ESRF	**Experiment title:** *The influence of Pu local environment on the non ideality of $(U,Pu)O_2$ solid solution*	**Experiment number**: CH - 619
Beamline: BM 20	**Date of experiment**: from: 15 May 2000 to: 17 May 2000	**Date of report**: 31/08/2000
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Report:

The aim of this experiment was to observe by EXAFS if structural changes occur when plutonium concentration varies in the $(U,Pu)O_2$ system, accounting that $(U,Pu)O_2$ is not an ideal solid solution [1].

Due to safety authorisation, cerium, an analogue of plutonium, had to be used. These six new shifts, allowed by the Review Committee on BM20 using a Si(111) double-crystal monochromator in channel-cut mode, were a continuation of our previous measurements on $(U_{1-y},Ce_y)O_2$ samples in june and july 1999. Four samples (with cerium amount of 5, 8, 10, and 12 at.%) were analysed at U and Ce L_{III} edges (17.17 and 5.72 keV respectively). Because of higher fluorescence efficency and then better statistics, Ce L_{III} edge was this time preferred to L_I one. The fluorescence signal was measured by a multichannel germanium detector with a sample orientation of 45°. Because of the Ce L_{II} edge position (6.165 keV), accumulations were recorded between 5.520 keV and 6.140 keV.

The XAS spectra of Ce^{4+} compounds are characterised by the presence of two undesired additional phenomena : final-state mixed valence behaviour and intense multi-electron excitations. The final-state mixed valence behaviour in Ce^{4+} induces a splitting of the white line caused by two different configurations in the initial state [2]. The first peak corresponds to the initial configuration $4f^1\underline{L}$ and the second one to $4f^0\underline{L}$, but both peaks can be described by a 2p-5d transition. In order to determine the relative intensity and energy position of the two transitions for all the samples, the XANES spectra were deconvoluated by using 2 arctan functions which describe the transitions from the 2p to the continuum state and 2 lorentzian functions that takes into account both the 5d density of unoccupied states and the finite lifetime of the 2p core hole [3]. An example is given in Figure 1. For all the 4 compositions, we determined a shift of 8 eV and a relative height of 60% between the two excitation channels. By comparison, we found a 7 eV and 66 % for pure CeO_2. This mixed-valence behaviour is due to the interaction between 4f orbitals of the metal and 2p orbitals of the ligands in its initial state [4], thus the difference observed is due to the presence of the uranium ions which

can modify the hybridation of the 2p orbitals of oxygen atoms. To clarify this effect, spectra at O K-edge on the same samples (plus others with different Ce contents), were recorded in july 2000 at LURE.

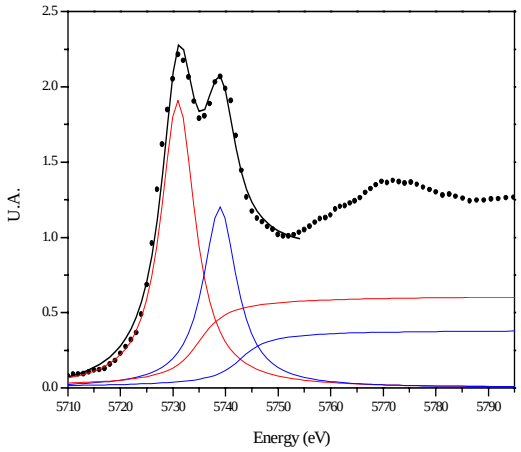

Figure 1 : Deconvolution of the Ce L_{III}-edge of $(U_{0,88}Ce_{0,12})O_2$.

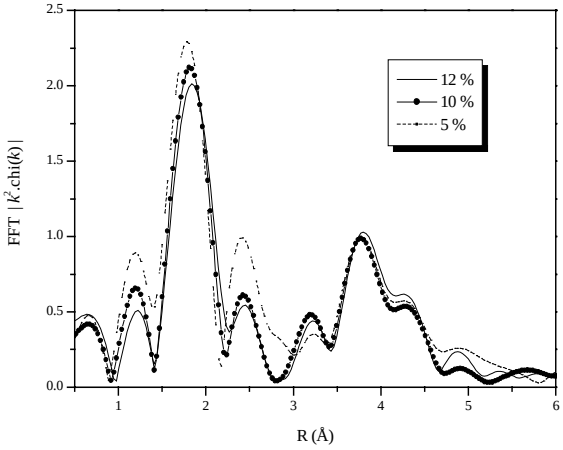

Figure 2 : Fourier Transform of $(U_{1-y},Ce_y)O_2$ samples with different cerium content.

The strong resonant-like features which is superimposed on all the EXAFS signal at about 125 eV over the edge is connected to multi-electron excitations. To obtain correct information, in particular on the first coordination shell, we substracted this behaviour on all our spectra, using a lorentzian function as indicated in [3, 5]. The Fourier transforms of this corrected EXAFS signal are gathered in figure 2. We clearly see that differences appear mainly on the first peak.

As described by Fonda *et al.* [5], we used two sets of phase and amplitude with different k-scale origins. The energy difference between the origins was 8 eV. We also assigned a 60% relative height to the phase and amplitude with the origin at lowest energy. The simulated EXAFS data were generated using FEFF8.10 code and fitting process was performed on k^2 weighted data in r space using FEFFIT program.

While the space group of $(U_{1-y},Ce_y)O_2$ solid solution is Fm3m (n° 225), the first coodination shell of metal atom should be 8 oxygen atoms at about 2.364 Å for a 12% Ce content. These distances do not agree with experimental data. The first coordination shell consists in more than one Ce-O bond (at least one at 2.20 Å and another around 2.80 Å). It appears to be consistent with the UO_{2+x} defect structure proposed by Murray and Willis[6], where oxygen atoms are located in interstitial positions. Further data analysis is in progress on this base.

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