EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Thermal recovery of self-irradiation induced defects	**Experiment number**: 20-01-739
Beamline: BM20	**Date of experiment**: from: 09.06.2015 to: 14.06.2015	**Date of report**: 24.01.2017
Shifts: 12	**Local contact(s)**: A. Scheinost	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

During in-pile, irradiation-induced damage occurs in nuclear fuel and results in a deterioration of its properties, which can affect the margin to melt of the fuel. Damage also occurs in fresh fuel through the self-irradiation process, and thus provides a convenient means to investigate changes in the material. A 10 uranium-plutonium mixed nitride fuel made over 25 years ago, and stored in the JRC archives has been retrieved and studied by XRD, EXAFS and TEM [1].

XAS data acquisition was performed on the damaged U0.78Pu0.22N powder mixed with BN, the latter being essentially transparent to X-rays. XAS measurements were conducted at the ROBL 20 beamline dedicated to actinide elements at the European Synchrotron Radiation Facility (ESRF, France).

The U L3 and Pu L3 edges XANES spectra of the damaged U0.78Pu0.22N NIMPHE fuel are presented in the Figure 1. At the U L3 edge, one can observed that the shape and the energy position of the damaged U0.78Pu0.22N XANES spectrum are similar to the UN reference materials. Thus the oxidation state of U in mixed (U,Pu)N is the same as in pure UN. Note that the U valence is not influenced by the presence of Pu, as would have been expected. Comparing with the UO2 XANES spectra, one can observe a shift of 3.2 eV.
At the Pu L3 edge, a shift of ~ 3 eV toward the lower energies was observed between the XANES spectrum of U0.78Pu0.22N and PuO2. As a similar shift was reported for PuN and PuO2, it can be supposed that Pu exhibit the same valence in PuN and (U,Pu)N materials.

In accordance with the XRD, both U LIII and Pu LII EXAFS spectra were fitted considering a NaCl type structure (*Fm-3m*). The experimental and fitted EXAFS spectra are presented in the Figure 2. A good agreement between the experimental and fitted data is observed, confirming the validity of the structural model used for the analysis. No additional Me-N or Me-Me distances were needed to reproduce the experimental data, confirming the complete local integration of Pu in the rocksalt structure. Considering the experimental uncertainty, this shows that the anion and cation atoms are still located on the theoretical atomic

positions of the NaCl structure, i.e. no atoms ejected in interstitial positions through the energy of the self-irradiation process could be detected. The EXAFS data analysis provides element-specific Me - N bond lengths. Indeed, the first U - N1 interatomic distance is equal to 2.440 (5) Å while the Pu – N1 is about 0.03 Å higher. Besides, the U – N1 distance is consistent with previous EXAFS measurement on UN. This bimodal distribution in the cation sublattice was expected, as different U-N1 and Zr-N1 bond lengths have been reported for analogous (U,Zr)N compounds. One should note that equal U-O1 and Pu-O1 interatomic distances have been observed in only U0.50Pu0.50O2. Indeed, a multimodal distribution, explained by the presence of cuboctahedral oxygen defects, was reported for mixed oxides with lower content of Am (> 30%).

