HAL
open science

Study of the 5f electronic states in u, np, pu and am and (u,pu) oxides using high resolution xanes

P. Martin, D. Prieur, R. Bes, R. Belin, M. Strach, D. Manara, C. Valot, T. Vitova, T. Prussman, K. Dardenne, et al.

To cite this version:

P. Martin, D. Prieur, R. Bes, R. Belin, M. Strach, et al.. Study of the 5f electronic states in u, np, pu and am and (u,pu) oxides using high resolution xanes. NuMat2016 The Nuclear Materials Conference, Nov 2016, Montpellier, France. cea-02437087

HAL Id: cea-02437087

https://cea.hal.science/cea-02437087v1

Submitted on 13 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Study of the 5f electronic states in U, Np, Pu and Am and (U,Pu) oxides using high resolution XANES

Ph. M. Martin[1], D. Prieur[2], R. Bès[3], R. Belin[4], M. Strach[1], D. Manara[2], Ch. Valot[1], T. Vitova[5], T. Prüßmann[5], K. Dardenne[5], J. Rothe[5]

1-CEA, DEN/DTEC/SECA/LCC, Bagnol sur Cèze, France; 2-European Commission, JRC-Karlsruhe, Germany; 3-Antimatter and Nuclear engineering, Department of applied Physics, Aalto University, Finland; 4- CEA, DEN/DEC/SESC/LLCC, Cadarache, France; 5-Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany

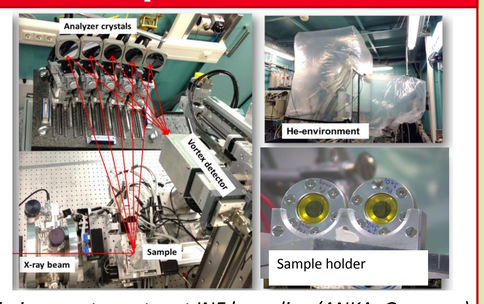
Context and Objectives

Uranium−plutonium mixed oxide fuels $U_{1-y}Pu_yO_{2-x}$ are currently studied within the frame of the fourth generation (GEN-IV) of nuclear reactors and more specifically for sodium-cooled fast neutron reactors (SFRs). Because of their specific neutronic spectrum, SFRs will also be able to burn long-lived minor actinides (MAs) such as Am and Np. One of the considered options is to add them homogeneously to the fuel in significant amounts (2−6%). In such complex mixed oxide systems, both the homogeneity of the cation distribution into the fluorite UO_2 structure and the oxygen stoichiometry significantly affects most of the fuel properties (thermal conductivity, melting temperature, diffusion phenomena, etc.). These properties depend mainly on the complexity of actinide electronic structures, in particular the unfilled actinide 5f valence shells. The latter can be directly probe with **High Resolution X-ray spectroscopy performed at the $M_{4,5}$** (3d→5f transition) edges of actinides. Here, we show results obtained on binary oxides (**UO_2, NpO_2, PuO_2** and **AmO_2**) and **$U_{1-y}Pu_yO_2$ (y=0.24, 0.44 and 0.62)** samples combined with theoretical calculations with **FDMNES [1]** code.

Methods

HERFD-XANES experimental Setup

To overcome the core-hole limitation in standard XANES measurements , an emission spectrometer can be used to collect High Energy Fluorescence Detected XANES (HERFD-XANES). Such experimental set-up is now available at the INE beamline [2,3] located at the synchrotron source ANKA (Karlsruhe, Germany) and application of HERFD-XANES on highly radioactive materials such as $(U,Pu)O_2$ is now possible.



Emission spectrometer at INE beamline (ANKA, Germany)

Samples

HERFD spectra collected on stoichiometric samples

- UO_2, NpO_2, PuO_2 and AmO_2
- $(U,Pu)O_{2.00}$ prepared by powder metallurgy process [4]

Purity checked by XRD results

➔ single face centered cubic phase

Calculations

Finite **D**ifference **M**ethod for **N**ear **E**dge **S**tructure (**FDMNES**) code [1]

Local Density Approximation (LDA) - Green Formalism (Multiple scattering)

Input data :

