 <b>ESRF</b>	<b>Experiment title:</b> High pressure x-ray diffraction studies of Am/Cm alloys.	<b>Experiment number:</b> HS-913
	<b>Beamline:</b> ID30	<b>Date of experiment:</b> from: 17 June 1999 to: 22 June 1999
<b>Shifts:</b> 12	<b>Local contact(s):</b> T. Le Bihan	<b>Received at ESRF:</b> 24 JAN. 2000
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**Report:**

For this experiment samples of  $^{243}\text{Am}$  and  $^{248}\text{Cm}$  as well as Am/Cm alloys of 50% and 75% Cm were loaded into two types of high pressure cell (Holzapfel and Cornell types) at the Oak Ridge National Laboratory in the USA and shipped to the ESRF where they were mounted in specially made containers for experiment HS-913 at ID30. Special precautions were taken to ensure that these samples remained confined during the experiments by the use of double or triple sealing of the cells with Mylar, Kapton or Be windows. The experiments were performed by a team from ITU, Karlsruhe and Oak Ridge National Laboratory, USA on smaller than 5  $\mu\text{g}$  samples. We used the ID30 high pressure beam line in angle dispersive mode and collected data containing the full diffraction cones on the Fast Scan Image Plate Detector. A micro-focused beam of  $25 \times 25 \mu\text{m}^2$  obtained with two bent mirrors and passed through a pinhole was used for the Cornell cells.

**Motivation.**

The physicochemical properties of the actinide metals at ambient pressure vary widely across the series, due largely to the changing nature of the 5f electrons. In principle, the filling of 5f orbitals begins after thorium and it is generally accepted that the 5f electrons are involved to varying degrees in the bonding (itinerant 5f electrons) for protactinium, uranium, neptunium and plutonium. These four elements display quite different properties from the elements with non-bonding (localised) 5f electrons such as americium and the remaining elements of the actinide series. In this sense americium occupies a pivotal position in the 5f series.

**Results for  $^{243}\text{Am}$ :**

New insights into the nature of americium's f-electrons with regard to its metallic bonding and the relationship to that in other f elements were acquired through studies of the metal under pressure up to 100 GPa.

The initial structure of the americium used in the high-pressure studies was the standard dhcp form ( $P6_3/mmc$ ; Am (I),  $a=0.3467$ ,  $c=1.1240$  nm). At 6.1 GPa, the dhcp form of americium converts to an fcc structure ( $Fm\bar{3}m$ ; Am (II),  $a=0.454$  nm at 9.0 GPa). With additional pressure, we observed that the fcc Am (II) phase transformed to an Am (III) phase at 10.0 GPa, which was retained up to 15.0 GPa. Given the quality of our diffraction data for this phase especially using  $\text{N}_2$  as the hydrostatic pressure-transmitting medium we determined that the structure has a face centred orthorhombic cell (space group  $Fddd$ , Am on 8a sites). At pressures above 15 GPa we observe the formation of a fourth phase Am (IV) which was accompanied by a 7% volume collapse.

Using Rietveld refinement programs, we were able to assign this Am (IV) structure as being orthorhombic, but in contrast to Am (III), with a primitive orthorhombic cell (space group  $Pnma$ , Am on 4c sites). Rietveld fits and difference profiles are shown for the Am (III) and (IV) phases in (Figure 1).

