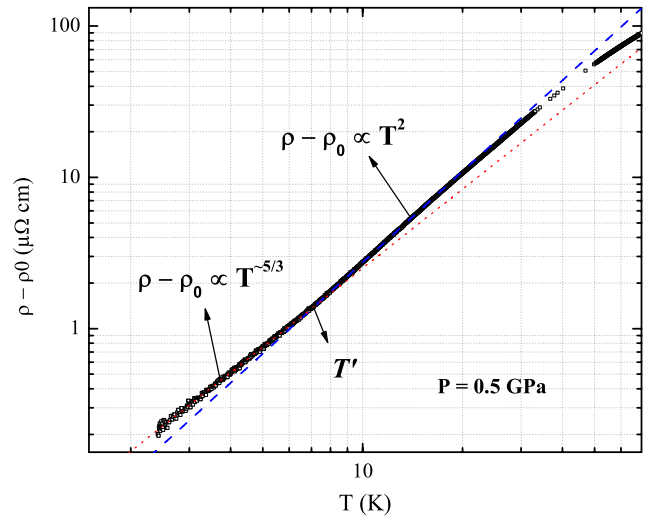
**Figure 6.** Resistivity curves of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy up to  $P = 0.6$  GPa. At these pressures, the curves are identical on cooling and heating the sample.

states: Pu is actually found to be a mixed valence metal with charge fluctuations between  $5f^5$  and  $5f^6$  configurations, with an average  $f$  occupation close to 5.2 [25]. Similarly, we can infer that the relative probabilities of each configuration (characterized by different volumes) evolve with pressure and temperature, thus leading to the anomalous compressibility behaviour observed for the  $\delta$  phase.

### 3.2. High pressure resistivity study

Resistivity curves obtained for the pure  $\delta$  phase ( $P < 0.7$  GPa, figure 6) are in very good agreement with the room pressure resistivity curve previously obtained by Dormeval (down to 4 K) [3], and also with the data reported by Gomez-Marín on a  $\text{Pu}_{0.9}\text{Am}_{0.1}$  alloy (down to 1.5 K) [26]. Surprisingly, no structural phase transition (that would have led to a discontinuity on the curve) was observed at low temperature under pressure. This result indicates that thermal stability of the  $\delta$  phase is very high in  $\text{Pu}_{0.92}\text{Am}_{0.08}$ , unlike what is observed in  $\delta$  Pu–Ga, Pu–Ce and Pu–Al alloys [3]. We can thus infer that the  $\delta$  phase is a stable (and not a metastable) phase in  $\text{Pu}_{0.92}\text{Am}_{0.08}$  (unlike what was shown for the  $\delta$  phase in the Pu–Ga system, for example [27]).

The three curves recorded at  $P = 0, 0.5$  and  $0.6$  GPa (figure 6) are very similar, showing no drastic evolution of electronic structure in this temperature range. They are characterized by a broad maximum of resistivity around  $T_{\text{max}} \sim 200$  K, followed by a rapid decrease of  $\rho$  under  $\sim 100$  K. This maximum of  $\rho$  may result from the influence of spin fluctuations, as reported for pure  $\alpha$ -Pu [39], but it can also be explained by the existence of a Kondo effect, as shown earlier by Gomez-Marín in his thesis [26]: at ambient pressure, the magnetic contribution to resistivity of a  $\text{Pu}_{0.9}\text{Am}_{0.1}$  alloy could be fitted following a Kondo-type dependence ( $\rho_{\text{mag}} = a - b \cdot \ln T$ ) for  $230 < T < 500$  K, suggesting an intermediate valence system. The latter interpretation is very well supported by the recent theoretical results published by Shim *et al* [25]; and note that it would be also consistent



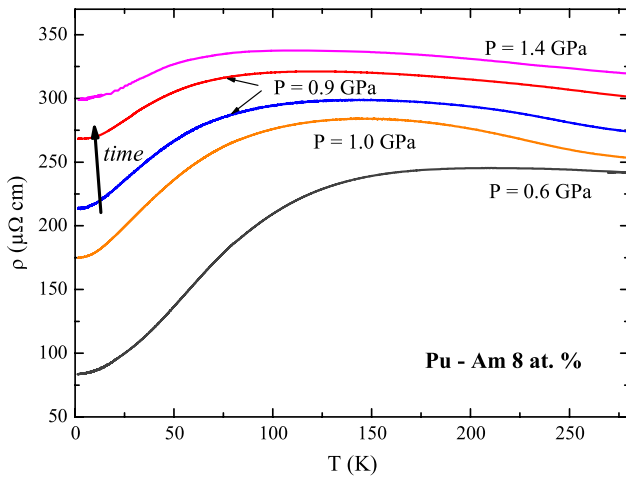
**Figure 7.** Low temperature electrical resistivity of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy at  $P = 0.5$  GPa on a logarithmic scale. The dashed line corresponds to the fit above  $T'$ , and the dotted line to the fit below  $T'$ .