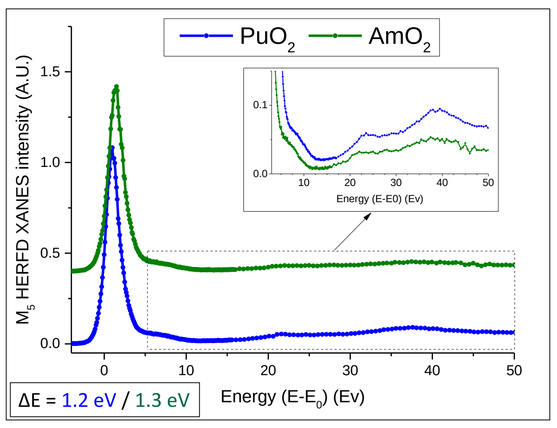
- Crystallographic structure
- Cluster radius = 8 Å (143 atoms)
- An and O electronic configuration

Results on binary systems

Measurements on AnO_2

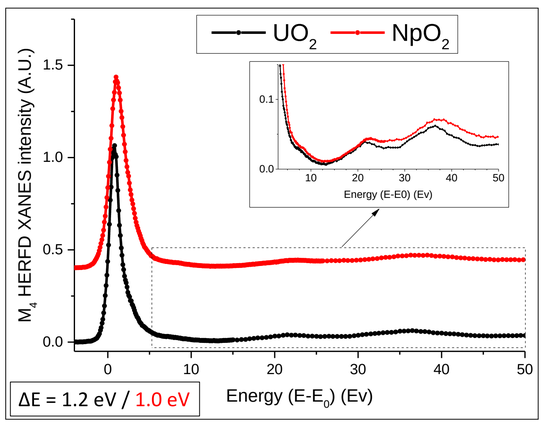
PuO_2 & AmO_2 ⇔ M_5N_7 line (M_α or $3d_{5/2}$-$4f_{7/2}$)

Pu: [Rn] $5f^6 6d^0 s^2$ | **Am**: [Rn] $5f^7 6d^0 s^2$



UO_2 & NpO_2 ⇔ M_4N_6 line (M_β or $3d_{3/2}$-$4f_{5/2}$)

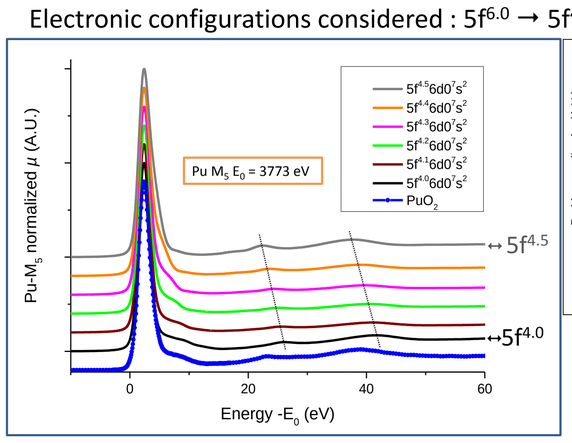
U : [Rn] $5f^3 6d^1 s^2$ | **Np**: [Rn] $5f^4 6d^1 s^2$

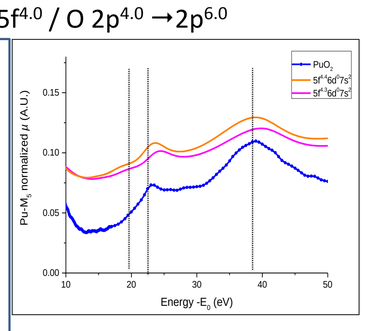


FDMNES calculations for elements with $6d^0$ ground states

PuO_2 ⇔ Pu^{+4} / $5f^4 6d^0$

Electronic configurations considered : $5f^{6.0} \rightarrow 5f^{4.0}$ / O $2p^{4.0} \rightarrow 2p^{6.0}$



