ESRF	**Experiment title: Local environment of iodine implanted in uranium dioxide**	**Experiment number**: ME 169
Beamline: BM 8	**Date of experiment**: from: 22/03/2001 to: 29/03/2001	**Date of report**: 31/08/2001
Shifts: 18	**Local contact(s)**: F. d'Acapito	*Received at ESRF:*

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Report:

The main aim of this experiment was to determine by EXAFS:

1) if iodine forms I_2 bubbles or/and is trapped in the UO_2 matrix
2) if presence of caesium modifies the iodine behaviour.

First of all, we analysed at the iodine K-edge (33.17 keV), different iodine concentrations ranging between 0.75 to 2.0 atomic per cent before and after annealing at 700°C for 4 hours. The spectra were collected in fluorescense detection mode at the nitrogen liquid temperature to improve their quality.

The first observation on as implanted samples was that whatever the iodine concentration is, the EXAFS signal is extremely weak and cannot be extracted from the atomic background.

The structural signal has been calculated using standard curved wave EXAFS equations and the whole data-analysis has been performed using the GNXAS code[1].

Different iodine environments have been tested such as molecular I_2, the most stable uranium iodide UI_3 and iodine in substitutional and vacant crystallographic positions in UO_2 lattice.

We introduced the atomic background correction due to double-electron excitation channels as described by Buontempo *et al*[2]. The result for the 2 at.% concentration is presented in the figure 1. Despite the high noise level, oscillations are well reproduced (residual function $R = 1.4.10^{-5}$). In this case, the iodine environment is described by only one coordination shell corresponding to 2 uranium atoms at 3.20 Å ± 0.02 Å with $\sigma^2 = 0.011$ Å^2 ± 0.007 Å^2.

Our first conclusions are the following:

- the I-I bond of 2.7 Å, characteristic of I_2 molecule, is not suitable with our data.
- the I-O bonds of 2.37 and I-U of 3.84 Å, characteristic of UO_2 fluorite lattice, does not appear in our data.
- the environment found is closed to the UI_3 one.

Hocking *et al*[3] studied by SIMS the iodine thermal diffusion using ion implantation in UO_2. They showed that at concentrations above 10^{16} at.cm^{-3}, iodine is trapped in the matrix. Accordingly, iodine does not diffuse thermally any more. To explain this phenomenon, they put forward a probable formation of I_2 microscopic bubbles, but cannot demonstrate it experimentally.

On the opposite, our observations seem to point out the absence of I_2 bubbles. But because of the signal weakness, new measurements are needed at helium-liquid temperature to verify this result with better statistics.

When caesium is present, the iodine behaviour is completely different as we can see in figure 2. This time, two components appear in the Fourier transform :

- the first peak is attributed to a I-U bond, but at a distance shorter than for iodine alone,
- the second one at around 3.9 Å corresponds to the I-Cs bond length in the CsI compound.

This is the first experimental evidence of CsI occurrence in UO_2 fuel.

Further data analysis is under way.

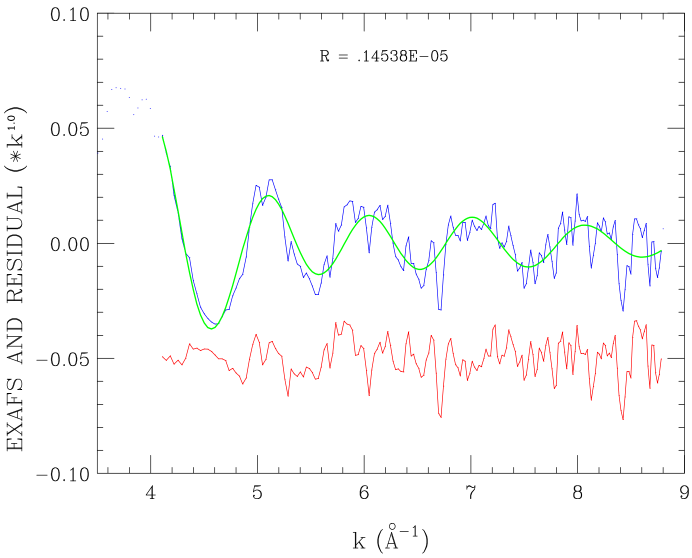

Figure 1: Best fit and residual function of the EXAFS spectrum of 2% I in UO_2 after annealing at 700°C for 4 hours.

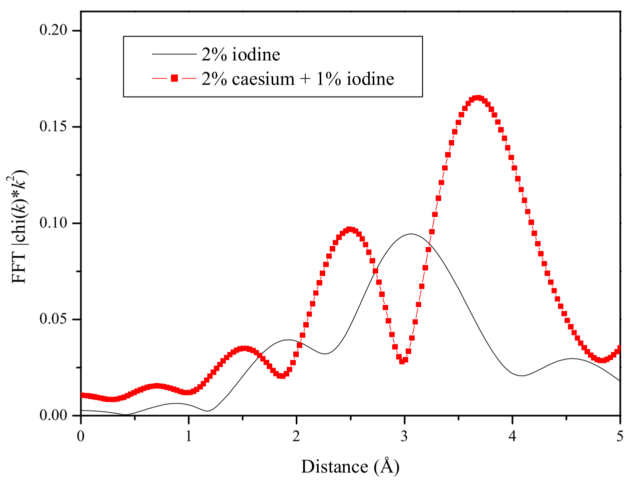

Figure 2: UO_2 samples with or without caesium Evolution of the iodine environment.

Références bibliographiques

[1] : "X-Ray-Absorption Spectroscopy and N-Body Distribution Functions in Condensed Matter .2. Data Analysis and Applications", FILIPPONI, A. et DICICCO, A.; Physical Review B, 52-21 (1995) 15135-15149.

[2] : "Determination of the I_2 Bond-Length Distribution in Liquid, Solid and Solution, by Extended X-Ray Absorption Fine Structure Spectroscopy", BUONTEMPO, U.; DICICCO, A.; FILIPPONI, A.; NARDONE, M. et POSTORINO, P.; Journal of Chemical Physics, 107-15 (1997) 5720-5726.

[3] : "Migration Behaviour of Iodine in Nuclear Fuel", HOCKING, W. H.; VERRALL, R. A. et MUIR, I. J.; Journal of Nuclear Materials, 294-1-2 (2001) 45-52.