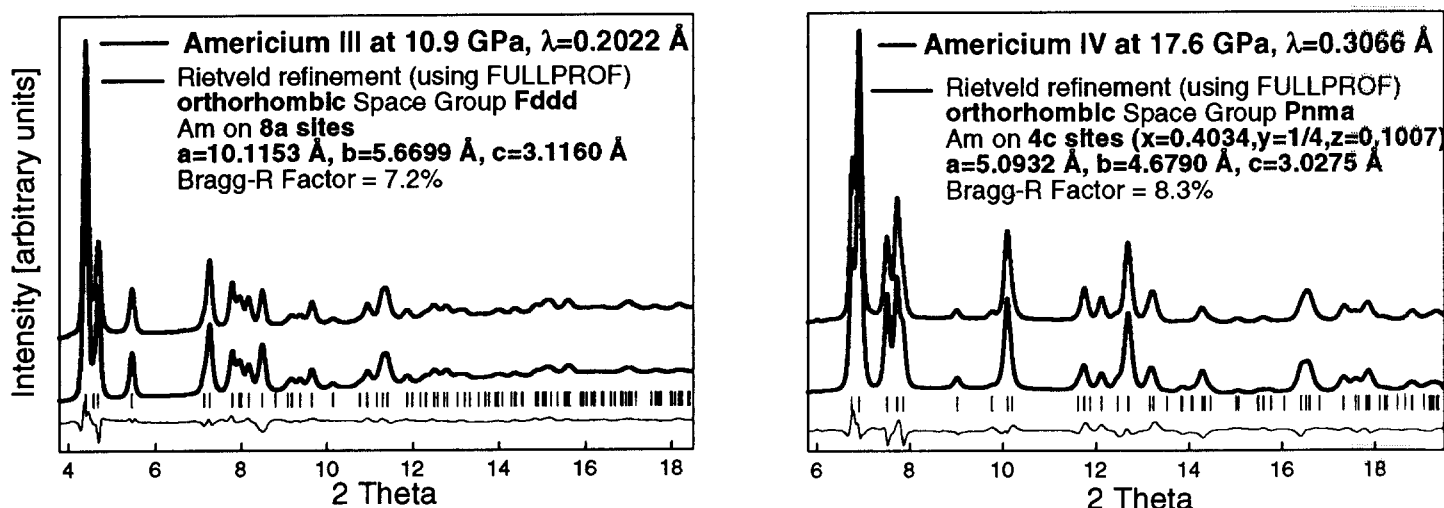


Figure 1: Rietveld fit and difference profiles of the face centred orthorhombic Am (III) structure (space group  $Fddd$ ) and the primitive orthorhombic Am (IV) structure (space group  $Pnma$ ) to the integrated profiles obtained at 10.9 and 17.6 GPa. The tick marks under the profile indicate the reflections allowed for this space group.

The four different americium structures observed in this work are shown as dhcp (Am (I)), fcc (Am (II)), Am (III) and Am (IV) in (Figure 2), and permit one to envision the transformation process occurring under pressure. In principle, the structures are composed of close-packed hexagonal or distorted close-packed hexagonal planes with a certain stacking sequence that changes from one structure to the next. In the case of Am (IV) there is an additional “ZIG-ZAG” bending of the hexagonal planes. This work has established two critical findings about the Am (III) and the Am (IV) structures formed under pressure. First, the Am (III) phase has the same structure as the  $\gamma$ -phase of plutonium [1] where the bonding involves itinerant 5f electrons. Second, the Am (IV) structure is a primitive orthorhombic structure, rather than the base centred orthorhombic  $\alpha$ -Uranium structure as reported previously, and is stable up to at least 100 GPa. The Am (IV) structure shows a rather small compressibility with pressure, as expected for a metal having 5f-electron character in its bonding.