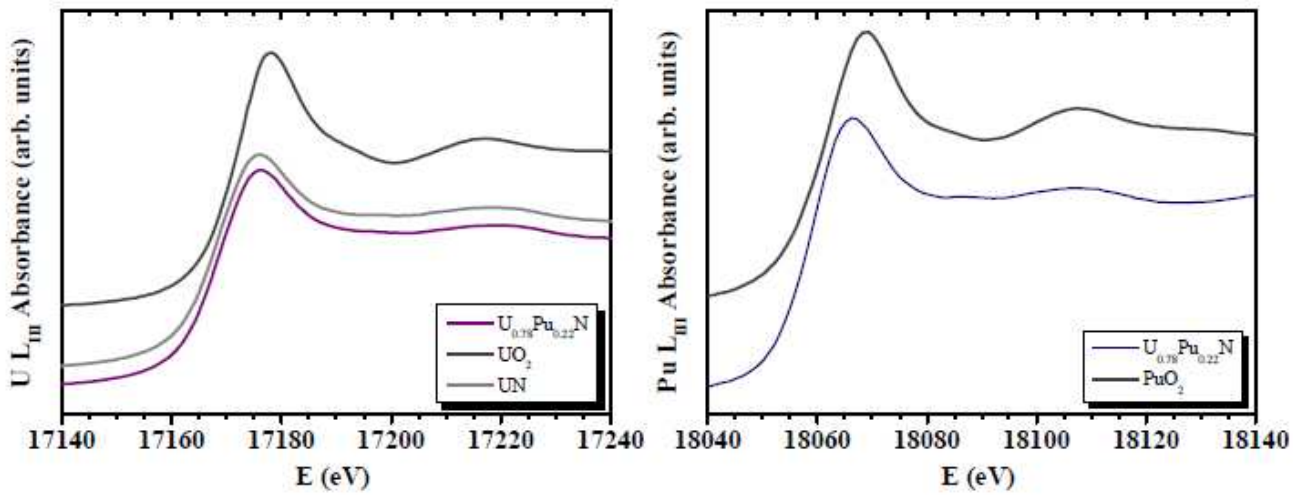

Fig 1 XANES spectra of damaged $U_{0.78}Pu_{0.22}N$ NIMPHE fuel at U L_{III} and Pu L_{III} edges (The XANES spectra of UN, UO_2 and PuO_2 are presented as reference materials).

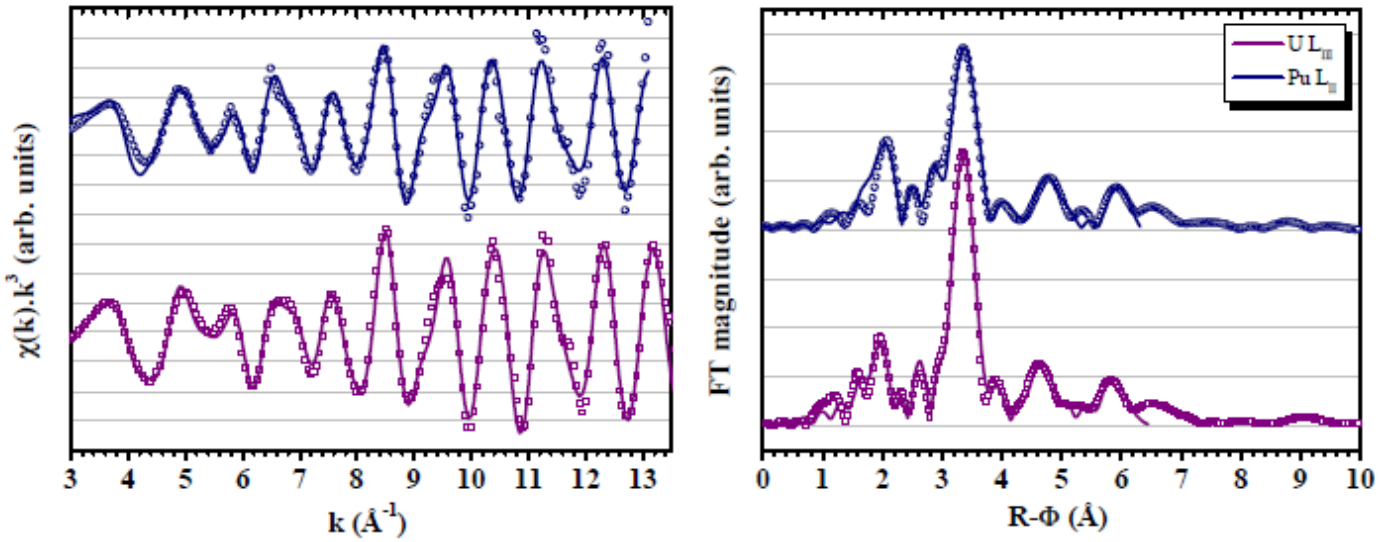

Fig 5 U L_{III} and Pu L_{II} k^3-weighed EXAFS spectra of damaged $U_{0.78}Pu_{0.22}N$ NIMPHE fuel.

Coupling XRD, EXAFS and TEM has shown that this material was still well-crystallized [1]. However, an increase of 0.3 % of the lattice parameter was found. As shown by the EXAFS, the U-N and Pu-N as well as the metal - metal distances are similarly affected. However, no significant modification of both anion and cation sublattice was found.

References:

1. Carvajal-Nunez, U.; Prieur, D.; Janssen, A.; Wiss, T.; Cambriani, A.; Vermorel, E.; Scheinost, A.; Somers, J., *Journal of Nuclear Materials* **2013,** *443*, 491-496.