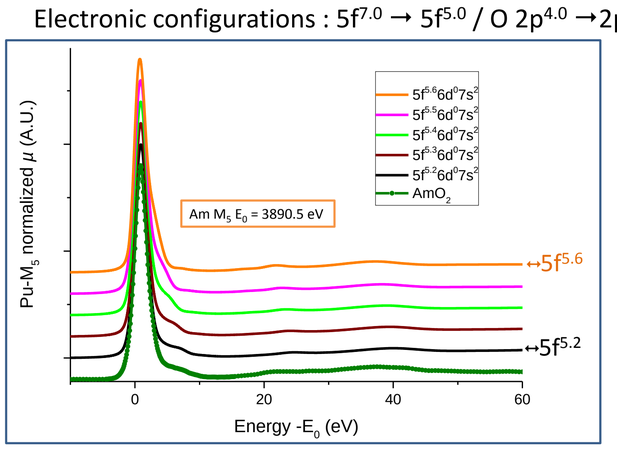


➔ **best results = Pu $5f^{4.4}$**

➔ **Charge transfer : Pu 5f – O 2p ⇔ +1.6 e⁻ / -0,8 e⁻**

AmO_2 ⇔ Am^{+4} / $5f^5 6d^0$

Electronic configurations : $5f^{7.0} \rightarrow 5f^{5.0}$ / O $2p^{4.0} \rightarrow 2p^{6.0}$



➔ **Best results obtained for Am $5f^{5.6}$**

Charge transfer = Am 5f – O p: +1.4 e⁻ / -0,7 e⁻

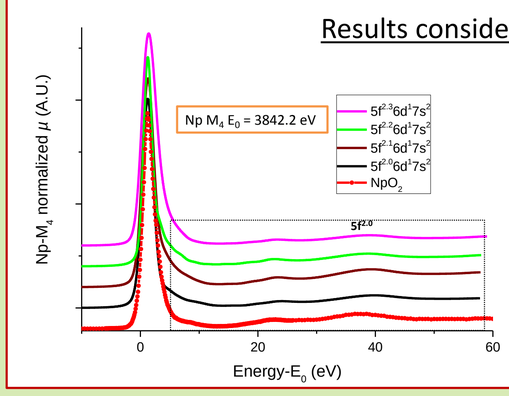
➔ **Slight decrease of the charge transfer between Pu and Am (Δ = 0.2 e⁻)**

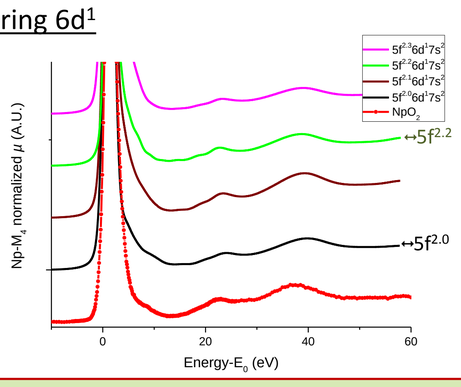
⇔ in agreement with 0.14 e⁻ obtained by Yu et al [5] extracted from GGA+U calculations

FDMNES calculations for elements with $6d^1$ ground states

NpO_2 ⇔ Np^{+4} / $5f^3 6d^0$

Results considering $6d^1$





If charge transfer is only considered Np 5f - O 2p :

➔ Experimental spectrum is not reproduced (WL & resonances)

Calculations with $6d^0$ ($5f^{3.0}$-$5f^{4.0}$) ➔ no improvement

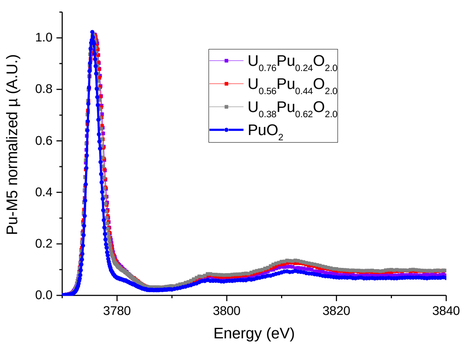
➔ **Charge transfer Np 5f and 6d and O 2p**

