ESRF	**Experiment title:** **Structural investigation of δ-stabilized plutonium alloys under pressure**	**Experiment number:** **HS-2775**
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Report:

The mechanism responsible for the stability of the δ-phase in plutonium alloys remains poorly understood despite previous extensive studies. In the present experiments, three alloys (Pu-8at%Am, Pu-15at%Am and Pu-2at%Ga) were studied under pressure by X-ray diffraction in diamond anvil cells and revealed i) a pressure-induced softening in the compressibility of the δ-phase and ii) the presence of an intermediate γ'-phase across the δ→α' phase transition. The softening, an anomalous behaviour, is shown to be coherent with other known unusual properties found for these alloys like NTE (Negative Thermal Expansion). Furthermore, it has been observed that the cell volume for the α'-phase formed under pressure depends on the rate of the pressure increase. This behaviour may be related to the diffusion of solute atoms to specific sites within the α'-phase unit cell. Such diffusion may also explain the α'-phase unit cell's volume shrinkage versus time in a Pu-2at%Ga sample kept at a constant pressure. These XRD results, obtained under pressure, may be used to test first-principle calculations or other general modelling which aim at predicting the solute's diffusion and/or self-irradiation effects in plutonium alloys. Examples of the spectra and structures obtained under pressure for some Pu-Am alloys are given in Figures 1 and 2.

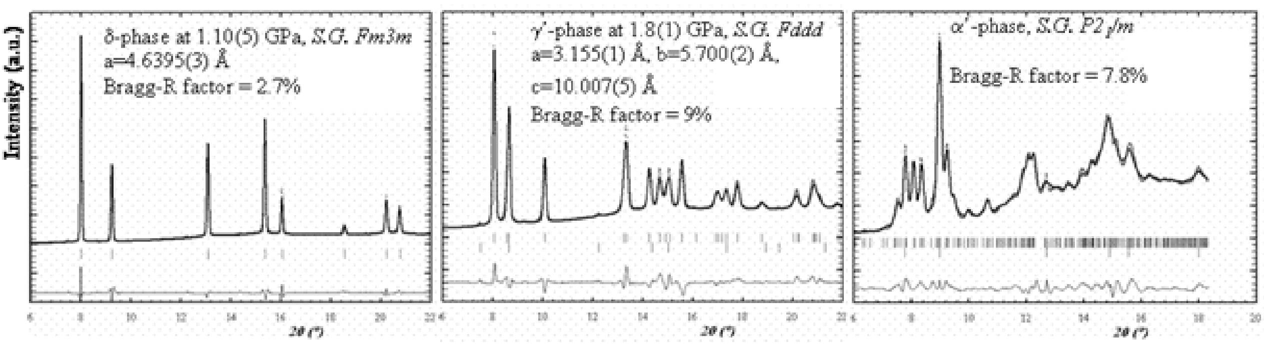

Figure 1: Rietveld refinements of Pu-15at.%Am under pressure. Vertical lines indicate the calculated *hkl* (Miller indices) positions, points are the experimental data, the top continuous lines are the calculated patterns and the lower continuous line are the difference profiles. Solidified argon (fcc structure) is observed with the α' and γ'-phases and its corresponding *hkl* positions are represented by the lower vertical lines.

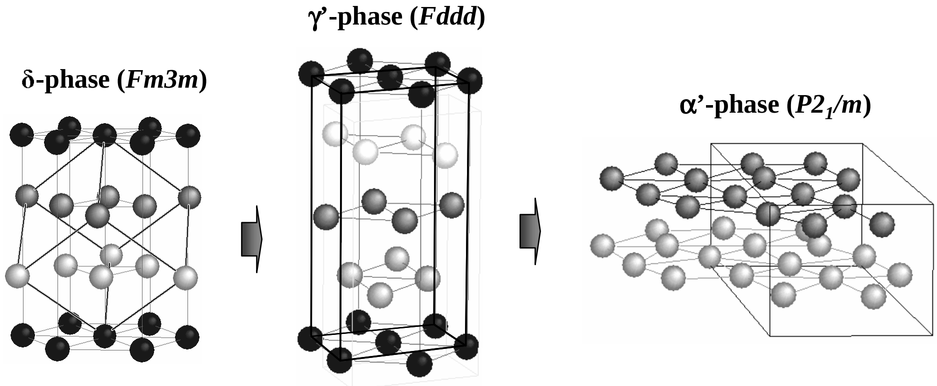

Figure 2: structural models for Pu-2at.%Ga, Pu-8at.%Am and Pu-15at.%Am under pressure. The structures can be viewed as being composed of close-packed hexagonal planes (δ-phase) or as distorted close-packed hexagonal planes (γ' and α'-phases).

The evolution of atomic volumes of three alloys with pressure (Figure 3) shows large volume collapses at the δ→γ' and γ'→α' phase transformations. These volume shrinkages may be linked to the sudden pressure induced delocalization of 5f electrons and a subsequent increase of 5f electron participation in the metallic bonding. The δ-phase is characterized by mainly localized 5f electrons, while the α'-phase has fully delocalized 5f electrons. The γ'-phase would therefore be expected to show an intermediate electronic state.

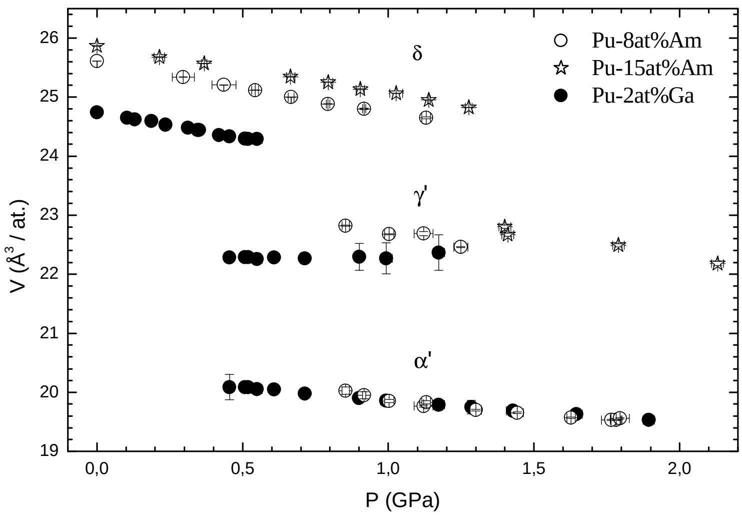

Figure 3: Atomic volumes as a function of pressure (up to 2GPa) for Pu-2at.%Ga, Pu-8at.%Am and Pu-15at.%Am.

During the 2 experimental periods on ID27 we have accurately determined the experimental α'-phase compressibility of these plutonium alloys. The results presented here indicate that the compressibility, as determined by static means, depends on the kinetics of the measurement. Slow pressure variations would lead to low volume, near equilibrium values, while rapid pressure changes would lead to non-equilibrium, high volumes, and therefore to an apparent higher compressibility. The δ-phase compressibility of several plutonium alloys reveals a pressure-induced "softening". This behaviour is shown to be coherent with other unusual properties found in these alloys, such as NTE. Furthermore, the δ→α' phase transformation, followed in several δ-Pu alloys by *in situ* XRD measurements, involves an intermediate γ'-phase.

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