with the Cooper model, considering that the Pu ‘ortho’ sites (totally localized) may develop magnetic moments and thus be treated as ‘magnetic impurities’. A Kondo effect may also originate from ‘non-equilibrium vacancy defects’ as postulated by Fluss *et al* [28]: regional site-specific electron localization would then be induced by non-equilibrium vacancy defects. Finally, it is worth noting that photoemission measurements performed on  $\delta$ -stabilized Pu [29] and, more recently, on a  $\text{Pu}_{0.67}\text{Am}_{0.33}$  alloy [6] have shown the existence of a narrow 5f-related feature at the Fermi level which can be interpreted as a quasiparticle (‘Kondo-like’) peak, as confirmed by DMFT calculations on ‘pure’  $\delta$ -Pu [25, 30].

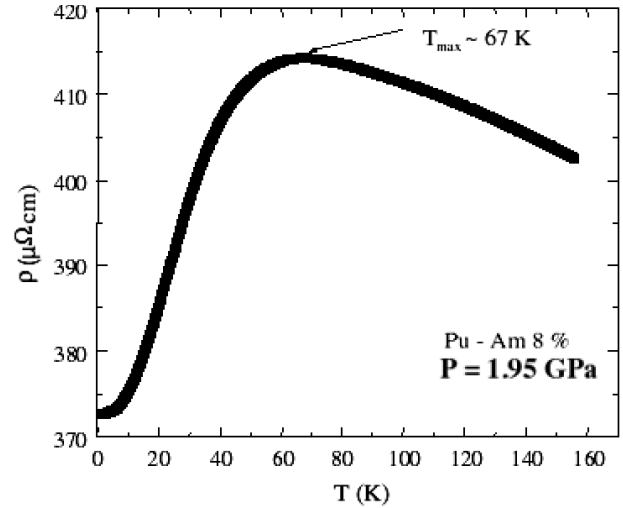
At low temperature, for  $T < T^*$  ( $\sim 25$  K), resistivity can be fitted, in a first approach, to a  $\rho = \rho_0 + AT^2$  law ( $\rho_0 =$  residual resistivity), characteristic of a Fermi liquid (FL) behaviour, and which may be associated here with spin fluctuations. However, a fine analysis of the lowest temperature part of the curves allows us to distinguish two regions delimited by a characteristic temperature  $T'$  (figure 7). For  $T' < T < T^*$  a FL law  $\rho = \rho_0 + AT^2$  can be applied, the  $A$  value (characteristic of electron–electron interaction) being  $\sim 3 \times 10^{-2} \Omega \text{ cm K}^{-2}$ . Using the Kadowaki–Wood relation  $A/\gamma^2$  [31] ( $\gamma$  is the Sommerfeld coefficient), one obtains  $\gamma \sim 50 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . From specific heat measurements, a value between 35 and 55  $\text{mJ mol}^{-1} \text{ K}^{-2}$  was recently deduced for this  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy [32].

For  $T < T'$  (down to 1.5 K), the exponent  $n$  to consider with a  $\rho = \rho_0 + bT^n$  law appears to be close to 5/3 (i.e. non-Fermi liquid (NFL) behaviour). The temperature range taken for this last fit is narrow ( $\Delta T < 8$  K), so complementary experiments at very low temperatures ( $T < 1.5$  K) would be useful to obtain a more precise value for  $n$ . This may not be easy since self-heating may then become non-negligible.

Several theoretical models have attempted to explain the existence of NFL behaviour in some compounds or alloys, generally linked to heavy fermion behaviour [33]: the



**Figure 8.** Resistivity curves of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy for  $P$  measured between 0.6 and 1.4 GPa.



**Figure 9.** Resistivity curve of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  alloy at  $P = 1.95$  GPa.

‘multichannel Kondo model’ (based on ‘overcompensation’ of a magnetic impurity spin), disorder-based models (e.g. disorder may involve local perturbations of the Kondo interaction and hence a distribution of Kondo temperatures), or the quantum critical point (QCP) theory for systems close to a magnetic instability. A QCP is a transition occurring at 0 K between a non-magnetic state (heavy fermion behaviour, Fermi liquid) and a magnetic state (generally antiferromagnetic). This transition can be induced by a slight change in a ‘tuning parameter’ that can be chemical composition, applied magnetic field or pressure [34, 35]. Recently, a new hypothesis emerged whose main idea is that the existence of a QCP could be the ‘key’ to explain the unusual properties of Pu, and especially of  $\delta$  stabilized Pu, which would then be an example of ‘quantum critical matter’ where defects and local disorder would play an essential role [28, 36, 37].

