ESRF	**Experiment title:** Thermal behaviour of xenon and krypton in uranium dioxide	**Experiment number:** 30 02 658
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Report:

The aim of this experiment was to study the thermal behaviour of xenon and krypton in uranium dioxide. the samples were polished UO_2 pellets implanted with Xe or Kr at a fluence of 10^{17} at.cm^{-2}. The heat treatments performed in a reducing atmosphere (Ar+10% H_2) at CEA Cadarache were : 800°C, 1000°C, 1200°C, 1400°C and 1500°C, with two hold times for each temperature: 2 and 12 hours.

All the measurements were performed at the Xe (34.56 keV) and Kr (14.32 keV) K edges with a 13 element fluorescence detector because at the experiment date the beamline's 30 element detector was not available. Acquisition was indeed longer than expected so the choice was to focus on Xe implanted samples. The measurements were performed at 11 K using a He cryostat. On one case, the He level in the experiment chamber dropped and some Xe K edge spectra were recorded at a higher temperature. The XAFS spectra obtained were completely flat: no EXAFS oscillation. On the same sample, once the He level reached its normal value, EXAFS oscillations were clearly observed. This accidental result demonstrates that when studying samples at the xenon K edge, experiments must be performed at or below 11 K.

The only results obtained from the fitting procedure that are presented here are those relative to the Xe implanted UO_2 samples, because previous experiments have enabled us to validate it. As regards Kr spectra, more effort is required in order to satisfactorily model and eliminate multi-excitation processes [1]. Figure 1 shows two Kr K edge XANES spectra of an as implanted sample and a sample annealed for 2 hours at 1200°C. A strong white line with weak EXAFS oscillations is seen in both cases. As described in [1,2] such features are characteristic of the presence of pressurised Kr inclusions. As expected, Kr atoms precipitate to form pressurised bubbles in UO_2. Based on a comparison of our results with those obtained by Di Cicco *et al.* [1], a Kr pressure in excess of 2.0 GPa is expected.

As regards the xenon spectra, our previous experiments [3] have enabled us to analyse these results in greater detail. Numerical values are obtained with Athena/Artemis software [4] using FEFF8.2 calculations.

The Fourier transform of k-weighted EXAFS spectra for an as implanted sample and two annealed ones ($2 \leq k \leq 7.5$ Å^{-1}) are shown in Figure 2. The narrow k interval is due to the poor signal to noise ratio relative to the as implanted sample.

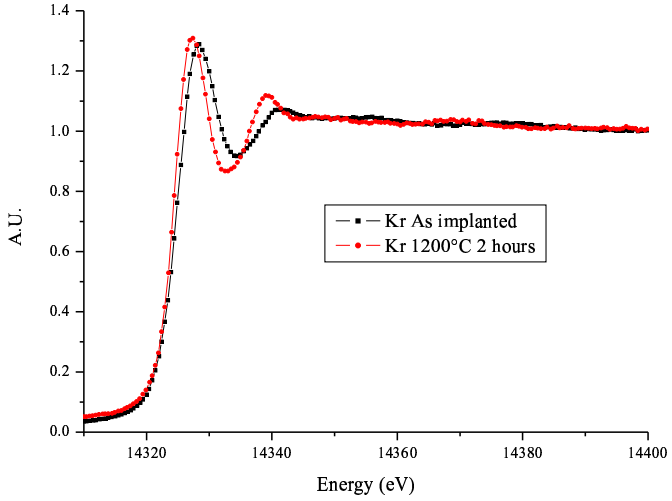

Figure 1 : XANES spectra obtained at the Kr K edge.

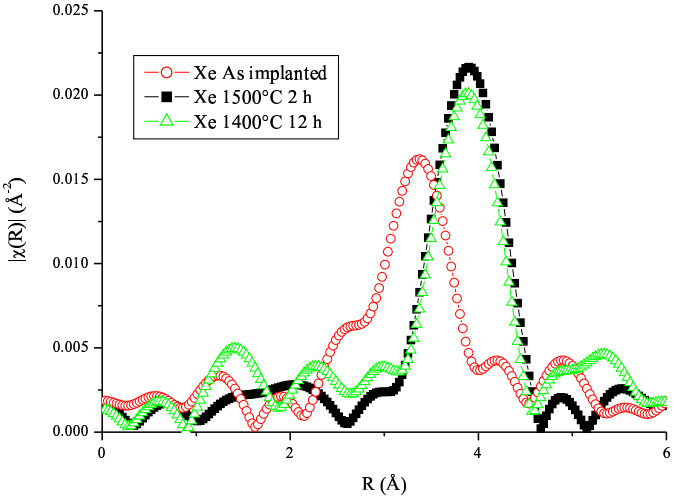

Figure 2 : Fourier transforms of the Xe K edge EXAFS spectra.

For each sample, only one coordination shell is clearly observed. For the as implanted sample the peak is broader and distance is shorter than for the two annealed samples. In each case, the peak is attributed to the presence of other surrounding Xe atoms. It is impossible to fit the experimental data by modelling Xe-U or Xe-O bonds. These results illustrate the fact that Xe is insoluble in UO_2 and readily forms aggregates (bubbles). A similar Xe-Xe distance appears to be observed for both annealed samples which could indicate a stabilisation of Xe aggregates. Furthermore, results of a PIXE analysis on sibbling samples have revealed xenon losses of 27% and 25% for the 1400°C and 1500°C samples respectively.

At 11 K, xenon precipitates in a cubic face centred crystal with a cell parameter of 6.20 Å. In this structure, the first coordination shell comprises 12 Xe atoms at 4.38 Å. Using the xenon equation of state, the pressure in the aggregates can be evaluated using the distance determined from the EXAFS fit. From the as-implanted spectrum, one can infer that each Xe atom is on average surrounded by 2.4±0.7 Xe atoms at a distance of 3.98±0.02 Å. The analysis of the spectra relative to the annealed samples reveals the presence around each Xe atom of 6±0.7 Xe atoms at 4.39±0.02 Å. One of the effects of the thermal treatments is clearly to reduce the pressure in the xenon aggregates. At these temperatures, inclusions would therefore be expected to contain xenon in a gaseous state.

These experimental results are highly relevant to the modelling of rare gas diffusion in UO_2. Indeed, by estimating the size distribution and concentration of gas bubbles resulting from these annealing conditions, it is then possible to estimate the fraction of gas atoms precipitated in bubbles. The remaining xenon atoms are then free to migrate in the bulk of the solid whence release is possible.

These experiments have demonstrated that the FAME beam line is particularly well suited for this subject. It is therefore planned to extend current research to the stability of rare gas bubbles under irradiation. This topic will make up the main part of our next application for beam time.

[1] A. D. Cicco, A. Filipponi, J. Itie and A. Polian, Physical Review B 54, 9086 (1996).

[2] A. Polian, J.P. Itie, E. Dartyge, A. Fontaine and G. Tourillon, Physical Review B 39, 3369 (1989).

[3] P. Martin, M. Ripert, G. Carlot and P. Garcia, ESRF BM8 experimental report ME 353, Febuary 2003 (2003).

[4] M. Newville, Synchrotron Radiation 8, 322 (2001).