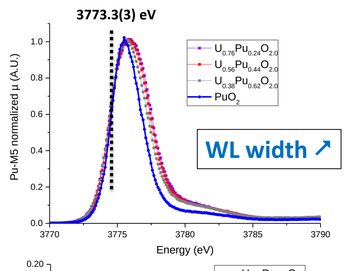
Same conclusion for UO_2

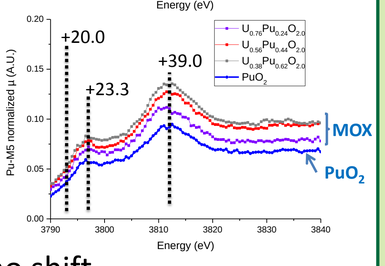
Calculations in progress

Results on $U_{1-y}Pu_yO_2$ (y=0.24, 0.44 and 0.62) samples

Pu-M_5 results

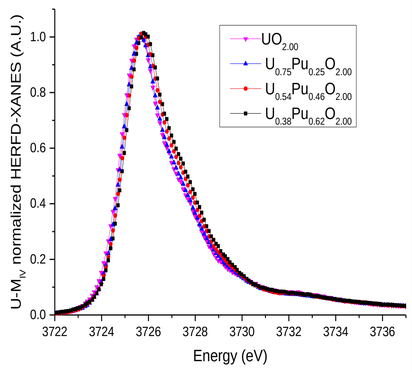






- Increase of the WL width but no shift
- No shift of resonance positions

U-M_4 results



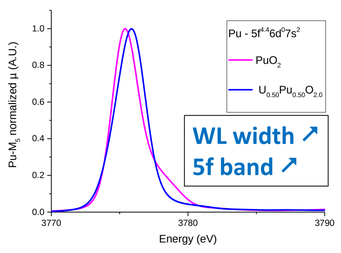
- No broadening of the WL
- Slight shift of the WL to higher energy

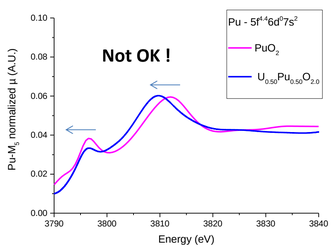
The substitution of U by Pu atoms is observed in both U and Pu experimental spectra

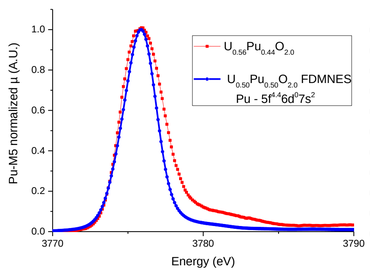
FDMNES simulation : PuO_2 Vs $U_{0.50}Pu_{0.50}O_{2.0}$

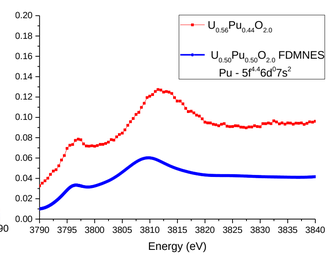
➔ Introduction of charge transfer Pu 5f – O2 p ⇔ $5f^{4.4}$

Comparison with PuO_2









First results on 50% Pu

- White line width is not reproduced
- Resonance are shifted

Next step = introduction of charge transfer U 5f-6d + Pu 5f

Conclusions

The gain in selectivity and resolution provided by HERFD at $M_{4,5}$ (3d →5f) edges of actinides (U-Am) allow to precisely probe the 5f (and 6d) occupancy experimentally. Charge transfer between An valence shells (5f – 6d) and O 2p must be considered in FDMNES calculations to reproduce experiment. **PuO_2 and AmO_2 (with $6d^0$ in the ground state) experimental spectra are well reproduced** with the following 5f configurations: **Pu = $5f^{4.4}$ and Am = $5f^{5.6}$**. For UO2 and NpO2 (with 6d1 in the ground state), 6d and 5f have to be taken into account in the charge transfer with O 2p but results obtained with $6d^0$ and $6d^1$ with different 5f occupancies are not satisfactory. Calculations with an intermediate 6d occupancy are in progress. **Contrary to the XANES measurements, the substitution of U by Pu atoms is observed at both U and Pu edges in HERFD-XANES spectra collected on $(U,Pu)O_{2.00}$ samples** [6]**.** First calculations show that charge transfer has to be introduced in both U (5f-6d) and Pu (5f).

[1] Bunau, O.; Joly, Y. J. Phys.: Condens. Matter 2009, 21, 345501 ; [2] T. Vitova *et al.*, J. Phys. Conf. Ser. 430 (2013) 012117 ; [3] J. Rothe *et al.*, Rev. Sci. Intrum. (2012) 043105 ; [4] T. Truphémus *et al.*, J. Nucl. Mater. 432 (2013) 378–387 ; [5] Y. Lu et al., J. Nucl. Mater. 441 (2013) 411 ; [6] R. Vauchy et al. , Inorg. Chem. 55 (2016) 2123.