In the present study, a slight decrease of temperature  $T'$  was observed, from  $\sim 8.5$  K at ambient pressure down to  $\sim 5$  K at  $P = 0.6$  GPa. But the observed  $(P, T)$  phase diagram of  $\text{Pu}_{0.92}\text{Am}_{0.08}$  appears exactly opposite to the phase diagram generally considered for a quantum critical system since  $\text{Pu}_{0.92}\text{Am}_{0.08}$  exhibits a transition at  $T'$  from FL behaviour to NFL behaviour with decreasing temperature. A very low temperature study is still required here. Moreover, the systematic occurrence of NFL behaviour will have to be established on other Pu–Am samples, and by other techniques, before we can make a statement about the possible occurrence of QCP in the Pu–Am system.

The resistivity curve recorded at  $P = 1$  GPa (during the heating of the sample after cooling down to 1.5 K) is somewhat different from the one recorded at 0.6 GPa (figure 8). Indeed the resistivity (especially the residual resistivity) is higher, its maximum is more pronounced and  $T_{\text{max}}$  is shifted to a lower value of about 150 K. For the rest of the experiment, no additional force was applied to the HPC and the sample was cooled down to 1.5 K one more time, and then re-heated. Surprisingly, the cooling curve (not shown) was still different from the previous one, with higher  $\rho$  values, and  $T_{\text{max}}$  back to  $\sim 200$  K. Measurement of  $P$ ,

using the superconducting transition temperature of lead, led to a slightly inferior value of about 0.9 GPa. This pressure decrease was probably due to the large volume contraction associated with the structural transformation occurring in this pressure range. The subsequent heating curve appeared similar to the former (heating) curve, although it was still shifted toward higher  $\rho$  values and was slightly flattened (figure 8). Further thermal cycling was performed without modifying the HPC, still leading to a continuous increase of  $\rho$  (and especially  $\rho_0$ ) and to the irreversibility between the cooling and the heating processes. These complex results should be considered, keeping in mind that in this pressure region the alloy contains at least two phases (and most probably three, as observed by XRD) which contribute to the total resistivity and whose amounts evolve with time, temperature and pressure. The flattening of the curves and the increase of residual resistivity can be attributed to disorder appearing during phase transformation, but also to modifications of the scattering processes of conduction electrons, and of the density of states at the Fermi level, depending on the nature of the 5f states in the crystallographic structures considered. When passing from the  $\delta$  phase to the  $\gamma'$  phase and then to the  $\alpha'$  phase, the 5f states become more and more delocalized, and build a narrow band at the Fermi level, thus increasing the influence of spin fluctuations and sd-type scattering on the resistivity [38] and destroying the Kondo effect. This results in a maximum of resistivity which becomes more pronounced, and at lower temperatures, compared with the maximum of resistivity observed with the  $\delta$  phase.

We would expect the curve recorded for a measured pressure  $P = 1.40(5)$  GPa (figure 8) to be representative of the electrical resistivity of the pure  $\alpha$  phase. However, due to the solid transmitting medium (steatite), pressure gradients are very likely within the HPC. So the whole sample was probably not totally transformed to the  $\alpha'$  phase, and small amounts of the  $\gamma'$  phase still remained. This is confirmed by the last curve recorded for  $P = 1.95(5)$  GPa, which is quite different from the latter (figure 9): the resistivity is still higher, and its maximum has decreased down to  $T_{\text{max}} \sim 67$  K. Let us

remember that pure  $\alpha$ -Pu is reported to exhibit a maximum of resistivity at about 100 K [39], the maximum generally being attributed to spin fluctuations.

#### 4. Conclusions

The evolution of atomic volume with pressure, especially at phase transformations, brings detailed information about the degree of localization of 5f states in the  $\delta$  phase and about their delocalization process under pressure. The quasi-linear  $V = f(P)$  dependence reflects subtle modifications of the electronic structure when  $P$  increases. A theoretical approach (especially by means of first-principles calculations) will help further analyse and explain these results.

The electrical resistivity measurements reveal the very high stability of the  $\delta$  phase for pressures less than 0.7 GPa, since no martensitic-like transformation occurs at low temperatures. Remarkable electronic behaviours, that remain to be elucidated by means of complementary experiments (especially at very low temperature) have also been observed with this alloy. The resistivity curves recorded between 0.7 and 1.3 GPa have shown the temperature dependence of the  $\delta \rightarrow \gamma' \rightarrow \alpha'$  transformation and unexpected kinetic effects.

#### Acknowledgments

The high pressure electrical resistivity study was made possible thanks to the support of the European Commission–Joint Research Centre’s FP6-Institutional Work Programme ‘Basic Actinide Research’ action (no. 3151) in financing access to the Actinide User Laboratory at the Institute for Transuranium, Karlsruhe, project no. AUL-62. VK wishes to thank A V Kolomiets (ITU) for fruitful discussions.

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