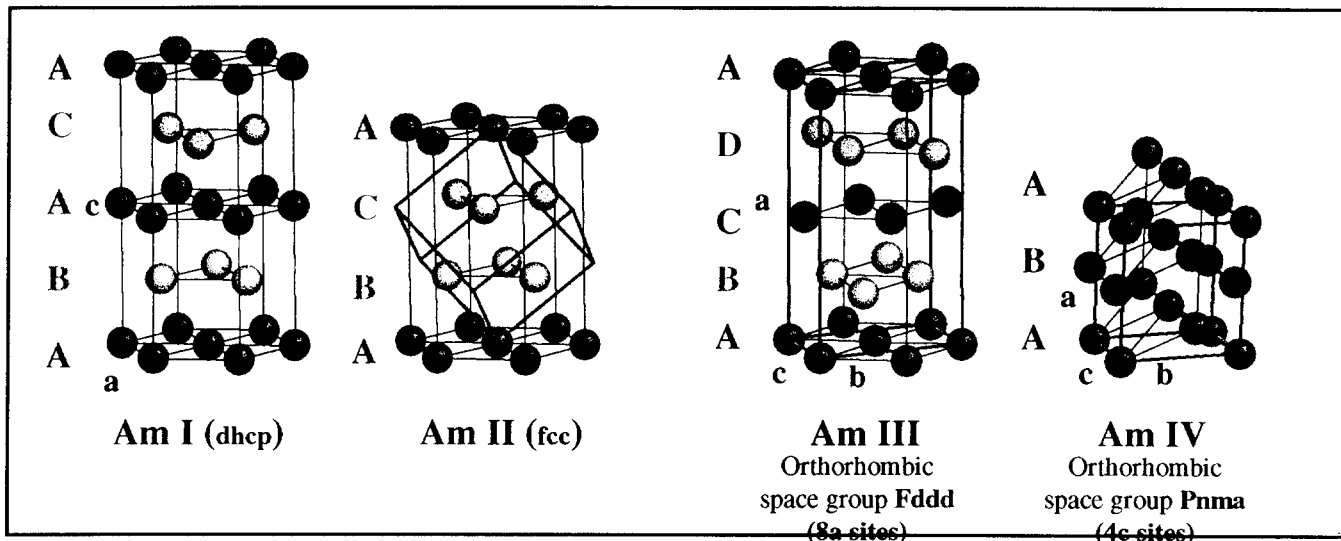


Figure 2: Models of the 4 structures of americium.

#### Results for pure $^{248}\text{Cm}$ and $\text{Cm}_{0.75}\text{Am}_{0.25}$ alloy:

Cm (element 96) is one of the most interesting transplutonium elements as it has a stabilizing ground state electronic configuration of : [Rn core]  $5f^7 6d 7s^2$ . This half-filled 5f-shell greatly influences the pressure behavior of Cm; which displays higher structural transition pressures and resists f-electron delocalisation.

The three experiments on pure Cm and a  $\text{Cm}_{0.75}\text{Am}_{0.25}$  alloy were only partially successful. For the pure Cm samples we were only able to study the lower pressure region up to 30 GPa. We were not able to further increase the pressure with these samples because of deformation of the gasket hole which could have eventually led to diamond breakage. The  $^{248}\text{Cm}$  samples studied remained in the dhcp phase throughout the measurements. For the 75% Cm alloy we collected data from both dhcp and fcc phases as well as a possible third phase but were not able to determine the pressures of these transformations as the reference signal from our Pt marker could not be measured after the first few pressure increases. Our goal of reaching the predicted fourth phase of Cm was therefore not realised in these measurements.

#### Results for $\text{Cm}_{0.5}\text{Am}_{0.5}$ alloy:

For this series of measurements we were successful in observing transitions from the dhcp to fcc phase at about 13 GPa and from the fcc to the same orthorhombic 3rd phase structure (space group Fddd ) as for pure Am at about 25 GPa. Figure 3 shows the diffraction spectra obtained for the 1st dhcp and 3rd orthorhombic phases of the  $\text{Cm}_{0.5}\text{Am}_{0.5}$  alloy. The transition pressures obtained for this alloy are as expected considerably higher than those for pure Am and will enable us to estimate better the probable transition pressures for pure Cm which will be the subject of further experiments.

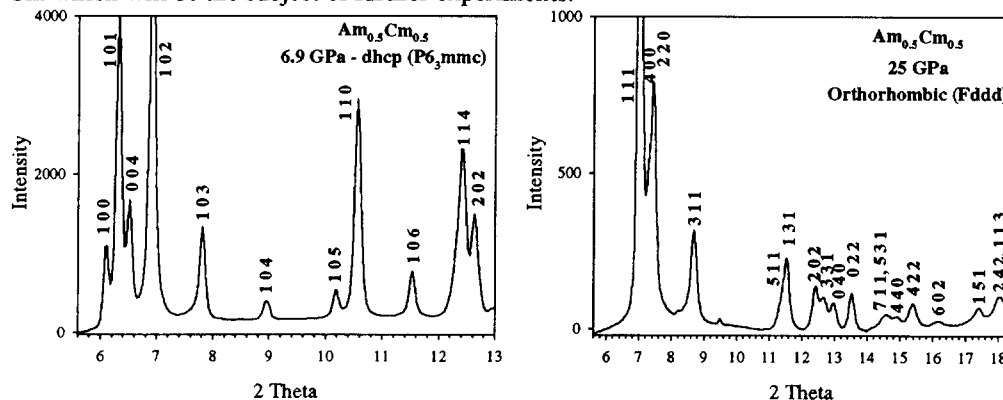


Figure 3: diffraction spectra obtained for the 1st dhcp and 3rd orthorhombic phases of the  $\text{Cm}_{0.5}\text{Am}_{0.5}$  alloy.

#### References

- [1] W.H. Zachariasen and F.H. Ellinger, *Acta Cryst.* 8 431-433 (1955)